Fraction C melted at 101.5–102.7° and was identical with authentic[7] *p-bromophenacyl chloroacetate* (m.p. 102.0–103.2°, lit.[7] m.p. 103.7°) by the criteria of mixture melting point and infrared spectral comparison. It amounted to 0.050 g. (16% on diene III).

Fraction B melted at 120.7–121.5° and was identical with an authentic sample of *p*-bromophenacyl β,β-dichloroacrylate by the criteria of mixture melting point and infrared spectral comparison. It amounted to 0.070 g. (19% on diene III).

Authentic *p-bromophenacyl β,β-dichloroacrylate* (m.p. 121.5–122.0°) was prepared by standard procedures[8] from β,β-dichloroacrylic acid (m.p. 74–75°, lit.[9] m.p. 76–76.5°) which was obtained as described by Levas.[9]

*Anal.* Calcd. for $C_{11}H_7BrCl_2O_3$: C, 39.08; H, 2.09. Found: C, 38.71; H, 2.30.

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(7) H. Lund and T. Langvad, *J. Am. Chem. Soc.*, **54**, 4107 (1932).

(8) Ref. 5, p. 200.

(9) M. Levas, *Ann. Chim.* [12], **7**, 713 (1952).

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# The Chemistry of Trinitromethane. II. Reactions with Esters of Unsaturated *N*-Methylolamides[1]

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*Received May 23, 1960*

Benzoate esters of various saturated *N*-methylolamides have been prepared for purposes of identification[2], but the reactions of these esters have apparently not been investigated. This note reports the results of the investigation of the reactions of esters of unsaturated *N*-methylolamides with trinitromethane (I) in polar and nonpolar solvents.

In an attempt to add compound I to *N*,*N*′-bis(benzoxymethyl)fumaramide[3](II) the desired reaction did not occur. Instead, the ester was cleaved and the only products isolated were benzoic acid (III) and *N*,*N*′-bis(trinitroethyl)fumaramide[4] (IV). The same products were obtained when two or three equivalents of compound I were employed. The reaction was carried out in nitromethane because it was the only solvent in which compound II was found to be appreciably soluble. (When a mixture of benzene and carbon tetrachloride was employed, ester II was recovered quantitatively). The formation of compound IV from the interaction of compounds I and II must have involved alkyl-oxygen fission. If ester I had undergone the usual acyl-oxygen fission, characteristic of esters of primary alcohols, the products would have been trinitromethyl phenyl ketone and *N*,*N*′-bis(methylol)fumaramide.

*N*,*N*′-Bis(acetoxymethyl)fumaramide,[3] for which no suitable solvent could be found was recovered unchanged when treated with compound I in a variety of organic solvents. When water was used as a solvent at 100° vigorous decomposition was observed. A small amount (2%) of compound IV was isolated and 90% of the ester was recovered unchanged. The formation of compound IV from the acetate ester on prolonged heating in water may not involve the same mechanism as the cleavage of the benzoate ester (II) under anhydrous conditions. It was observed that some of the acetate ester was cleaved by boiling water alone to *N*,*N*′-bis(methylol)fumaramide, and it has been established[4] that this compound reacts with compound I in a Mannich type reaction to yield compound IV.

The reaction of *N*-benzoxymethylmethacrylamide (V) with compound I to yield *N*-trinitroethylmethacrylamide (VI) and compound III occurred at 25° in anhydrous ethylene chloride as well as in water. The highest yield (65%) of compound VI was obtained when ester V was treated with two equivalents of compound I for three hours at 25°. When the reaction time was increased to twelve hours, compound III was obtained in an almost quantitative yield but none of compound VI. The only other product was a noncrystallizable red oil which probably was formed from a secondary reaction of compound VI with compound I. For we had observed that samples of compound VI, contaminated with compound I, decompose on standing to a noncrystallizable red oil.

In aqueous solution at 25° compound V reacted with compound I in thirty minutes to give compounds III and VI in yields of 33% and 63% respectively.

$$\underset{\text{V}}{H_2C{=}C(CH_3)CONHCH_2OCOC_6H_5} + \underset{\text{I}}{HC(NO_2)_3} \xrightarrow[25^\circ]{(CH_2Cl)_2 \text{ or } H_2O} \underset{\text{III}}{C_6H_5CO_2H} + \underset{\text{VI}}{H_2C{=}C(CH_3)CONHCH_2C(NO_2)_3}$$

In the case of *N*-benzoxymethylacrylamide (VII), no cleavage of this ester occurred at 40° in the absence of a solvent, instead compound I added across the double bond with the formation of *N*-benzoxymethyl-4,4,4-trinitrobutanamide (VIII).

$$\underset{\text{VII}}{H_2C = CHCONHCH_2OCOC_6H_5} \xrightarrow[40^\circ]{\text{I}} \underset{\text{VIII}}{(O_2N)_3C(CH_2)_2CONHCH_2OCOC_6H_5}$$

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(1) From the Ph.D. thesis of Una E. Lynch, Purdue University, 1952.

