aniline. It did not crystallize, however. The remainder of the residue was not investigated.

Caution should be exercised during the addition of the nitro compound to the alkoxide-alcohol solution. If the rate of addition is too rapid, a violent exothermic reaction often results. This is particularly the case at lower temperatures where an induction period has been observed before the reaction commenced. The temperature of the reaction is conveniently controlled by the rate of addition of the nitro compound.

When a carbonyl compound corresponding to the dehydrogenation product of the charged alcohol is employed in the reaction, it is added simultaneously with the nitro compound. This minimizes self-condensation products. The mole ratio of carbonyl compound to nitroaromatic was always 1:1. In those experiments where attempts were made to trap hydrocarbons from this reaction, two traps cooled in liquid nitrogen were placed at the head of the condenser. A T-tube was connected to the last trap, and a slow stream of nitrogen passed across the T to exclude moisture from the trap.

Frequently a deep purple coloration developed in the reaction mixture. This phenomenon was also observed by Gagnon and co-workers[6] during a study on the reduction of halonitroaromatics in alkaline solution. The color has been ascribed to impurities in the nitro compound, and in the case of *o*-chloronitrobenzene, has been shown to be due to the formation of a chlorotrihydroxydihydrophenazine.

An authentic sample of *N*-(*o*-chlorophenyl)alanine was prepared by heating 89 g. (0.68 mole) of *o*-chloroaniline and 100 g. (0.55 mole) of ethyl α-bromopropionate in a round-bottom flask on a steam bath for 4 hr. The hot solution was washed with water to remove the amine hydrobromide. The organic material was returned to the flask and refluxed with a solution of 50 g. (0.89 mole) of potassium hydroxide in 250 ml. of water. The cooled solution was extracted with ether, and the aqueous layer acidified. *N*-(*o*-Chlorophenyl)alanine was recovered in the amount of 82.1 g. (75.0%), m.p. 148.5–149.5°. *N*-(2,5-Dichlorophenyl)alanine prepared from 2,5-dichloroaniline by this method melted at 161–162.5°.

DAYTON 7, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Chemistry of Trinitromethane. I. Reactions with Unsaturated *N*-Methylolamides[1]

HENRY FEUER AND UNA E. LYNCH-HART

Received May 23, 1960

Unsaturated *N*-methylolamides, such as *N*-methylolmethacrylamide and *N*,*N'*-bis(methylol)fumaramide undergo a Mannich type reaction with trinitromethane to give *N*-trinitroethylmethacrylamide (II) and *N*,*N'*-bis(trinitroethyl)-fumaramide (X) respectively. The reaction of *N*-methylolacrylamide and trinitromethane affords *N*-trinitroethylacrylamide (IV) and *N*-methylol-4,4,4-trinitrobutanamide (VIII). Nitration of compounds II and IV yield *N*-nitro-*N*-trinitroethylmethacrylamide and *N*-nitro-*N*-trinitroethylacrylamide, respectively.

In 1953, we reported the preparation of unsaturated *N*-methylolamides.[2] The subject of this paper is their Mannich type reactions with trinitromethane (I).[3]

The synthesis of *N*-trinitroethylmethacrylamide (II) could not be accomplished by reacting methacrylamide with trinitroethanol or with a mixture of I and formaldehyde. Unstable oils were produced which were subsequently found to be reaction products of methacrylamide and I alone. However, treating *N*-methylolmethacrylamide (III) with I in aqueous medium gave compound II in an 80% crude yield.

The reaction of compounds III and I occurred over a wide *p*H range below 7. A *p*H range above 7 had to be avoided because it is well known that the trinitroethyl group is decomposed in basic medium to I and formaldehyde.[4] This also explains the failure to obtain II by reacting methacrylamide with I and formaldehyde, because the first step in this reaction, which is the formation of III, is base catalyzed[2] and the second step, the condensation of III with I can only proceed in acidic media.

The purification of II was difficult. The best results were obtained when small amounts of II (less than 2 g.) were treated at 2° with fuming nitric acid for 4 minutes and the mixture poured over crushed ice. Pure II decomposed on storage at 25° over a period of several months to a red semisolid. Upon nitrating II with a mixture of anhydrous nitric acid and trifluoroacetic anhydride, *N*-nitro-*N*-trinitroethylmethacrylamide was obtained as a stable compound which did not discolor starch-iodide paper when heated for one hour at 65°; nor did it decompose upon storage for one year at 25°.[5]

The synthesis of *N*-trinitroethylacrylamide (IV) was difficult because of the ease of addition of I across the double bond present in acrylamide (V) or in *N*-methylolacrylamide (VI). Fusion of V with

---

[1] From the Ph.D. Thesis of Una E. Lynch, Purdue University, 1952.

