## REACTION OF ALIPHATIC POLYNITRO COMPOUNDS

# WITH METAL HALIDES

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Previously we have briefly reported that the nitro group is replaced by the halogen atom (chlorine, bromine) when polynitro compounds are reacted with alkali metal halides (LiCl, KCl, KBr, etc.) in the medium of various aprotic dipolar solvents (dimethylformamide (DMF), acetone, acetonitrile) [1]. The present paper is devoted to a more detailed study of the reaction of metal halides with aliphatic polynitro compounds.

We found that replacement of the nitro group by the halogen atom (chlorine, bromine) is a general reaction in the series of aliphatic polynitro compounds, and proceeds both in aprotic dipolar solvents (DMF, acetone, acetonitrile) and in hydroxyl-containing solvents (methanol, ethanol, ethylene glycol).

Thus, from the reaction products of tetranitromethane with LiCl, KCl, RbCl, and CsCl in the medium of aprotic dipolar solvents was isolated chlorotrinitromethane in satisfactory yield (40-50%)

$$C(NO_2)_4 + MCI \rightarrow CIC(NO_2)_3 + MNO_2.$$
<sup>(1)</sup>

Dichlorodinitromethane is formed in 30% yield when a double excess of LiCl in DMF is used. Fluorotrinitromethane, chlorotrinitromethane and 1,1,1-trinitroethane were respectively converted to fluorodinitromethane, dichlorodinitromethane and 1-chloro-1,1-dinitroethane in an analogous manner and in approximately the same yields. Reaction between tetranitromethane and LiCl fails to go when dioxane is used as the solvent, despite the more drastic experimental conditions employed. However, vigorous reaction sets in when a small amount of DMF is added, and chlorotrinitromethane is formed in 50% yield.

Replacement of the nitro group by the chlorine atom under the influence of LiCl in hydroxyl-containing solvents (methanol, ethanol, ethylene glycol) proceeds much more slowly than in aprotic dipolar solvents, and requires higher temperatures and a larger excess of the metal chloride. For example, the reaction of tetranitromethane with a threefold amount of LiCl in refluxing 96% ethanol gave us chlorotrinitromethane in 44.5% yield; the yield of chlorotrinitromethane was low when equimolar amounts of the reactants were used in methanol, ethanol (at reflux), and ethylene glycol ( $100^{\circ}$ C); the compound could be recorded only by the GLC method.

The relatively low yields (40-50%) of the chloropolynitro compounds are apparently associated with the fact that the nitrite ion, formed in reaction (1), reacts with the starting polynitro compound [2, 3]

$$\mathrm{RC}(\mathrm{NO}_2)_2 + \mathrm{NO}_2^- \to \mathrm{RC}(\mathrm{NO}_2)_2^- + \mathrm{N}_2\mathrm{O}_4$$
<sup>(2)</sup>

The anion of the polynitro compounds under the reaction conditions — in aprotic dipolar solvents — decomposes to nitrogen oxides and carbon dioxide, which we also observed in the experiments. Confirmation of this is the fact that, for example, when tetranitromethane was reacted with LiCl in acetone\* we were able to record up to 10% of the trinitromethane anion by the spectrophotometric method, while in alcohol, where the anion is more stable, its amount is approximately 38%.

\*Besides this, when the reaction is run in acetone there is formed diacetone alcohol – the condensation product of acetone under the influence of alkaline agents [4]. We also detected  $\alpha$ -chloro- $\alpha$ -isonitroso-acetone in the reaction products.

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The formation of the anions of polynitro compounds under the influence of nitrite ion in protonic polar solvents, and their decomposition in aprotic solvents, was proved by us by special experiments. Thus, the vigorous evolution of nitrogen oxides and other gases begins when tetranitromethane is mixed with an acetone solution of  $LiNO_2$  (two equivalents), and within an hour the starting tetranitromethane can no longer be detected in the mixture, while the amount of the trinitromethane anion is approximately 10% (in the absence of  $LiNO_2$  the tetranitromethane remains without any special change even after refluxing for 10 h in acetone). The trinitromethyl anion is formed in 95% yield within an hour when tetranitromethane is reacted with two equivalents of  $LiNO_2$  in refluxing alcohol.