(2) A. Einhorn and R. Feibelmann, *Ann.*, **361**, 141 (1908).

(3) H. Feuer and Una E. Lynch, *J. Am. Chem. Soc.*, **75**, 5027 (1953).

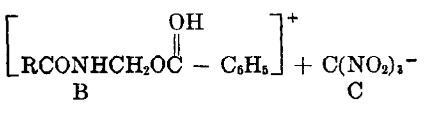
(4) H. Feuer and Una E. Lynch-Hart, *J. Org. Chem.*, **26**, 391 (1961).

The results of the reactions of compounds VII and I in various solvents are summarized in Table I. The experiments indicate that the cleavage of the ester VII occurs in polar and non-polar solvents. The products isolated were, besides compound III, compound VIII and *N*-trinitroethyl-4,4,4-trinitrobutanamide (IX). The formation of compound VIII was of course due to the rapid addition of compound I to the unsaturated ester VII. That this addition is faster than the ester cleavage is indicated by the results of the experiments in which only one equivalent of compound I was employed. In all these runs, in addition to compounds III and IX, ester VIII was isolated. When two equivalents of compound I were employed, only compounds III and IX were obtained, except when the solvent was water. In this case ester VIII was also isolated, because it precipitated during the reaction and was therefore cleaved more slowly to compound IX.

$$VII + I \longrightarrow \underset{IX}{(O_2N)_3C(CH_2)_2CONHCH_2C(NO_2)_3} + III + VIII$$

The mechanism of the cleavage reaction is not known, although it must involve fission of the alkyl oxygen bond. The reaction may occur by a displacement of the benzoate ion by the trinitromethide ion in an $S_N2$ type reaction. Evidence for the formation of the trinitromethide ion has been observed even in an anhydrous ethylene chloride solution. Compound IV is colorless in an ethylene chloride solution, but a yellow color develops when this solution is added to a colorless solution of *N*-benzoxymethylamide. Thus the following steps might be involved. The ionization of IV occurs by the acceptance of the proton by the ester, as indicated in step (1). The trinitromethide ion then attacks an unprotonated ester molecule in step (2), and in the final step a proton is transferred from the conjugate acid of the ester to the benzoate ion.

$$\underset{A}{R-CONHCH_2OCOC_6H_5} + HC(NO_2)_3 \rightleftarrows$$



$$\underset{B}{\left[RCONHCH_2O\overset{\overset{OH}{\|}}{C}-C_6H_5\right]^+} + \underset{C}{C(NO_2)_3^-} \qquad (1)$$

$$A + C \rightleftarrows RCONHCH_2C(NO_2)_3 + \underset{D}{C_6H_5CO_2^-} \qquad (2)$$

$$B + D \longrightarrow A + C_6H_5CO_2H \qquad (3)$$

Another possible mechanism involves an $S_N1$ type reaction with the intermediate formation of a resonance stabilized carbonium ion from the conjugate acid B.

TABLE I

REACTION OF *N*-BENZOXYMETHYLACRYLAMIDE WITH TRINITROMETHANE

| Equiv.[a] TNM | Solvent | Reaction Temp. | Reaction Time, Min. | Yield of A,[b] % | Yield of B,[c] % | Yield of C,[d] % |
|---|---|---|---|---|---|---|
| 2[e] | $CH_3NO_2$ | 101 | 15 | — | 70 | 49 |
| 1 | $CH_3NO_2$ | 101 | 30 | 19 | 69 | 12 |
| 2 | $(CH_2Cl)_2$ | 83 | 30 | — | 76 | 43 |
| 1 | $(CH_2Cl)_2$ | 83 | 30 | 22 | 46 | 4 |
| 2 | $C_2H_5OH$ | 78 | 30 | — | 66 | 55 |
| 2 | $H_2O$ | 25 | 240 | 47 | 34 | 10 |

[a] TNM, Trinitromethane. [b] A, Benzoxymethyl-4,4,4-trinitrobutanamide. [c] B, Benzoic acid. [d] C, *N*-Trinitroethyl-4,4,4-trinitrobutanamide. [e] Vigorous decomposition occurred with the evolution of oxides of nitrogen.