[2] H. Feuer and U. E. Lynch, *J. Am. Chem. Soc.*, **75**, 5027 (1953).

[3] After this work was completed, two patents were issued which deal with the reaction of saturated amides with I and formaldehyde. R. Schenck and G. A. Wetterholm, Swed. Patent **148,217**, Dec. 28, 1954, and Nitroglycerin Aktiebolaget, Brit. Patent **813,477**, May 21, 1959.

[4] J. Reinhart, J. G. Meitner, and R. W. Van Dolah, *J. Am. Chem. Soc.* **77**, 496 (1953).

[5] C. R. Koller (Ph.D. thesis, Purdue University, 1950) has found that the stability of compounds containing a *N*-trinitroethyl group can be increased considerably by its conversion to a *N*-nitro-*N*-trinitroethyl group.

trinitroethanol gave only 4,4,4-trinitrobutanamide trinitrobutanamide (VII). When VI was treated in aqueous medium with one equivalent of I at 5° there was obtained a mixture consisting of IV and *N*-methylol-4,4,4-trinitrobutanamide (VIII). Higher temperatures, afforded only compound VIII. This also was the case when the reactions were performed in acetic anhydride at 5° or at 25° in nitromethane containing anhydrous cupric sulfate. These conditions were chosen because it was hoped that the formation of compound IV would be favored in the presence of a dehydrating agent.

The separation of the mixture of compounds IV and VIII was accomplished by tedious fractionation from aqueous ethanol. From solvents such as ethylene chloride or benzene compounds IV and VIII co-crystallized yielding needles, m.p. 106–107°.

The structure of compound VIII was verified by its conversion to *N*,*N'*-methylenebis(4,4,4-trinitrobutanamide) (IX) on treatment with 4,4,4-trinitrobutanamide in acidic medium. Compound IX was also prepared by the addition of I to *N*,*N'*-methylenebisacrylamide.[2,6] Compound IX was converted to *N*,*N'*-dinitromethylenebis(4,4,4-trinitrobutanamide) on treatment with a mixture of anhydrous nitric acid and trifluoroacetic anhydride at 30°.

In contrast to compound II, IV did not decompose on standing at 25°. Compound IV was nitrated with fuming nitric acid at 20° to yield *N*-nitro-*N*-trinitroethylacrylamide. For the preparation of this compound the mixture consisting of compounds IV and VIII could be employed directly because the adduct VIII was decomposed to water soluble products during the nitration.

When compound VI was treated with two equivalents of I, *N*-trinitroethyl-4,4,4-trinitrobutanamide was obtained in almost quantitative yields.

The preparation of *N*,*N'*-bis(trinitroethyl)fumaramide (X) was accomplished in a manner similar to compounds II and IV. It was necessary to prepare the methylolamide[2] first and then treat it with I. Unlike the other *N*-methylol compounds, *N*,*N'*-bis(methylol)fumaramide (XI) did not react with aqueous solutions of I over a wide *p*H range. The reaction occurred only in the narrow *p*H range 0.55–0.85 as determined by potentiometric titration. Above and below this *p*H range violent decompositions occurred with the evolution of oxides of nitrogen. Furthermore, to obtain the optimum yield (50%) of X it was necessary to raise the reaction temperature to 70°; below this temperature XI was only sparingly soluble in water. The low yield of X was found to be due to partial demethylolation of XI at the required reaction conditions for the formation of X. The nitration of X was studied but it was not found possible to replace the amido hydrogens with nitro groups. Compound X was found to be unusually stable because even after treating it with fuming nitric acid at 80° for 24 hours, 90% of X was recovered.

Compound I added readily to *N*,*N'*-methylenebismethacrylamide to give *N*,*N'*-methylenebis(2-methyl-4,4,4-trinitrobutanamide). Further nitration of this compound was unsuccessful.