For a comparative<sup>\*</sup> qualitative estimate of using metal chlorides we studied the reaction of tetranitromethane with LiCl, KCl, RbCl, and CsCl in DMF under close initial conditions ( $30^{\circ}$ , approximately a 20% excess of the metal chloride). It was found that the reaction with LiCl is practically ended in 15-20 min, while the yield of chlorotrinitromethane is approximately 40%. In the reaction with KCl, RbCl, and CsCl the tetranitromethane is consumed at a much slower rate: in the first case the process is ended in 8 h, while in the case of RbCl and CsCl it is ended in 4 h. † The yield of chlorotrinitromethane is 57-60%. The comparative experiments using various solvents (DMF, acetone, acetonitrile) disclosed that the reaction of tetranitromethane with LiCl ( $50^{\circ}$ ) is ended in DMF in less than 10 min (the yield of chlorotrinitromethane is 40%), in acetone it is ended in 80 min (45% yield), while in acetonitrile 4.5 h is necessary to complete the reaction (56% yield).

In addition, experiments were run in which we compared the reaction of four different polynitro compounds (tetranitromethane, fluorotrinitromethane, chlorotrinitromethane and 1,1,1-trinitroethane) with LiCl in DMF at 30°. It was found that in the same length of time (30 min) the reaction of tetranitromethane is ended completely, fluorotrinitromethane is consumed to the extent of 70%, chlorotrinitromethane is consumed a total of only 40%, while 1,1,1-trinitroethane does not react at all under these conditions. For a successful progress of the reaction with 1,1,1-trinitroethane it is necessary to employ long heating (about 20 h) at a higher temperature (80-85°). The yield of 1-chloro-1,1-dinitroethane under such conditions is approximately 40%.

Bromotrinitromethane reacts differently with metal chlorides than do tetranitromethane, chlorotrinitromethane, and fluorotrinitromethane. Thus, the reaction of LiCl with bromotrinitromethane in either DMF or 96% alcohol gives chlorotrinitromethane in 50-60% yield, instead of the expected chlorobromodinitromethane. When this reaction was run in DMF we detected (by the GLC method) dichlorodinitromethane as an impurity in the chlorotrinitromethane, the amount of which increases with increase in the temperature. As a result, exchange of the bromine atom by chlorine occurs in the case of bromotrinitromethane.

Next we studied the reaction of polynitro compounds with metal bromides in various solvents. Replacement of a nitro group in tetranitromethane, fluorotrinitromethane, and bromotrinitromethane by the bromine atom occurs when reaction is with metal bromides (KBr, LiBr). This reaction goes both in aprotic dipolar solvents and in hydroxyl-containing solvents. The yields of the corresponding bromo derivatives are comparatively low. Thus, bromotrinitromethane is formed from tetranitromethane in DMF in approximately 23% yield, while in acetone or alcohol the yield is approximately 30%. In all cases dibromodinitromethane was recorded as being a second reaction product, the yield of which is approximately 6-18%. Dibromodinitromethane is the sole reaction product (40% yield) when excess LiBr is used (in refluxing 96% alcohol). The yield of dibromodinitromethane from bromotrinitromethane in alcohol is 52%. The yield of fluorobromodinitromethane from fluorotrinitromethane in DMF is 15-25%, while in acetone it is approximately 40%.