## EXPERIMENTAL

*Reaction of N,N'-bis(benzoxymethyl)fumaramide with trinitromethane.* N,N'-Bis(benzoxymethyl)fumaramide (0.38 g., 1.0 mmole) and trinitromethane (0.45 g., 3.0 mmoles) were dissolved in 50 ml. of dry, pure nitromethane. The solution was refluxed for 4 hr. and the solvent was then removed *in vacuo*. The solid residue was extracted with boiling carbon tetrachloride and upon evaporation of the solvent a yellow solid (66% yield) remained. It melted at 120–121° after recrystallization from petroleum ether (b.p. 50–60°), and was identified as benzoic acid. A mixed melting point with a pure sample of benzoic acid was not depressed.

The part of the residue which was insoluble in carbon tetrachloride was dissolved in absolute ethanol and upon the addition of water to the point of turbidity, 0.20 g. (47%) of solid, m.p. 197° dec. crystallized. It was identified as *N,N'-bis(trinitroethyl)fumaramide* (IV). A mixed melting point with an authentic sample[4] was not depressed.

*Reaction of N,N'-bis(acetoxymethyl)fumaramide with trinitromethane* (I). To 0.52 g. (2.0 mmoles) of *N,N'*-bis(acetoxymethyl)fumaramide was added a solution of 0.60 g. (4.0 mmoles) of compound I in 15 ml. of water. The reaction mixture was heated under reflux for 25 min., after which time the color of the solution changed from yellow to orange, and oxides of nitrogen were vigorously evolved. The suspension was cooled and filtered, yielding 0.47 g. of ester (90% recovery). A solid crystallized from the filtrate after several hours. After recrystallization from aqueous ethanol, 20 mg. (2% yield) of compound IV, m.p. 212° dec., was isolated. A mixed melting point with an authentic sample of this compound was not depressed.

*Reaction of N-benzoxymethylmethacrylamide* (V) *with one equivalent of trinitromethane* (I). *a. In ethylene chloride solution.* To 15 ml. of dry ethylene chloride were added 2.16 g. (0.01 mole) of compound V and 1.51 g. (0.01 mole) of compound I. Upon the addition of compound I, a yellow color developed. The solution was allowed to stand for 12 hr. at 25°, after which time the color had changed to orange. After the solvent was removed *in vacuo*, the orange semisolid residue was extracted twice with 20-ml. portions of boiling petroleum ether (b.p. 60–70°) and the supernatant liquid was carefully decanted from the insoluble red oil. Evaporation of the combined extracts almost to dryness yielded 1.12 g. (92%) of benzoic acid, m.p. 120–121°. A mixed melting point with an authentic sample of this acid was 121–122°.

The red oil which was insoluble in petroleum ether was dissolved in methylene chloride and this solution was filtered. Pentane was added to the clear filtrate to the point of turbidity, yielding 0.17 g. of an amber oil. The supernatant liquid was carefully decanted from the oil, and more pentane was added to it. A lighter colored oil separated from solution which weighed 0.22 g. When this procedure was repeated a third time, 0.06 g. of a light yellow oil was obtained. From the fourth fraction, 0.27 g. of crude *N*-trinitroethylmethacrylamide (VI), m.p. 65–67° crystallized. A mixed melting point with an authentic sample,[4] m.p.

73–74° was 70–71°. Addition of more pentane to the filtrate from these crystals yielded 0.98 g. of compound VI, m.p. 70–71°, which separated from solution in the form of hexagonal platelets. The melting point of a mixture of this material with an authentic sample of compound VI was not depressed. The total yield of compound VI was 50%.

The oils obtained could not be crystallized from methylene chloride and pentane, nor from aqueous ethanol. Seeding with crystals of pure compound VI did not induce crystallization.

(*b*) *In water.* In 20 ml. of water was suspended 2.16 g. (0.01 mole) of ester V and 1.51 g. (0.01 mole) of compound I was added. The suspension was stirred at 25° for 0.5 hr., after which time a change in crystalline form occurred, and short needles appeared. The solid was filtered and weighed 2.15 g. It was extracted twice with 20 ml. of boiling petroleum ether (b.p. 50–60°), and the supernatent liquid was carefully decanted from the oil which formed. From these extracts 1.01 g. (83%) of benzoic acid, m.p. 119–120° was isolated. A mixed melting point of this solid with an authentic sample of benzoic acid was 121–122°.

The oil which was insoluble in petroleum ether was dissolved in methylene chloride and the solution was filtered. To the filtrate pentane was added to the point of turbidity, and an oil separated from solution. The supernatant liquid was carefully decanted, and this procedure was repeated twice yielding progressively lighter-colored oils. When this operation was carried out for the third time 0.52 g. of colorless hexagonal platelets of compound VI slowly crystallized from solution, m.p. 69–70°. A mixed melting point with an authentic sample of this compound was 71–72°.

From the original aqueous filtrate of the reaction mixture, 1.06 g. of pure compound VI, m.p. 73–74°, crystallized upon standing for 24 hr.

The total yield of compound VI was 1.58 g. (64%).

