REACTION OF HALOADAMANTANES WITH SALTS OF NITRO COMPOUNDS

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Silver and mercury salts of nitro compounds react with bromo- or chloroadamantanes with the formation of products of C- and/or O-alkylation, the ratio of which depends on the structure of the initial reactants. The direct experimental evidence of nitronic esters to be isomerized into nitro derivatives and of their role as intermediates in the formation of the nitro derivatives in the alkylation of nitro compounds has been presented for the first time.

Keywords: haloadamantanes, trinitromethyladamantanes, nitronic esters, alkylation, isomerization.

The reaction of alkyl halides with the salts of nitro compounds leads, depending on the structure of the initial reactants, to alkylated nitro compounds, nitronic esters, or their mixture [1]. The opinion has been expressed in [2-4] that in many instances nitro compounds are obtained hereby by the rearrangement of initially formed nitronic esters; however, no experimental evidence has been offered. Moreover, the methyl ester of dinitromethanenitronic acid (DNMNA) has been synthesized in [5], assumed to appear as intermediate in the formation of trinitroethane [2], but showed no rearrangement tendency.

By assuming that, thanks to the relative thermodynamic stability of the adamantyl as well as the polynitroalkyl ions, this rearrangement can occur in the reaction of haloadamantanes with the salts of polynitro compounds, we have investigated this reaction.

The nitro compounds used were trinitromethane (TNM), dinitromethane (DNM), and dimethylnitromalonate (DMNM), while 1-bromoadamantane(1), 1-bromo-3-methoxycarbonyladamantane(2), 1-bromo-3-hydroxymethyladamantane(3), 1-chloro-3-(1'-hydroxyminoethyl)adamantane (4), and 1-chloro-3-acetyladamantane (5) served as the alkylating agents.

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Compound	Y 1,3-Ad X		IR spectrum (v, cm ⁻¹)	UV spectrum, λ_{max} , in the 300-330 nm region
	Y	х		
6 b	C (NO ₂) 3	Н	1610, 1585 (doublet) 1305,	_
6a	$ \underset{O}{\overset{V}{=}} ON = C(NO_2)_2 $	н	1610, 1570, 830	305
7b	C (NO ₂) 3	CO ₂ CH ₃	1610, 1590 (doublet) 1310,	-
7a	$ \underset{\downarrow}{\overset{\downarrow}{\text{ON}}} = C(\text{NO}_2)_2 $	CO ₂ CH ₃	1610, 1570, 1350, 1320	310 (12 700)
11	ON≕C(NO₂)H ↓ ♀	Н	1615, 1520, 1320	302

 TABLE 1. Absorption in IR and UV Spectra of Some Trinitromethyladamantanes and

 Adamantyl Esters of Nitro- and Dinitromethanenitronic Acids

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It was found that the K salt of TNM with 1 in DMF, EtOH, or ether does not react; this is easily explained by the fact that the reaction cannot proceed according to the S_N^2 mechanism. On the other hand, the Ag salt of TNM (Ag-TNM) reacts vigorously with 1; in ether the reaction is completed virtually immediately after mixing of the reactants. After removal of the solvent a colorless crystalline substance is obtained with a yield of ~80% which according to elemental analysis, IR, and UV spectra, turns out to be 1-trinitromethyladamantane (**6b**) (Table 1). The same compound is obtained when the reaction is performed in another solvent (for instance, hexane) or when Hg-TNM is used instead of Ag-TNM.

On the other hand, in the alkylation of Ag-TNM 2 a mixture is formed of the corresponding colorless trinitromethyl derivative (7b) and the yellow, relatively stable 3-methoxycarbonyladamantyl ester of DNMNA (7a) is formed. The summary yield of the alkylation products is more than 80%, whereby the nitronic ester (7a) is the main component (7a:7b ratio ~ 5 :1).



One of the causes for the considerable differences in the character of the products, formed in the alkylation of Ag-TNM 1 and 2 could be the rearrangement of the initially formed adamantyl ester of DNMNA 6a and 6b. These considerations led us to check the IR and UV spectra of the reaction mixture immediately after mixing of the original reactants. It was found that in this instance 6a was the main reaction product, with a yield of $\sim 80\%$.* According to the IR spectrum, even if 6b was present in the reaction products, its amount would be less than 10%.

The compound **6a** was found to be relatively stable in solutions: its amount decreased from 80% to $\sim 60\%$ in 24 h and to $\sim 5\%$ in 11 days. However, the rate of isomerization decreased sharply after removal of the solvent; if the product obtained hereby was dissolved after 0.5 h again in ether, only **6b** was detected instead of **6a**.