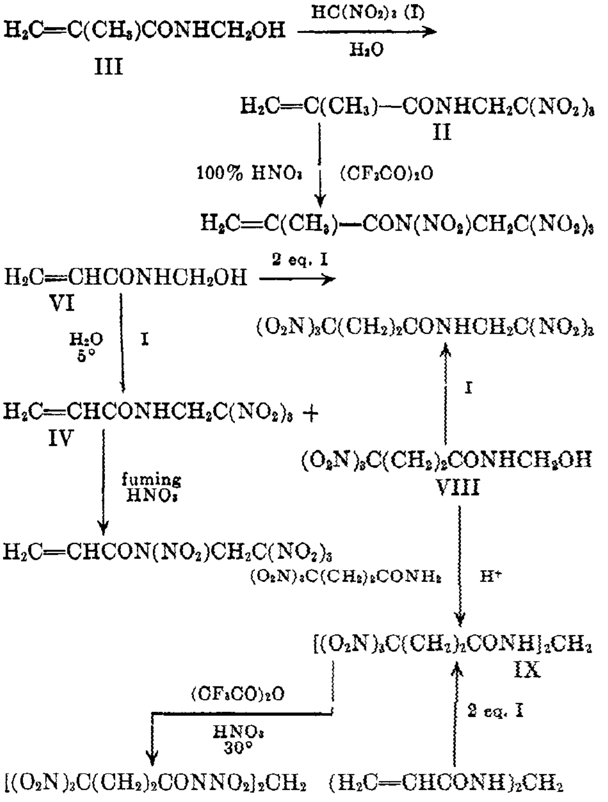

Fig. 1 Reactions of unsaturated *N*-methylolamides with trinitromethane

EXPERIMENTAL

Preparation of N-trinitroethylmethacrylamide (II). (a) *From N-methylolmethacrylamide* (III). In 50 ml. of ice water was dissolved 11.5 g. (0.10 mole) of *N*-methylolmethacrylamide. While this solution was stirred, a solution of 15.1 g. (0.10 mole) of trinitromethane in 50 ml. of cold water was slowly added over a period of 2 hr. The reaction mixture was stirred for 24 hr. at 25° and then filtered. The light yellow solid product which formed was filtered, washed with several portions of water, and dried *in vacuo*. It weighed 18.9 g. The deep red-colored filtrate was heated at 40° for 1 hr. and an additional 2.5 g. of product was obtained. Total yield was 21.4 g. (87%).

The crude product (m.p. 67–69°) can be purified by a number of methods. On a large scale, the best procedure is fractional crystallization from methylene chloride and pentane. Twelve g. of impure *N*-trinitroethylmethacrylamide was dissolved in 50 ml. of methylene chloride, and the solution was filtered. Pentane was added to the point of turbidity, and the cloudy solution was allowed to stand for 10 min. Some product separated from solution which was yellow-colored and slightly sticky. The supernatant liquid was carefully decanted, and more pentane was added to it. The second crop of product was obtained as almost white platelets, m.p. 73–74°. The mother liquor was again carefully decanted and pentane added to the point of turbidity. Pure *N*-trinitroethylmethacrylamide crystallized

---

(6) L. Lundbert, U. S. Patent 2,475,846 (1949).

from solution in the form of hexagonal platelets, m.p. 74–75°.

Anal. Calcd. for $C_6H_8N_4O_7$: C, 29.03; H, 3.20; N, 22.58. Found: C, 29.11; H, 3.14; N, 22.80.

This procedure can be successfully applied to the purification of very crude material, and the first fractions obtained are oils, and the last fraction, the fourth or fifth is pure II. Recrystallization is also possible from aqueous ethanol, but large losses of product result.

A small sample is most efficiently purified by dissolving it in fuming nitric acid at 2° and allowing the solution to stand at 2° for 4 min. before pouring it over crushed ice. The following experiment will illustrate this method.

One gram of crude, orange-colored *N*-trinitroethylmethacrylamide (m.p. 65–67°) was added to 1 ml. of fuming nitric acid at 2° and the solution was allowed to stand at this temperature for 4 min. Two drops of fuming sulfuric acid were added and the reaction mixture was allowed to stand at 4° for 2 min., before being poured over crushed ice. The product was washed and dried. After recrystallization from methylene chloride and pentane, 0.93 g. (93%) of white crystals, m.p. 73–74°, were obtained.

It is necessary to purify *N*-trinitroethylmethacrylamide carefully, otherwise it decomposes rapidly. The color of the impure product changes from yellow to orange on standing several days at 25°, and on being stored for 10 days, it is transformed into a red semisolid. The pure product, on the other hand, does not decompose appreciably in one month.

