DUAL REACTIVITY OF THE ANIONS OF 1,1-DINITROALKANES IN THE REACTION OF ALKYLATION WITH ALKYL HALIDES

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Recently it was shown by us that in the alkylation of the silver salt of trinitromethane (TNM) with primary alkyl halides the anion of TNM is alkylated simultaneously in both of the possible directions — by the schemes of both C- and O-alkylation [1], whereas secondary and tertiary alkyl halides give only the O-alkyl products [2]. As a continuation of our study of the dual reactivity of ambident polynitro carbanions we made a study of the alkylation of the Ag salts of some 1,1-dinitroalkanes, and specifically of dinitromethane (DNM) and dinitroethane (DNE), using alkyl halides.

Only two papers are known where brief mention is made of the alkylation of the salts of 1,1-dinitroalkanes with alkyl halides [3, 4]. When the author of one of these papers [3] reacted the Ag salt of DNE with methyl iodide or ethyl iodide in the absence of a solvent he was able to isolate the C-alkylation product, namely, 2,2-dinitropropane, only in the case of CH_3I ; the principal reaction products were ethylnitrolic acid and the corresponding aldehyde (formaldehyde or acetaldehyde), formed as the result of the decomposition of the O-alkyl esters of DNE. In [4] it was mentioned that the Ag salt of DNM reacts with methyl iodide or ethyl iodide (also in the absence of a solvent) to give the C-alkyl derivatives – the 1,1-dinitroalkanes; the O-alkylation products were not identified, although it was mentioned that unstable oily substances were formed.

In the present paper we made a detailed study of the reaction of the Ag salts of DNM and DNE with alkyl halides of variable structure for the purpose of detecting both possible directions of the reaction, i.e., both C- and O-alkylation.

When the Ag salt of DNM is alkylated with primary alkyl iodides, and specifically with methyl iodide and ethyl iodide (in benzene, 1,2-dimethoxyethane (DME), and also without a solvent – in excess alkyl halide), there simultaneously occurs both C-alkylation (with the formation of 1,1-dinitroethane and 1,1dinitropropane, respectively) and O-alkylation of the ambident DNM anion. In order to fix the O-alkyl esters of DNM (I) we employed the 1,3-dipolar cycloaddition reaction with styrene [5]. It is known that the (I) compounds with styrene give 3-nitro-5-phenylisoxazoline (II), in which connection, as is assumed by the authors of [5], the reaction goes through the intermediate formation of the N-alkoxy-3-nitro-5phenylisoxazolidine (III), which then, via the cleavage of a molecule of the corresponding alcohol, is converted to (II). Product (II) was actually isolated by us from the reaction mixture. In addition, the O-esters were identified via one of their decomposition products, namely, methylnitrolic acid (IV).

The yield of the C-alkylation product in the reaction of the Ag salt of DNM with CH_3I is: in DME 25%, in benzene 34%, and in the absence of a solvent (more accurately, in excess CH_3I) 50%. When the Ag salt of DNM is alkylated with ethyl iodide the yield of the C-alkylation product, namely, 1,1-dinitropropane, is: 9% in DME and 15% in excess C_2H_5I . It should be mentioned that varying the ratios of the Ag salt of DNM and alkyl iodide (from 1:1 to 1:4) is practically without effect on the yield of the C-alkylation products. On the example of $i-C_3H_7I$ and $t-C_4H_9CI$ it was shown that the reaction of the Ag salt of DNM with secondary and tertiary alkyl halides proceeds exclusively by the O-alkylation scheme. In these experiments the

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O-esters of DNM were fixed as the adducts with styrene, in which connection, if the (II) adduct was isolated in the case of $i-C_3H_7I$, then N-(tert-butoxy)-3-nitro-5-phenylisoxazolidine (Vb) was obtained when $t-C_4H_9CI$ was used as the alkylating agent. Consequently, when the tert-butyloxy grouping is attached to the nitrogen atom of the isoxazolidine ring the cleavage of a molecule of alcohol from the cycloaddition product (Vb), as took place in the case of the other O-esters, fails to occur. When treated with gaseous NH_3 (in ether), (Vb) is converted quantitatively to (II).