Thus, direct and unambiguous experimental evidence has been obtained for the first time that some nitronic esters are capable of rearranging themselves into nitro compounds and to act as intermediates in the formation of nitro derivatives in the alkylation of salts of nitro compounds.

Compound 7a is much more stable toward isomerization, which permitted its separation in pure form and its characterization; it was observed, however, that when stored for 9 months in a weighing bottle at $\sim 20^{\circ}$ C, 7a was virtually completely rearranged into 7b. These data lead us to the conclusion that in the alkylation of Ag-TNM 2; at least the main part of 7b is formed not by the rearrangement of 7a, but directly at the nucleophilic substitution stage.

Thus, the reaction of Ag-TNM with haloadamantanes is a relatively universal reaction for the preparation of trinitromethyladamantanes, whereby the yield of the latter is determined to a large degree by the character of the substituents in the haloadamantanes: the more electronegative they are, the lower the yield of the C-alkylation products; the methoxycarbonyl group can be considered as a unique calibration substituents, which gives C-alkylation products with a yield of 10-20% (immediately after completion of the reaction of the original reactants). The examples given below evidently confirm these considerations.

^{*}Calculated from the optical density of the solution at the condition that the molar extinction coefficients of 6a and 7a were equal.



Naturally, the structure of the nitro component must have a very strong influence on the course of the reaction; substitution of the nitro group in TNM by substituents, less prone to delocalization of the negative charge, must create a strong tendency to O-alkylation. The reactions of 1 with the Ag salts of DNM and DMNM, which lead to the exclusive formation of nitronic esters, confirm this statement.

$$1-\operatorname{BrAd}_{\top} \operatorname{AgC(NO_2)} XY \longrightarrow 1-\operatorname{AdON}=CXY$$

$$\downarrow \\ 0$$
(11, 12)
$$X=\operatorname{NO_2}, Y=H (11); \quad X=Y=\operatorname{CO_2CH_3} (12).$$

The trinitromethyladamantanes represent colorless crystalline substances. The trinitromethyl group gives them an increased chemical stability in comparison with the aliphatic trinitromethyl compounds. Thus, **6b** is inert toward a denitrating agent such as KI in methanol and can be chromatographed on Al_2O_3 without decomposition. However, denitration can be carried out by means of H_2O_2 in an alkaline medium; this makes it possible to obtain 1-dinitromethyladamantane (13) which, has been shown above, cannot be synthesized by the reaction of 1 with Ag-DNM.

$$6b \xrightarrow[\text{KOH}]{\text{H}_2O_2} 1-\text{AdC}(\text{NO}_2)_2\text{H}$$
(13)

Trinitromethyladamantanes can also be used to obtain derivatives, containing several polynitroalkyl radicals. The nitration of 9 to 1-trinitromethyl-3-(1', 1'-dinitroethyl)adamantane (14) can serve as an example.



Among the compounds described in the present article the stable ester of DNMNA (7a) was of particular interest, of which, by analogy with the methyl ester of DNMNA, an easy 1,3-dipolar cycloaddition to olefins could be expected [5]. However, to our astonishment 7a did not react with methylacrylate, which can be attributed to the steric effect of the adamantyl radical.

The compounds 4 and 5, used in the work, we synthesized according to the following scheme:



In both approaches the yields of 5 were approximately the same; however, a cleaner product was obtained when using the malonic ester.

EXPERIMENTAL

The IR spectra were recorded on a UR-10 spectrometer; products 1 and 2 were obtained according to [6, 7].

1-Chloro-3-Acetyladamantane (5). a. A solution of 35.16 g of the acid chloride of 1-chloroadamantanecarboxylic acid in 100 ml C_6H_6 is treated at 10°C dropwise with 120 ml of a benzene solution of 42.2 g $C_2H_5OMgCH(COOC_2H_5)_2$; the reaction mixture is refluxed for 1 h, cooled, and poured into ice water. 2 N H₂SO₄ is added until dissolution of the precipitate formed, the organic layer was separated, washed with H₂O, and the C_6H_6 stripped off. The residue (51.4 g) was mixed with 300 ml of a mixture (CH₃COOH:conc. H₂SO₄:conc. HCl:H₂O in the ratio 100:3:40:30 by volume), refluxed for 2 h, cooled, and poured into ice water; the crystals formed were filtered off and washed with water. Obtained 20.9 g (65%) 5, mp 50.5-51.5°C (from isooctane).