The comparatively low yields of the corresponding bromo derivatives are explained, on the one hand, by the reaction of the starting polynitro compound and the formed bromo derivative with the nitrite ion (Scheme 2), and on the other hand, by the oxidation — reduction reaction between the bromopolynitro compound and metal bromides:

$$RC(NO_2)_2Br + MBr \rightleftharpoons Br_2 + RC(NO_2)_2^{-M^+}.$$
(3)

<sup>\*</sup>In running the comparative experiments using various metal halides, solvents, and polynitro compounds we employed the spectrophotometric method to follow the course of the reaction. The given yields were calculated on the basis of the data of the UV spectra.

<sup>†</sup>The reaction of tetranitromethane with LiCl in DMF proceeds under homogeneous conditions, while with KCl, RbCl, and CsCl it proceeds under heterogeneous conditions.

Confirmation of the above said is the fact that when the reaction is run in DMF a sharp increase in the temperature is observed, which is accompanied by the brisk evolution of nitrogen oxides, probably, due to decomposition of the anions of the polynitro compounds, and free bromine<sup>†</sup> always appears in the reaction products.

Chlorotrinitromethane reacts with LiBr in a different manner than do tetranitromethane or the fluoroand bromotrinitromethanes. Bromotrinitromethane was isolated in 40% yield when chlorotrinitromethane was reacted with LiBr in 96% ethanol.

As a result, replacement of the chlorine atom by the bromine atoms occurs here. This fact, together with the above described reaction of bromotrinitromethane with LiCl, serves as evidence that we were able to observe a new type of reaction for aliphatic  $\alpha$ -halopolynitro compounds, namely the reciprocal exchange of halogen atoms under the influence of nucleophilic agents (halide anions); this reaction, as is clear from our experiments, bears a reversible character (see [5] for more details on this reaction)

 $BrC(NO_2)_3 + LiCl \simeq ClC(NO_2)_3 + LiBr.$ 

## EXPERIMENTAL

In all of the experiments the reaction products were characterized by the melting point, refractive index and the GLC method. The methods, designated by an \*, may be recommended as being preparative methods.

## Reaction of Tetranitromethane (TNM) with

### Metal Chlorides

With Lithium Chloride in Dimethylformamide (DMF) Medium<sup>\*</sup>. (Expt. a). To a solution of 19.6 g of TNM in 20 ml of dry DMF, with stirring and cooling in ice water, was added a solution of 4.67 g of freshly ignited LiCl in 50 ml of dry DMF at such a rate that the temperature of the reaction mixture did not exceed  $30^{\circ}$  (~10 min). The reaction goes with the evolution of nitrogen oxides and other gases. The solution was stirred for 40 min at  $30^{\circ}$  and then poured into 400 ml of ice water. The obtained oil was extracted with ether (4×50 ml), and the combined ether extracts were washed with water (4×50 ml) and dried over anhydrous MgSO<sub>4</sub>. The ether was removed under reduced pressure. The residue was distilled. We obtained 7.29 g (39.3%) of chromatographically pure chlorotrinitromethane, bp 55-56° (40 mm);  $n_D^{20}$  1.4500. From [6]: bp 56° (40 mm);  $n_D^{20}$  1.4500.

(Expt. b). To a solution of 10.4 g of freshly ignited LiCl in 100 ml of dry DMF, with stirring and cooling in water, was added 19.6 g of TNM, maintaining the temperature of the reaction mixture at 50-55° (~1 h). Then the mixture was stirred for another 4 h at 50-55°, cooled, and poured into 400 ml of water. The obtained oil was extracted with ether (4×50 ml), and the combined ether extracts were washed in succession with 5% Na<sub>2</sub>CO<sub>3</sub> solution (3×30 ml) and water (2×50 ml), and dried over anhydrous MgSO<sub>4</sub>. The ether was removed at atmospheric pressure, using a fractionating column with a length of at least 25 cm. The residue was vacuum-distilled. We obtained 5.14 g (29.4%) of chromatographically pure dichlorodinitromethane, bp 54-56° (50 mm);  $n_D^{20}$  1.4560. From [7]: bp 54-56° (50 mm);  $n_D^{20}$  1.4560.