When the Ag salt of DNE is alkylated with alkyl halides the same rules hold as in the case of the Ag salt of DNM. Thus, primary alkyl halides, like methyl and ethyl iodides, give both the C- and O-alkyl derivatives. When the reaction is run in DME the yield of 2,2-dinitropropane is 9.3%, while that of 2,2-dinitrobutane is even less, namely, 2-3%; 2,2-dinitropropane is formed in 13% yield when CH_3I is used as the solvent and reagent. As can be seen, the yield of the C-alkylation products is essentially lower than in the case of the Ag salt of DNM. Secondary (i- C_3H_7I) and tertiary (t- C_4H_9CI) alkyl halides react with the Ag salt of DNE only by the O-alkylation scheme. Due to the extreme instability of the O-alkyl esters of DNE [6], they were not taken for the 1,3-cycloaddition reaction, for which reason their formation in the reaction mixture during the alkylation of the Ag salt of DNE was judged on the basis of their decomposition product, namely, ethylnitrolic acid (VI).



Ethylnitrolic acid was not found in the reaction products of the Ag salt of DNE with $t-C_4H_3Cl$. From the reaction mixture was isolated the O-tert-butyl ester of ethylnitrolic acid, $CH_3C(NO_2) = NOC(CH_3)_3$ (VII), the formation of which can apparently be explained by the loss of the oxygen of the N-oxide atom by the Oester (analogous to the theory advanced by us recently to explain the formation of the acetate and benzoate of ethylnitrolic acid from the corresponding O-acyl derivatives of DNE [7]). The structure of (VII) was confirmed by alkaline hydrolysis of ethylnitrolic acid (VI). It is known [8] that the esters of ethylnitrolic acid when treated with aqueous and alcoholic solutions of alkalies are converted to the salts of ethylnitrolic acid.

It should be mentioned that in all of the studied reactions (with the exception of the reaction of the Ag salt of DNM with CH_3I) the corresponding dinitroalkanes, namely, DNM and DNE, were detected. In the experiments using t- C_4H_3Cl their formation could be caused by the decomposition of the corresponding O-alkyl esters.

 $\operatorname{RC}(\operatorname{NO}_{2})_{2}^{-}\operatorname{Ag}^{+} + (\operatorname{CH}_{3})_{3}\operatorname{CCl} \rightarrow \begin{bmatrix} & & \\ &$

Apparently, partial dehydrohalogenation of the alkyl halides (leading to a displacement of the dinitroalkanes from their Ag salts) occurs in the other cases, although this route is not the sole one possible. It also cannot be excluded that in the case of $t-C_4H_9Cl$ the dinitroalkanes are formed only via decomposition of the O-alkyl esters, but also due to partial dehydrohalogenation.

A comparison of the data, obtained in the alkylation of the Ag salts of 1,1-dinitroalkanes, on the one hand, and the Ag salt of TNM [1, 2], on the other hand, makes it possible to formulate a definite rule. In the series TNM, DNM, and DNE a substantial reduction in the amount of C-alkylation is observed when the Ag salts of polynitroalkanes are reacted with primary alkyl halides; for example, in the reaction with CH_{3I} (in the same medium, namely, DME, at 20-25°) the yields of the C-alkylation products in the mentioned series are respectively 85, 25, and 9%; the same rule is also observed for ethyl iodide. This suggests that the character of the polynitro carbanion exerts an important effect on the ratio of the C- and O-alkylation products.