b. A Grignard solution, obtained from 0.124 g Mg in 10 ml ether and 1 g CH₃I was treated with 0.7 g ZnCl₂ powder; the solution was refluxed for 45 min and 1 g of the acid chloride of 1-chloroadamantanecarboxylic acid added rapidly at -30 to -40° C. The mixture was refluxed for 1 h, cooled, poured on ice with water, and treated with 2 N H₂SO₄ until dissolution of the precipitate formed. The organic layer was separated, washed with H₂O, and the solvent stripped off. Yield 0.71 g of a crystallizing product which according to GLC data contained ~90% 5.

1-Chloro-3-(1'-hydroxyiminoethyl)adamantane (4). A solution of 50.9 g 5 in a mixture of $CH_3OH:C_2H_5OH$ (2:1 by volume) was treated at 20°C with a solution of 1.8 g NH₂OH·HCl and 1.22 g Na₂CO₃ in a minimum amount of water. The reaction mixture was stirred for 3.5 h, the precipitate was filtered off, and washed with water. Obtained 4.38 g (80.5%) 4, mp 148-150°C (from isooctane). Found, %: C 63.52; H 8.05; Cl 15.70; N 6.05. $C_{12}H_{18}NOCl$. Calculated, %: C 63.31; H 7.92; Cl 15.62; N 6.16.

Trinitromethyladamantane (6b). a. A solution of 1.32 g 1 in 50 ml ether was treated at 20°C by vigorous stirring dropwise with a solution of 1.9 g Ag-TNM in 20 ml ether. After 1 h AgBr was filtered off, the filtrate was washed with H₂O until the washing water was colorless, dried over MgSO₄, and the solvent stripped off. Obtained 1.41 g (80.7%) 6b, mp 137-138°C. In order to purify it, 6b was passed through a column of Al_2O_3 in C_6H_6 and recrystallized from hexane or CH_3OH , mp 161-162°C (decomposes). Found, %: C 46.52; H 5.20; N 14.74. $C_{11}H_{15}N_3O_6$. Calculated, %: C 46.31; H 5.30; N 14.73.

b. A solution of 2.15 g 1 and 2.25 g TNM in 20 ml ether was treated with 2.6 g Ag_2O with cooling with water and vigorous stirring. The stirring was continued for 2 h and the mixture allowed to stand for 12 h; the precipitate was filtered off, the filtrate washed with H₂O, dried, and the solvent removed. Obtained 1.72 g (6b), mp 124-126°C, after purification 162°C.

c. A solution of 11 g 1 in 40 ml ether was treated with a solution of 17.8 g Hg-TNM in 70 ml ether. The mixture was allowed to stand 12 h. The precipitate was filtered off, the filtrate was evaporated to dryness and extracted with hot hexane; the solvent was removed and the residue in C_6H_6 passed through a column packed with Al_2O_3 . Obtained 10.6 g (75%) (6b), mp 161-162°C (from CH₃OH).

3-Methoxycarbonyladamantyl Ester of Dinitromethanenitronic Acid (7a) and 1-Trinitromethyl-3methoxycarbonyladamantane (7b). A solution of 1.34 g 2 in 25 ml ether was treated with 1.6 g Ag-TNM in 30 ml ether with vigorous stirring. After 2 h AgBr (0.86 g) was filtered off, the filtrate was washed with H₂O, dried, and the solvent removed. Obtained 1.42 g of a mixture of 7a and 7b. After two recrystallizations from hexane 0.68 g 7a, mp 71-71.5°C, was isolated. Found, %: C 45.48; H 5.04; N 11.90. $C_{13}H_{17}O_8N_3$. Calculated, %: C 45.48; H 4.99; N 12.24. After evaporation of the hexane filtrate 0.49 g of a partially crystallized oil remained. The crystals were separated and recrystallized from hexane. Obtained 7b, mp 87.5-88°C. Found, %: C 45.64; H 5.00; N 12.24. $C_{13}H_{17}O_8N_3$. Calculated, %: C 45.48; H 4.99; N 12.24.

1-Trinitromethyl-3-hydroxymethyladamantane (8). To a solution of 1.27 g 3 in 15 ml ether 1.7 g Ag-TNM was added. After 2 h the precipitate was filtered off, the filtrate was washed with water, dried, and the solvent removed. Obtained 0.98 g (60%) 8, mp 112-114°C. For cleaning, 0.25 g 8 in CHCl₃ was passed through a column of Al_2O_3 . Obtained 0.21 g 8, mp 117-119°C (hexane). Found, %: N 12.93. $C_{12}H_{17}O_7N_3$. Calculated, %: N 13.33.