With the Chlorides of Potassium, Rubidium, and Cesium in DMF Medium\*. To a suspension of 8.95 g of finely ground KCl, freshly ignited in vacuo at 300°, in 48 ml of dry DMF, with stirring and cooling in water, was added at one time 19.6 g of TNM. The mixture was stirred at 30° for 8 h. The remainder of the workup was the same as in Expt.a. We isolated 9.3 g (50%) of chromatographically pure chlorotrinitromethane.

The use of RbCl and CsCl respectively gave, after holding for 4 h, 49 and 48.6% of chromatographically pure chlorotrinitromethane.

With Lithium Chloride in Acetone, Acetonitrile, or a Mixture of Dioxane and DMF. To a suspension of 5.1 g of finely ground LiCl, freshly ignited at approximately 300°, in 48 ml of dry acetone, with stirring, was added 19.6 g of TNM as one portion. The temperature of the reaction mixture rose to 50°, and the copious evolution of gases was observed. The mixture was stirred at 50° (cooling with water) for 3 h. The remainder of the workup was the same as in Expt.a. The yield of chlorotrinitromethane was 6.5 g (35%).

 $\dagger$ In acetone medium, together with the bromopolynitro compound, is detected a certain amount of bromoacetone. The latter proves to be the sole reaction product when the reaction is run for a long time. The residue (1.3 g), obtained as white crystals with mp 104° (from  $CCl_4$ ), is  $\alpha$ -chloro- $\alpha$ -isonitrosoacetone. The mixed melting point with an authentic sample was not depressed. From [8]: mp 105-106°.

When the reaction is run in either acetonitrile or a mixture of dioxane and DMF (composition 7:1) the yield of chlorotrinitromethane, after stirring at 50° for 6 h, is respectively 51.5 and 50%.

With Lithium Chloride in Aqueous Alcohol Medium. To a solution of 12.7 g of anhydrous LiCl in 100 ml of 96% ethanol was added 19.6 g of TNM. After refluxing for 5 h the reaction mass was worked up in the same manner as in Expt.a. The yield of chlorotrinitromethane was 8.23 g (44.5%). Based on the GLC data, the product contains about 15% of dichlorodinitromethane.

## Reaction of Tetranitromethane with Metal Bromides

With Potassium Bromide in DMF Medium. To a suspension of 16.3 g of finely ground freshly ignited KBr in 48 ml of dry DMF, with stirring and cooling in water, was added 19.6 g of TNM. The mixture was stirred for 4 h, maintaining the temperature at 30°. The copious evolution of nitrogen oxides, free bromine, and other gases was observed. The remainder of the procedure was the same as in Expt.a. After removal of the ether in vacuo we obtained 6.76 g of an oil, which, based on the GLC data, contains 77.5% of bromotrinitromethane and 22.5% of dibromodinitromethane. They could not be separated by distillation. The yield of bromotrinitromethane when based on starting TNM is 22.8%, and that of dibromodinitromethane is 5.76%.

With Lithium Bromide in Acetone Medium. To a solution of 4.34 g of anhydrous LiBr in 50 ml of dry acetone was added 9.8 g of TNM in three portions. Vigorous reaction sets in when the TNM is added and the reaction mixture begins to boil. At the end of 25 min the reaction mass was cooled rapidly and poured into 300 ml of water. The obtained oil was separated, washed well with water ( $6 \times 30$  ml), and dried over anhydrous MgSO<sub>4</sub>. Distillation gave 3.45 g (30%) of bromotrinitromethane with bp 74-78° (32 mm) and  $n_D^{20}$  1.4900. Based on the GLC data, the product contains about 15% dibromodinitromethane.

Bromoacetone was isolated as the sole reaction product when the experiment was run for 4 h. Yield 4 g (58.4%); bp 42-45° (15 mm);  $n_D^{20}$  1.4690. From [9]: bp 40-42° (13 mm).