It should be mentioned that although the reaction of the Ag salts of the gem-dinitroalkanes with CH₃I in DME was run in suspension, while the reaction of the Ag salt of TNM was run in solution, this does change the observed rule. Thus, we found that when the reaction of the Ag salts of polynitroalkanes with $CH_{3}I$ is run in DME solution* (with close initial concentrations of the Ag salts) the yields of the C-alkylation products are practically the same as those given above: in the case of the Ag salt of TNM the yield of the C-alkyl derivative is 83.5%, and in the case of the Ag salt of DNM it is 28% (determined spectrophotometrically[†]). It is necessary to emphasize that in all three cases the reacting particle is the anion (either "free" or bound in an ionic pair) of the corresponding polynitroalkane, and not the covalently built Ag derivative. ‡ Actually, although an equilibrium does exist between the ionic and organometallic forms in the solutions of all three Ag salts in DME, as is evidenced by the low value of the molar extinction coefficients (ɛ) in the absorption maxima (6300 for the Ag salt of TNM, 5100 for the Ag salt of DNM, and 1200 for the Ag salt of DNE), still complete ionization of the Ag salts occurs when CH₃I is added, as is evidenced by the exceedingly rapid increase in z up to the following values: 14,500 for TNM, 20,100 for DNM, and 16,500 for DNE, which values are characteristic for the anions of these polynitroalkanes. The ionization of the Ag derivatives under the influence of CH₃I is evidently caused by the great tendency of alkyl iodides to form complexes with the Ag ion (see, for example, [10]).

When going from primary to secondary and tertiary alkyl halides, an increase in the amount of Oalkylation of the Ag salts of 1,1-dinitroalkanes, the same as in the case of the Ag salt of TNM [1, 2], is explained by the fact that in the series of halide derivatives: $CH_3X < RCH_2X < R_1R_2CHX < R_1R_2R_3CX$, the carbonium character of the transition state of the alkylation reaction increases in the presence of silver ions, which, in harmony with contemporary concepts [11, 12], should increase the probability of alkylating ambident polynitro carbanions at the oxygen atom of the nitro group.

In principle, the obtained results can also be explained by the fact that due to the presence of considerable steric hindrance in the case of secondary and tertiary alkyl halides the alkylation of the polynitroalkyl anion at the carbon atom is greatly hindered. However, this assumption is less probable, since in *The solubility of the Ag salts of DNM and DNE in DME is low(0.15 and 0.1 g/liter, respectively), for which reason the reaction was run in very dilute solutions (at 20°).

 \dagger For the spectrophotometric determination of 1,1,1-trinitroethane the latter was converted to the DNE anion by treatment with alkaline H_2O_2 .

The existence in solutions of covalently built Ag derivatives of polynitroalkanes was shown in [9].

the present paper it was specially shown by us that benzyl bromide and p-nitrobenzyl bromide, where the same steric conditions exist at the reaction center, but where the tendency to manifest a carbonium character in the transition state is different [11], when reacted with the Ag salt of TNM* (under the same conditions – in ether, at 20°†) give completely different amounts of the C-alkylation products. Thus, the yield of the C-alkyl derivative in the case of $p-NO_2C_6H_4CH_2Br$ is approximately 40% [15], whereas in the reaction with $C_6H_5CH_2Br$ it does not exceed 1%. Consequently, the amount of C-alkylation drops rapidly with increase in the tendency to manifest a carbonium character in the transition state.

EXPERIMENTAL

The Ag salt of DNM was obtained as described in [4], while the Ag salt of DNE was obtained as described in [16].

Reaction of Ag Salt of DNM with $CH_{3}I$. To a suspension of 8.5 g of the Ag salt of DNM in 50 ml of dimethoxyethane (DME) was added 6.25 g of styrene, and then, with stirring, 11.4 g of $CH_{3}I$ was added. The mixture was stirred at 20-25° for 5 h and then allowed to stand overnight. In this, and in all of the subsequent experiments, the reaction mixture was allowed to stand in order to complete the cycloaddition reaction. The precipitate of AgI was separated (weight 9.4 g, i.e., the theoretical amount), and the filtrate was diluted with 300 ml of 1% NaCl solution and extracted with ether (2×100 ml). The ether extracts were washed with water (2×50 ml), dried over MgSO₄, and then saturated with gaseous NH₃. The obtained ammonium salt of DNE was separated (the filtrate was kept) and washed with ether (weight 1.5 g). Treatment of a suspension of this salt in 30 ml of water and 150 ml of ether with 10% H₂SO₄ solution gave the free 1,1-dinitroethane; yield 1.2 g (25%); bp 54-55° (4 mm); n_D^{20} 1.4348. From [17]: bp 55.5-56° (4.5 mm); n_D^{20} 1.4346.