(b) *From the calcium chloride complex of N-methylolmethacrylamide.*[2] In 100 ml. of water was dissolved 21 g. of the calcium chloride complex of *N*-methylolmethacrylamide, and to this solution was added 18.9 g. (0.125 mole) of trinitromethane. The reaction mixture was warmed to 45° and allowed to stand for 12 hr. The solid which separated from solution was filtered, washed, and dried *in vacuo.* It weighed 25.4 g. (82% yield based on methacrylamide) and melted at 69–70°. After recrystallization from methylene chloride and pentane by the procedure given above, hexagonal platelets, m.p. 73–74° dec., were obtained.

Preparation of N-nitro-N-trinitroethylmethacrylamide. Trifluoroacetic anhydride (10 ml.) was placed in a 50-ml. three necked round bottom flask fitted with a calcium chloride drying tube. The liquid was cooled to −20° and 14 ml. of anhydrous nitric acid was slowly added with stirring. The nitrating medium was allowed to warm to −10° and 1.24 g. (5.0 mmoles) of pure *N*-trinitroethylmethacrylamide (m.p. 74–75°) was added. The temperature of the reaction mixture rose slowly to 0°, and then rapidly to 25°, despite being cooled in a Dry Ice–trichloroethylene bath. The temperature then dropped to 17° over a period of 2 min. After standing at 17° for 15 min., the mixture was very slowly poured over 200 ml. of crushed ice which was stirred rapidly. A cloudy solution was obtained from which the product crystallized after 3 hr. in the form of needles, m.p. 128–128.5°. After being thoroughly washed with water and dried, it weighed 0.62 g. (43% yield). Recrystallization from methylene chloride and pentane did not raise its melting point further.

Anal. Calcd. for $C_6H_7N_5O_9$: C, 24.58; H, 2.41; N, 23.94. Found: C, 24.54; H, 2.51; N, 23.92.

When this experiment was repeated using 6.0 g. (24 mmoles) of pure *N*-trinitroethylmethacrylamide, 30 ml. of trifluoroacetic anhydride and 40 ml. of anhydrous nitric acid, a 73% yield of crude product, m.p. 122–123°, was obtained when the nitration mixture was poured over 800 ml. of crushed ice. This time the product immediately separated from solution as a white solid. Upon recrystallization from methylene chloride and pentane, 2.49 g. (35% yield) of pure product was obtained. The first two fractions obtained melted at 118–120° and 122–123° respectively, and the third one was the pure product.

Preparation of N-methylol-4,4,4-trinitrobutanamide (VIII). In 5 ml. of acetic anhydride were dissolved 1.01 g. (0.01 mole) of *N*-methylolacrylamide and 1.51 g. (0.01 mole) of trinitromethane. The mixture was cooled to 5° and allowed to stand at this temperature for 48 hr. After this time, the color of the mixture had changed from yellow to red. When the reaction mixture was poured into 30 ml. of ice water, a yellow semisolid separated from solution which solidified on standing. The crude product weighed 1.94 g. and was recrystallized by dissolving it in chloroform and adding pentane to the point of turbidity to the filtered solution. The white crystalline solid, m.p. 132–133°, which separated from solution weighed 1.10 g. (44%).

Anal. Calcd. for $C_5H_8N_4O_8$: C, 23.82; H, 3.20; N, 22.22. Found: C, 24.13; H, 2.96; N, 22.21.

Preparation of N,N′-methylenebis(4,4,4-trinitrobutanamide) (IX). (a) *From N-methylol-4,4,4-trinitrobutanamide and 4,4,4-trinitrobutanamide.* To 1 ml. of ethylene chloride were added 0.10 g. (0.4 mmole) of *N*-methylol-4,4,4-trinitrobutanamide, 0.09 g. (0.4 mmole) of 4,4,4-trinitrobutanamide and 1 drop of concd. hydrochloric acid. Upon heating the mixture on a steam cone, the solids dissolved and after one-half hour, needles crystallized from solution. The mixture was cooled, and 90 mg. of *N,N′*-methylene-bis(4,4,4-trinitrobutanamide), m.p. 183–183.5°, was obtained after filtration. Upon evaporation of the filtrate almost to dryness, an additional 70 mg. of product having the same melting point was isolated. The total yield was 0.16 g. (94%).

(b) *From N,N′-methylenebisacrylamide and trinitromethane. N,N′*-Methylenebisacrylamide (3.45 g., 0.023 mole) was dissolved in 20 ml. of methanol and a solution of 6.77 g. (0.045 mole) of trinitromethane in 20 ml. of methanol was added slowly. The reaction mixture was warmed to 40° for an hour and then allowed to cool. Compound IX crystallized slowly from the solution in 80% yield, m.p. 183–184°. A mixed melting point determination with a sample of IX prepared by procedure (a) gave no depression.