With Lithium Bromide in Aqueous Alcohol Medium. A solution of 10.4 g of anhydrous LiBr and 19.6 g of TNM in 65 ml of 96% ethanol was refluxed for 90 min, cooled, and then worked up the same as in Expt. a. After removal of the ether we obtained 10.9 g of an oil, which contained, based on the GLC data, 56% of bromotrinitromethane and 44% of dibromodinitromethane. The yield of bromotrinitromethane when based on taken TNM is 26.5%, and that of dibromodinitromethane is 18.1%.

To a solution\* of 26 g of anhydrous LiBr in 80 ml of 96% ethanol was added 19.6 g of TNM and the mixture was refluxed for 3 h. Then the reaction mass was worked up the same as in Expt.b. We obtained 10.7 g (40%) of dibromodinitromethane (the degree of purity, based on the GLC data, was approximately 95%); bp 67-68° (13 mm);  $n_D^{20}$  1.5260. From [7]: bp 67-67.5° (12 mm);  $n_D^{20}$  1.5240.

## Reaction of Fluorotrinitromethane (FTNM) with

#### Metal Halides

With Lithium Chloride in DMF Medium<sup>\*</sup>. To a solution of 5.1 g of freshly ignited LiCl in 50 ml of dry DMF, with stirring, was added at one time 16.9 g of FTNM, and the mixture was stirred at 30° for 3 h (the evolution of nitrogen oxides and other gases was observed during the course of the reaction). The subsequent procedure was the same as in Expt.a. We obtained 7.6 g (48%) of chromatographically pure fluoro-chlorodinitromethane, bp 85-87°;  $n_D^{20}$  1.4000. From [10]: bp 85-87° (752 mm);  $n_D^{20}$  1.3992.

<u>With Potassium Bromide in DMF Medium</u>. To a suspension of 7.15 g of finely ground freshly ignited KBr in 25 ml of dry DMF, with stirring, was added 8.45 g of FTNM, after which the mixture was stirred at 50° for 12 h and then worked up the same as in Expt.a. We obtained 2.54 g (25%) of fluorobromodinitromethane, bp 34-36° (40 mm);  $n_D^{20}$  1.4330. From [10]: bp 35-36° (40 mm)  $n_D^{20}$  1.4351.

With Lithium Bromide in DMF Medium. To a solution of 5.2 g of anhydrous LiBr in 25 ml of dry DMF, with stirring, at 50-55°. was added 8.45 g of FTNM in 20-30 min, and the mixture was stirred at 50° for 2 h. The subsequent workup was the same as in Expt.a. We obtained 1.47 g (14.5%) of fluorobromodinitromethane.

With Lithium Bromide in Acetone Medium<sup>\*</sup>. A solution of 6 g of anhydrous LiBr and 8.45 g of FTNM in 50 ml of dry acetone was refluxed for 3 h and then worked up the same as in Expt.a. The yield of fluoro-bromodinitromethane was 4.1 g (40.1%). A double distillation gave the chromatographically pure substance, bp 35-36° (40 mm);  $n_D^{20}$  1.4350.

## Reaction of Chlorotrinitromethane (CTNM) with

### Metal Halides

<u>With Lithium Chloride in DMF Medium\*</u>. To a solution of 5.3 g of freshly ignited LiCl in 50 ml of dry DMF, with stirring, was added 18.54 g of CTNM, after which the mixture was stirred at 30° for 6 h and then allowed to stand overnight at room temperature. The subsequent workup was the same as in Expt. b. The yield of chromatographically pure dichlorodinitromethane was 9.81 g (56%), bp 54-56° (40 mm);  $n_D^{20}$  1.4560.