The ether filtrate (after separation of the NH_4 salt of DNE) was washed with 5% Na_2CO_3 solution until the soda extracts remained colorless (4-5 times with 30-ml portions), then with water, and dried over $MgSO_4$. From the oil, remaining after removal (under reduced pressure) of the ether and excess styrene, by preparative TLC on acid Al_2O_3 (pH 4, III activity)[‡] was isolated (using benzene as the eluant) 0.8 g of 3-nitro-5-phenylisoxazoline; yield 10.4% when based on the Ag salt of DNM; mp 64-65° (from CCl₄). From [5]: mp 64.5-65.5°. The mixed melting point with an authentic sample [5] was not depressed; the identity of the compounds was also confirmed by means of the IR spectra and TLC.

In an analogous experiment (but omitting the styrene), after separating the AgI, the filtrate under cooling (0°) was saturated with gaseous NH_3 (here the NH_4 salt of DNE remains in solution). The obtained red salt was separated, washed with $CHCl_3$ and then with ether, dissolved in CH_3OH , and to the obtained solution was added a solution of KI in CH_3OH . We obtained 0.1 g of the potassium salt of methylnitrolic acid. Found: K 29.8; 30.2%. CHO_3N_2K . Calculated: K 30.5%.

When the reaction of the Ag salt of DNM (8.5 g) with CH_{3I} (11.4 g) was run in benzene (the mixture was stirred at 25° for 8 h and then allowed to stand at 20°C for 3 days), in the presence of styrene, we obtained 1.65 g (34.4%) of DNE and 0.8 g (10.4%) of (II).

When the same reaction was run without a solvent (in excess $CH_3I - using 20 \text{ ml}$ of CH_3I per 0.02 mole of the Ag salt of DNM) for 30 min (20°) the yield of DNE was 50%.

Reaction of the Ag Salt of DNM with Ethyl Iodide. To a suspension of 8.5 g of the Ag salt of DNM in 50 ml of DME were added 6.25 g of styrene and 25 g of C_2H_5I . The mixture was stirred at 20-25° for 8 h and then allowed to stand for 3 days. The precipitate of AgI was separated (weight 9.35 g, or 99.5% of theory), while the filtrate was worked up in the same manner as in the preceding experiment. We obtained 0.5 g (9.3%) of 1,1-dinitropropane; bp 69-70° (3 mm); n_D^{20} 1.4335 (from [18]: bp 67-68° (2.5 mm); n_D^{20} 1.4321), and 0.9 g (11.7%) of 3-nitro-5-phenylisoxazoline (II).

When the same reaction was run without a solvent (in excess C_2H_5I – using 26 ml of C_2H_5I per 0.02 mole of the Ag salt of DNM) for 1.5 h (20-23°) the yield of 1,1-dinitropropane was 14.9%.

*Of all of the anions studied by us, the TNM anion is sterically least favorable for C-alkylation: on the basis of purely steric considerations the TNM anion should be nonplanar, which is corroborated by the data of x-ray structure analysis [13], whereas the anions of the gem-dinitro compounds are practically planar [14].

†The quantitative precipitation of AgBr was observed in both cases.

 \ddagger The size of the plate was 20 × 25 cm, and the layer thickness was 1 mm; the chromatogram was developed in UV light.

Reaction of the Ag Salt of DNM with Isopropyl Iodide. To a suspension of 8.5 g of the Ag salt of DNM in 50 ml of DME was added 6.25 g of styrene, and then, with stirring and cooling (0°), was added 18.6 g (8 ml) of $i-C_3H_7I$ in drops. The mixture was stirred at 0-5° for 5 h and then allowed to stand at the same temperature for 3 days. The precipitate of AgI was separated (weight 9.2 g, or 98% of theory), while the filtrate was poured with stirring into a mixture of 200 ml of ether and 300 ml of ice water, and the ether layer was separated immediately and dried over MgSO₄. The passage of gaseous NH₃ into the ether solution gave 0.7 g of the NH₄ salt of DNM (identified by conversion to the potassium salt. Found: K 27.0; 27.1%. CHO₄N₂K. Calculated: K 27.2%).