1-Trinitromethyl-3-(1'-hydroxyiminoethyl)adamantane (9). A solution of 4.9 g 4 and 6.4 g Ag-TNM in 70 ml ether was mixed for 4 days, the precipitate was filtered off, the ether was evaporated; the residue was thoroughly mixed with H_2O , dried, and passed in ether through a column with Al_2O_3 for purification. Obtained 3.42 g (46.4%) 9, mp 169-170°C (from isooctane). Found, %: C 45.45; H 5.43. $C_{13}H_{18}N_4O_7$. Calculated, %: C 45.61; H 5.30.

1-Trinitromethyl-3-acetyladamantane (10). A sample of 2.3 g 5 in 45 ml ether was treated with 3.5 g Ag-TNM. After 3 days the precipitate was filtered off, the ether solution washed six times with H₂O, dried, and the ether evaporated. From the residue the crystalline part was recrystallized from hexane. Obtained 0.69 g (19.5%) **10**, mp 89°C. Found, %: C 47.91; H 5.17; N 12.96. $C_{13}H_{17}O_7N_3$. Calculated, %: C 47.71; H 5.23; N 12.84.

Adamantyl Ester of Nitromethanenitronic Acid (11). A solution of 7 g 1 in 15 ml ether was treated with 8.5 g Ag-DNM in 150 ml ether with vigorous stirring. After 24 h the AgBr was filtered off, the filtrate washed with water, dried, and the solvent removed. Obtained 7.27 g 11, together with a small amount of adamantol-1; mp of 11 51-52°C. Found, %: C 55.09; H 7.76; N 11.26. C₁₁H₁₆O₄N₂. Calculated, %: C 54.99; H 6.71; N 11.66.

Adamantyl Ester of Bis(methoxycarbonyl)methanenitronic Acid (12). A sample of 1.21 g 1 in 45 ml ether was treated with 1.92 g Ag-DMNM. The mixture was stirred for 48 h, filtered, the filtrate washed with water, dried, and the solvent removed. Obtained 1.4 g of oily crystals of 12, mp 50-51°C (from hexane). Found, %: C 58.15; H 6.90; N 4.53. $C_{15}H_{21}O_6N$. Calculated, %: C 57.86; H 6.80; N 4.50.

1-Dinitromethyladamantane (13). A suspension of 0.7 g **6b** in 13 ml CH₃OH was treated with 1.3 ml 30% H_2O_2 , followed by the dropwise addition at 5-10°C of a solution of 1 g KOH in 5 ml CH₃OH. The mixture was stirred for 3 h at 20°C, filtered, and acidified with 20% H_2SO_4 ; the precipitate was separated, the filtrate diluted with the equal volume of water, and the precipitated compound 13 filtered off. Obtained 0.3 g (51.8%) 13, mp 34-35°C. After freezing-out from hexane and reprecipitation from C_2H_5OH with water, 13 melted at 38°C. Found, %: C 54.89; H 6.74; N 11.96. $C_{11}H_{16}N_2O_4$. Calculated, %: C 54.99; H 6.71; N 11.66.

1-Trinitromethyl-3-(1',1'-dinitroethyl)adamantane (14). A solution of 3 ml HNO₃ (d = 1.5) in 70 ml dry CCl₄ was treated at -10 to -5° C dropwise with 1.72 ml (CH₃CO)₂O; the mixture was kept for 20 min at 0°C, 15 min at 20°C, and rapidly heated to 60°C; after that a suspension of 1.24 g 9 in 50 ml CCl₄ was added. After 0.5 h the mixture was poured on ice, the organic layer was separated, washed with water and with NaHCO₃ solution, dried, and the solvent evaporated. TLC on Al₂O₃ (eluent benzene – ether 1:1, elution repeated) was used to obtain from the residue 0.34 g (28.7%) 10 and 0.32 g (22%) 14, mp 99-101°C (from isooctane). Found, %: C 39.10; H 4.63; N 17.08. C₁₃H₁₇N₅O₁₀. Calculated, %: C 38.71; H 4.25; N 17.37. IR spectrum (ν , cm⁻¹): 800, 1305, 1590, and 1610 [C(NO₂)₃]; 1330 and 1570 [C(NO₂)₂].

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