With Lithium Bromide in Aqueous Alcohol Medium. To a solution of 26 g of anhydrous LiBr in 80 ml of 96% ethanol was added 9.26 g of CTNM, and the mixture was allowed to stand at room temperature for 20 h. Then it was worked up the same as in Expt.a. We obtained 8.6 g of an oil, which, based on the GLC data, contained 77% of bromotrinitromethane and 23% of chlorotrinitromethane. As a result, the yield of bromotrinitromethane, when calculated on the CTNM, is 55%. By vacuum-distillation were isolated: a mixture of chloro- and bromotrinitromethanes, bp 45-70° (32 mm);  $n_D^{20}$  1.4670; 3.5 g, and 4.66 g (40.5% yield) of pure bromotrinitromethane, bp 71-72° (32 mm);  $n_D^{20}$  1.4808.

## Reaction of Bromotrinitromethane (BTNM)

## with Metal Halides

With Lithium Chloride in DMF Medium. To a solution of 2.34 g of freshly ignited LiCl in 25 ml of dry DMF, with stirring and cooling in ice water, was added 11.5 g of BTNM. The mixture was stirred at 30-35° for 6 h. A quite brisk evolution of gases was observed for approximately an hour and the temperature rose, but the temperature could be kept within the range  $30-35^{\circ}$  by good cooling. The cooled mixture was poured into 200 ml of water and worked up the same as in Expt.a. We obtained 5 g (53.2%) of chlorotrinitromethane, which contained about 10% of dichlorodinitromethane, bp 54-56° (40 mm);  $n_D^{20}$  1.4508.

With Lithium Chloride in Aqueous Alcohol Medium. To a solution of 8.48 g of anhydrous LiCl in 50 ml of 96% ethanol at room temperature was added 11.5 g of BTNM, and the mixture was allowed to stand for 3 h. Then the solution was worked up the same as in Expt.a. We obtained 6.8 g of an oil, which contained 90% of chlorotrinitromethane and 10% of bromotrinitromethane. By distillation were isolated: chlorotrinitromethane, bp 53-55° (39 mm);  $n_D^{20}$  1.4520; 5.55 g; yield 60%, and a mixture of the chloro- and bromotrinitromethanes in a 1:1 ratio (GLC), bp 55-68° (39 mm);  $n_D^{20}$  1.4600; 1.3 g.

With Lithium Bromide in Aqueous Alcohol Medium<sup>\*</sup>. To a solution of 4.34 g of anhydrous LiBr in 20 ml of 96% ethanol was added 6.75 g of BTNM, after which the mixture was refluxed for 3 h, cooled, and poured into 100 ml of water. The subsequent workup was the same as in Expt. b. We obtained 3.5 g (52.4%) of dibromodinitromethane, bp 67-68° (13 mm); np 1.5260.

#### Reaction of 1,1,1-Trinitroethane with Lithium

#### Chloride in DMF Medium

To a solution of 4.24 g of freshly ignited LiCl in 48 ml of dry DMF was added 8.25 g of 1,1,1-trinitroethane, and the stirred mixture was heated at 80-85°, with overnight interruption, for 20 h, after which it was cooled to room temperature and poured into 200 ml of water. The subsequent workup was the same as in Expt.a. We obtained 3 g (38.9%) of 1-chloro-1,1-dinitroethane, bp 65-67° (26 mm);  $n_D^{20}$  1.4439. From [11]: bp 59-61° (22 mm);  $n_D^{20}$  1.4439.

## CONCLUSIONS

1. Replacement of the nitro group by the halogen atom (chlorine, bromine) in aliphatic polynitro compounds under the influence of metal halides bears a general character, and proceeds both in aprotic dipolar solvents and in protonic solvents. 2. A new reaction was discovered for aliphatic  $\alpha$ -halopolynitro compounds, namely the reciprocal exchange of unlike halogen atoms (chlorine, bromine) under the influence of metal halides.

3. Simple preparative methods for the synthesis of certain  $\alpha$ -halopolynitro compounds were proposed on the basis of the obtained results.

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