From the filtrate (after separation of the NH_4 salt of DNM) by the above-described method (see the experiment with CH_3I) was isolated 1.2 g (15.6%) of 3-nitro-5-phenylisoxazoline (II).

Reaction of the Ag Salt of DNM with Tert-Butyl Chloride. To a suspension of 8.5 g of the Ag salt of DNM in 50 ml of DME was added 6.25 g of styrene, and then, with stirring and cooling (0°), was added 7.4 g of t-C₄H₉Cl in drops. The mixture was stirred at 0-5° for 6 h, and then allowed to stand at the same temperature for 2 days. The precipitate of AgCl was separated (weight 5.6 g, or 97.5% of theory). In the filtrate by means of GLC was detected DNM. Then the reaction mixture was worked up in the same manner as in the preceding experiment to give 0.4 g of the NH₄ salt of DNM. The ether filtrate (after separation of the NH₄ salt) was washed with 5% Na₂CO₃ solution (4 × 30 ml), then with water, and dried over MgSO₄. After removal of the ether and excess styrene under reduced pressure the residue was stirred with a small amount of chilled (-10°) pentane, and the obtained colorless crystals were separated. We obtained 3.5 g (33%, when based on the Ag salt of DNM) of N-(tert-butoxy)-3-nitro-5-phenylisoxazolidine (Vb) with mp 91-92° (from n-pentane). Found: C 58.39; 58.40; H 6.68; 6.67; N 10.74; 10.63%; mol. wt. 264 (in benzene). C₁₃H₁₈ \cdot O₄N₂. Calculated: C 58.63; H 6.81; N 10.52%; mol. wt. 266.

Infrared spectrum: 13701375, 1575, cm^{-1} (dinitromethylene grouping); 1015 cm⁻¹ (O - N - O fragment in N-alkoxyisoxazolidines [19]).

The passage of gaseous NH_3 (20°, 30 min) into an ether solution of (Vb) and subsequent evaporation of the ether gave (II) in quantitative yield, mp 64-65° (from CCl_4). The identity of the compound with an authentic specimen [5] was proved by the mixed melting point and by TLC.

Reaction of the Ag Salt of DNE with Methyl Iodide. With stirring, to a suspension of 9.1 g of the Ag salt of DNE in 50 ml of DME was added 11.4 g of CH_3I , keeping the temperature below 25°. The mixture was stirred at 20-25° for 8 h, after which the precipitate of AgI was separated (weight 9.2 g, or 98% of theory). In the filtrate by means of GLC were detected 2,2-dinitropropane and DNE. The filtrate was evaporated in vacuo (not exceeding 30°), while the residue was diluted with ether (150 ml) and washed with cold 2% NaOH solution (5×30 ml), * then with water, and dried over MgSO₄. After distilling off the solvent we obtained 0.5 g (9.3%) of 2,2-dinitropropane with mp 53-54° (from hexane). From [20]: mp 53°. The mixed melting point with an authentic specimen was not depressed; the identity of the compounds was also proved by GLC.

The alkaline extracts (see above) were stirred with 150 ml of ether and then, with stirring and cooling $(0-5^{\circ})$, were acidified with 10% H₂SO₄ solution. The ether layer was separated, while the aqueous layer was extracted with an additional 100 ml of ether. The ether extracts were dried over MgSO₄, and the ether was removed under reduced pressure. The residual oil was repeatedly extracted with warm (30°) hexane (the hexane extracts were saved). The residue represented 0.25 g (6%, when based on the Ag salt of DNE) of ethylnitrolic acid (VI), mp 86–87°. From [21]: mp 87–88°. The mixed melting point with an authentic specimen was not depressed. The identity of the compounds was also proved by TLC.

The hexane extracts (see above) were evaporated, while the residue was treated (under cooling) with alcoholic KOH solution. We obtained 1.7 g (27%, when based on the Ag salt of DNE) of the potassium salt of DNE. Found: K 24.6; 24.5%. $C_2H_3O_4N_2K$. Calculated: K 24.7%.