Anal. Calcd. for $C_9H_{12}O_{14}N_8$: C, 23.68; H, 2.63; N, 24.56. Found: C, 24.01; H, 2.48; N, 24.23.

Preparation of N,N′-dinitro-N,N′-methylenebis(4,4,4-trinitrobutanamide). To 7 ml. of trifluoroacetic anhydride cooled to −10° was slowly added 5 ml. of anhydrous nitric acid. Compound IX (0.50 g., 1 mmole) was added to the mixture and the temperature was raised to 30° (oxides of nitrogen were evolved above 20°). After 5 min., the reaction mixture was poured over crushed ice, causing the precipitation of 0.24 g. (44% yield) of *N,N′*-dinitro-*N,N′*-methylenebis(4,4,4-trinitrobutanamide), m.p. 109–110°. After two recrystallizations from aqueous ethanol the melting point was raised to 110–110.5°.

Anal. Calcd. for $C_9H_{10}O_{18}N_{10}$: C, 19.78; H, 1.83; N, 25.64. Found: C, 20.11; H, 1.85; N, 25.43.

Reaction of N-methylolacrylamide with one equivalent of trinitromethane in aqueous solution. N-Methylolacrylamide (10.1 g., 0.10 mole) was dissolved in 30 ml. of distilled water at 0°. A solution of 15.1 g. (0.10 mole) of trinitromethane in 50 ml. of distilled water was added dropwise to the stirred, cooled solution of the methylol compound over a period of 8–10 hr. while the temperature of the reaction mixture was kept at 1–2° with an ice bath. After all the trinitromethane solution had been added, the reaction mixture was stirred for 48 hr. while maintaining the temperature below 5°. The white solid (A) which formed was filtered, washed, and dried. It weighed 16.9 g. and melted at 101–102°. The filtrate was stored for 10 days at 5° and an additional 2.15 g. of product (B), m.p. 96–97° was obtained. The solids produced were mixtures of *N*-trinitroethylacrylamide (IV) and *N*-methylol-4,4,4-trinitrobutanamide (VIII) which were separated by tedious fractional crystallizations which follow.

Ten grams of solid (A), m.p. 101–102° was dissolved in absolute ethanol and water was added to the point of turbidity. After standing at 5° for 4 hr., 0.60 g. of crystals, m.p. 126–127° were obtained. This operation was repeated three times and a total of 5.09 g. of compound VIII, m.p.

124–127°, was isolated. After recrystallization from chloroform, needles, m.p. 130–131°, were obtained.

When no more product was obtained by the addition of water to the alcoholic filtrate, the latter was evaporated *in vacuo* to one half its original volume, and 2.41 g. of very impure VIII, m.p. 114–117°, separated. It could not be crystallized from chloroform, but upon recrystallization from aqueous ethanol, its melting point was raised to 129–130°. This operation resulted in a considerable loss (50%) of material.

For the separation of *N*-trinitroethylacrylamide (IV), the following procedure had to be adopted. Upon recrystallization of the product, m.p. 101–102°, from chloroform, crystals were obtained which softened at 92–93° and melted at 105–106°. These crystals were dissolved in absolute ethanol after filtration of the solution and distilled water was added to the point of turbidity. The first crop of white crystals, melting at 106–107° was a mixture of compounds IV and VIII. Addition of more water to the filtrate yielded a second crop of crystals, m.p. 90–92°. Recrystallization of this material from chloroform yielded *N*-trinitroethylacrylamide, m.p. 90.5–91°.

Anal. Calcd. for $C_5H_6N_4O_7$: C, 25.63; H, 2.56; N, 23.94. Found: C, 25.58; H, 2.30; N, 23.5.

Solid (B), m.p. 96–97° was fractionated in the following way. Recrystallization from chloroform yielded 1.12 g. of pure IV. Evaporation of the filtrate in a stream of air to one half its original volume gave 0.53 g. of crystals, m.p. 101–102°. They were further purified by the procedure given above. The total yield of *N*-trinitroethylacrylamide which was isolated was 5% and the yield of *N*-methylol-4,4,4-trinitrobutyramide obtained was 22%.