*Reaction of ester* V *with two equivalents of compound* I. Ester V (2.16 g., 0.01 mole) and compound I (3.02 g., 0.01 mole) were added to 15 ml. of dry ethylene chloride and the solution was allowed to stand for 3 hr. at 25°.

The solvent was removed *in vacuo,* and the light yellow solid residue was extracted twice with 20-ml. portions of petroleum ether (b.p. 50–60°). The solid obtained upon evaporation of the petroleum ether weighed 1.55 g. and was a mixture. Separation was achieved by dissolution in absolute ethanol and addition of water to the point of turbidity. The first crop of crystals which precipitated was unreacted ester V, m.p. 87–88°, and weighed 0.35 g. (16%). Partial evaporation of the filtrate *in vacuo* yielded 0.70 g. (57%) of benzoic acid, m.p. 121–122°.

The residue which was insoluble in petroleum ether was fractionated from methylene chloride and pentane by the procedure given above. Again the first three fractions were oils, weighing 0.22 g., 0.10 g., and 0.11 g., respectively. The fourth fraction was slightly impure compound VI, m.p. 67–68°, and weighed 0.37 g. The fifth fraction separated as colorless crystals, m.p. 72–73°, which weighed 1.24 g. The total yield of compound VI was 1.61 g. (65%).

*Reaction of N-benzoxymethylacrylamide* (VII) *with compound* I. Ester VII (2.02 g., 0.01 mole) was heated under reflux in 15 ml. of dry ethylene chloride with 1.51 g. (0.01 mole) of compound I. After 30 min., heating was discontinued because the evolution of oxides of nitrogen was observed. The reaction mixture was allowed to cool and the solvent was removed *in vacuo.* The residue was extracted several times with petroleum ether (b.p. 50–60°) from which 0.56 g. (46%) of benzoic acid was isolated upon evaporation almost to dryness.

The residue which was insoluble in petroleum ether was extracted with hot chloroform. The part of the solid which was insoluble in chloroform melted at 146–147°, and was identified as *N*-trinitroethyl-4,4,4-trinitrobutanamide[4] (IX) by a mixed melting point determination with an authentic sample which gave no depression. It weighed 0.15 g. (4% yield). From the chloroform extract an oil separated on cooling which slowly crystallized, yielding 1.14 g. of solid, m.p. 85–90°. After three recrystallizations from absolute ethanol, *N*-benzoxymethyl-4,4,4-trinitrobutanamide (VIII), m.p. 132–133°, was obtained. A mixed melting point determination with an authentic sample of this compound was not depressed. Evaporation of the chloroform filtrate yielded a sticky, orange product from which more compound VIII was obtained after several crystallizations from absolute ethanol. The total yield of compound VIII was 0.68 g. (22%).

*Preparation of N-benzoxymethyl-4,4,4-trinitrobutanamide* (VIII). Ester VII (0.20 g., 1.0 mmole) and 0.15 g. (1.0 mmole) compound I were fused by gentle heating on a steam cone to a yellow liquid. It solidified on cooling, and after recrystallization from benzene, 0.29 g. (83% yield) of *N-benzoxymethyl-4,4,4-trinitrobutanamide* (VIII), m.p. 126–127° was obtained. Two additional recrystallizations from aqueous ethanol raised the m.p. to 133–133.5°.

*Anal.* Calcd. for $C_{12}H_{12}O_9N_4$: C, 40.45; H, 3.40; N, 15.73. Found: C, 40.58; H, 3.36; N, 15.76.

*Acknowledgment.* The authors are indebted to the Office of Naval Research for the financial support of this work.

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## 1,1-Bis(2-hydroxyethyl)hydrazones

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*Received March 23, 1960*

Although 1,1-bis(2-hydroxyethyl)hydrazine (I) has been reported[1] as an unisolated product from the reaction of ethylene oxide and hydrazine hydrate, neither it nor any of its derivatives have been isolated and identified as pure chemical individuals. The reaction of diethanolamine with chloroamine, using the techniques previously described[2,3] for other secondary amines, offers an unexplored synthetic route to this hydrazine and its derivatives.

Our study of this reaction has shown that the hydrazine (I) is formed from chloroamine and diethanolamine and can be isolated in the form of certain hydrazone derivatives. Other hydrazone derivatives are thermally unstable, as is also the hydrazine (I) itself, and cannot be isolated. The yields, 9–94%, and characteristics of twelve such hydrazones are given in Table I. Higher alkyl derivatives, such as that from undecanal, undergo decomposition at temperatures required for distillation. The phenyl and pyridyl derivatives must be carefully fractionated to avoid decomposition. 2-Ethoxypropanal, methacrylaldehyde, tiglaldehyde, alkoxybenzaldehydes, and naphthaldehyde gave

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