When the same reaction was run without a solvent (in excess $CH_3I - using 25 \text{ ml of } CH_3I \text{ per } 0.02 \text{ mole}$ of the Ag salt of DNE) for 2 h (0°) the yield of 2,2-dinitropropane was 13%.

Reaction of the Ag Salt of DNE with Ethyl Iodide. With stirring, to a suspension of 9.1 g of the Ag salt of DNE in 50 ml of DME was added 12.5 g of C_2H_5I , keeping the temperature below 25°. The mixture

*The alkaline extracts were kept.

was stirred at $23-25^{\circ}$ for 8 h and then allowed to stand at room temperature overnight. The precipitate of AgI was separated (weight 9.4 g, i.e., the theoretical amount). In the filtrate by means of GLC were detected 2,2-dinitrobutane and DNE. Then the reaction mixture was worked up the same as in the preceding experiment. We obtained 2,2-dinitrobutane (yield 2-3%, estimated by means of GLC*), ethylnitrolic acid (VI) (yield 0.1 g, or 2.4%) and DNE (isolated as the K salt; yield 36%).

<u>Reaction of the Ag Salt of DNE with Isopropyl Iodide</u>. To a suspension of 9.1 g of the Ag salt of DNE in 50 ml of DME, with cooling (0°) and stirring, was added 18.6 g (8 ml) of $i-C_3H_7I$. The mixture was stirred at 0-5° for 3 h, the precipitate of AgI was separated (weight 9.3 g, or 99% of theory), and the filtrate was worked up in the same manner as described above. We obtained 2.2 g (53%, when based on the Ag salt of DNE) of (VI) and 0.1 g (1.6% of the K salt of DNE.

<u>Reaction of the Ag Salt of DNE with Tert-Butyl Chloride</u>. To a suspension of 16.0 g of the Ag salt of DNE in 80 ml of DME, with cooling (0°) and stirring, was added 13.0 g of $t-C_4H_9Cl$. The mixture was stirred at 0° for 2 h and at 20° for 3 h, after which the precipitate of AgCl was separated (weight 9.9 g, or 99% of theory). The filtrate was evaporated in vacuo (not exceeding 20°), and the residue was immediately diluted with 150 ml of ether and washed with 1% NaOH solution (6 × 30 ml⁺), then with water, and dried over MgSO₄. The ether was removed under reduced pressure, while the flask with the residual liquid was placed in a water bath (15-20°). After some time the evolution of nitrogen oxides began, which was accompanied by warming up of the mixture. When the gas evolution had ceased, the liquid was blown with dry air and then distilled. We obtained 2.0 g (19.6%, when based on the Ag salt of DNE) of the O-tert-butyl ester of ethylnitrolic acid (VII) with bp 43-45° (1 mm); n_D^{20} 1.4476. Judging by the data of GLC and TLC, the compound is devoid of impurities. Found: C 44.74; 44.82; H 7.57; 7.46; N 17.94; 17.69%; ml. wt. 164 (in benzene). $C_6H_{12}O_3N_2$. Calculated: C 44.99; H 7.55; N 17.49%; mol. wt. 160. Infrared spectrum: 1342, 1549 cm⁻¹ (NO₂ group); 1603 cm⁻¹ (C = N); 1040 cm⁻¹ (N - O).

Ethylnitrolic acid (VI) was isolated when the compound was dissolved in saturated alcoholic KOH solution and subsequent acidification.

CONCLUSIONS

1. The alkylation of the Ag salts of 1,1-dinitroalkanes (dinitromethane and dinitroethane) with primary alkyl iodides proceeds simultaneously in two directions — by both the C- and O-alkylation schemes. Sec- ondary and tertiary alkyl halides give only the O-alkyl derivatives.

2. In the presence of silver ions the trinitromethane anion is more inclined toward C-alkylation by primary alkyl halides than are the anions of gem-dinitroalkanes.

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*The 2,2-dinitrobutane, needed as a standard, was obtained as described in [17]. †The alkaline extracts were saved.

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