Preparation of N-nitro-N-trinitroethylacrylamide. To 20 ml. of fuming nitric acid cooled to −20° was added 5.80 g. of a mixture of *N*-trinitroethylacrylamide and *N*-methylol-4,4,4-trinitrobutyramide, m.p. 101–102°. The temperature of the reaction was allowed to rise slowly to 20° and the solid dissolved. After standing at 20° for 0.5 hr., the mixture was poured over crushed ice. The white solid obtained, m.p. 155–156°, was thoroughly washed with water and dried. After two recrystallizations from aqueous ethanol, 0.40 g. (8% yield) of needles, m.p. 178–179°, were obtained. One more recrystallization from this solvent raised the melting point to 179–179.5°.

Anal. Calcd. for $C_5H_5N_5O_9$: C, 21.51; H, 1.79; N, 25.09. Found: C, 21.52; H, 1.83; N, 24.95.

Preparation of N-trinitroethyl-4,4,4-trinitrobutanamide. (a) *From N-methylolacrylamide and two equivalents of trinitromethane.* To a solution of 6.3 g. (0.063 mole) of *N*-methylolacrylamide dissolved in 25 ml. of absolute ethanol was added 18.6 g. (0.125 mole) of trinitromethane. The temperature of the reaction mixture rose rapidly to 60° and the solution was cooled in an ice bath. After standing for 12 hr. at 25°, the solvent was removed *in vacuo*, leaving an oil. This oil crystallized on standing at 5° and after being washed with water and dried yielded 19.9 g. (88%) of *N*-trinitroethyl-4,4,4-trinitrobutanamide, m.p. 150–151°. Upon recrystallization from ethylene chloride, needles, m.p. 152–152.5° were obtained.

Anal. Calcd. for $C_6H_7N_7O_{13}$: C, 18.71; H, 1.82; N, 25.42. Found: C, 18.36; H, 1.89; N, 25.38.

(b) *From N-methylol-4,4,4-trinitrobutanamide and trinitromethane.* *N*-Methylol-4,4,4-trinitrobutanamide (50 mg., 0.2 mmole) and trinitromethane (30 mg., 0.2 mmole) were dissolved in 1 ml. of methanol. The solution was gently heated on a steam cone for 5 min. and water was added to the point of turbidity. Upon standing for 12 hr., 60 mg. (80%) of *N*-trinitroethyl-4,4,4-trinitrobutanamide, m.p. 150-151°, crystallized from solution in the form of long, white needles.

Preparation of N,N′-bis(trinitroethyl)fumaramide (X). In 7 ml. of distilled water was dissolved 1.05 g. (6.95 mmoles) of trinitromethane and the *p*H of this solution was adjusted to 0.7–0.8 by the addition of barium hydroxide. The solution was then heated to 70° and 0.20 g. (1.15 mmoles) of *N*,*N*′-bis(methylol)fumaramide was added. After heating the reaction mixture for 5 min., the solution turned red and small needle-like crystals appeared. The *p*H was continuously adjusted to 0.7–0.8 by the dropwise addition of hydrochloric acid while the mixture was heated for 90 min. The suspension was cooled, and the insoluble solid was filtered, thoroughly washed with water, and dried. The yield was 0.24 g. (48%). After recrystallization by dissolving the solid in dioxane and adding water to the point of turbidity, needles, m.p. 212° dec., were obtained.

Anal. Calcd. for $C_8H_8N_8O_{14}$: C, 21.78; H, 1.83; N, 25.45. Found: C, 21.92; H, 1.83; N, 25.42.

Preparation of N,N′-methylenebis(2-methyl-4,4,4-trinitrobutanamide). *N*,*N*′-Methylenebismethacrylamide (1.0 g., 5 mmoles) was added to a solution of 1.5 g. (10 mmoles) of trinitromethane in 15 ml. of water. The reaction mixture was heated at 50° for 10 min. and a semisolid material separated from the solution. It solidified after standing for several hours at 5° and amounted to 1.6 g. (64% yield). Purification was accomplished either by recrystallizing it from ethylene chloride or aqueous ethanol, or by dissolving it in a mixture of fuming nitric and sulfuric acids at 45° and then pouring the solution over crushed ice. The melting point of pure *N*,*N*′-methylenebis(2-methyl-4,4,4-trinitrobutanamide) is 179–179.5°.

Anal. Calcd. for $C_{11}H_{16}O_{14}N_8$: C, 27.30; H, 3.33; N, 23.14. Found: C, 27.23; H, 3.49; N, 23.00.

Acknowledgment. We are indebted to the Office of Naval Research for the financial support of this work.

LAFAYETTE, IND.