REACTION OF O-ACYL DERIVATIVES OF POLYNITROALKANES WITH ELECTROPHILIC REAGENTS

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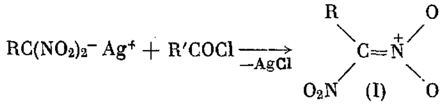
It is known [1-3] that the reaction of the ambident anions of polynitroalkanes with acyl halides proceeds by the O-acylation scheme; the O-acyl derivatives (I) that are formed here can undergo a number of further transformations. Thus, the reaction of the O-acetyl derivative of trinitromethane (Ia) with halogens (chlorine or bromine) gave the corresponding chloro- and bromotrinitromethanes [1], while the chlorination of the O-acetyl derivative of dinitromethane (Ib) led to the chloro-derivatives of dinitromethane [3]:



(1)

$R=NO_2$, $R'=CH_3$(a); $R=H$; $R'=CH_3$ (b); $R = CH_3$, $R' = CH_3$ (c)

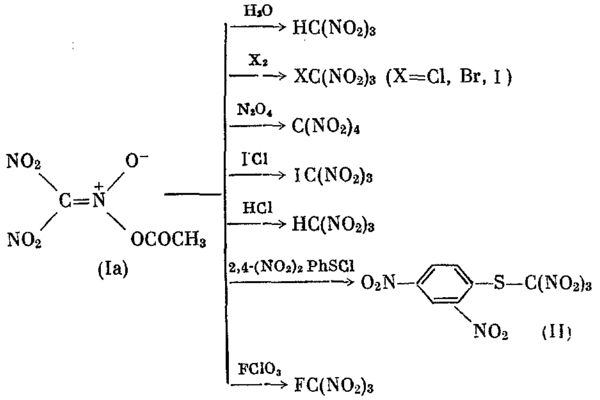
$$(I) \xrightarrow{X_2} RC(NO_2)_2X \qquad (2)$$

$R=NO_2$, $X=Cl$, Br(a); $R=H$, $X=Cl$ (b)

In the present paper we studied the reaction of (I) with a broader gamut of electrophilic reagents (halogens, ICl, N_2O_4, HCl, $FClO_3$, sulfenyl chloride, N-chloropiperidine) and found that the type (2) reaction has a general character.*

The reaction of the O-acetyl derivative of trinitromethane (Ia) was studied in greatest detail. When freshly prepared (Ia) is treated with water it is quantitatively hydrolyzed to trinitromethane (TNM) (determined spectrophotometrically), which can serve as a convenient method for the analysis of (Ia). This observation made it possible to estimate the stability of (Ia) in CH_3CN, in which it is usually prepared [1]. We proved to ourselves that (Ia) is stable in CH_3CN for at least 7-8 h at –20° and a concentration of ~0.2 mole/liter; (Ia) remains unchanged for ~2-3 h when the temperature is raised up to 0°, while at 20° only 5-7% of (Ia) remains in the solution even after an hour. Starting with these data, all of the reactions of (Ia) with the electrophiles were usually run at –20 to –10°.

The corresponding halotrinitromethanes, $XC(NO_2)_3$, are formed when (Ia) is reacted with halogens (Cl_2, Br_2, I_2), the yield of which is 60% in the case of X = Cl or Br, and 8% when X = I:



(3)

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*See [4] for preliminary communication.

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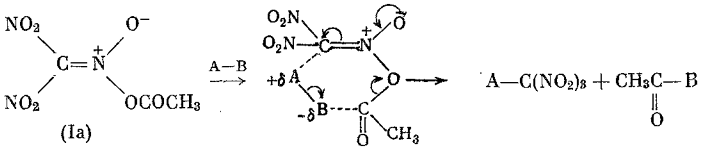
Tetranitromethane is formed when (Ia) is treated with N_2O_4. Another possible route for the formation of $C(NO_2)_4$, namely the reaction of N_2O_4 with the $(CH_3CO)_2O$ that is formed in the decomposition of (Ia) [1], is not realized in the given case, as was shown by special experiment.

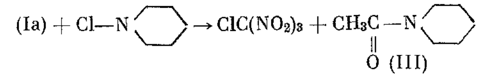
In [1], the theory was expressed that (Ia) reacts with electrophilic reagents (Cl_2 and Br_2) by the 1,3-addition scheme, and specifically the "electrophilic" portion of the reagent attacks the oxygen atom of the N-oxide of (Ia). In order to verify the validity of this hypothesis we studied the reaction of (Ia) with those electrophiles in whose molecules (in contrast to the halogen and N_2O_4 molecules) the "nucleophilic" ("anionoid") and "electrophilic" ("cationoid") portions were different. Only iodotrinitromethane was isolated when (Ia) was reacted with ICl. The reaction of (Ia) with dry HCl led to the formation of TNM (up to 80% yield). Another possible product of these reactions, namely chloronitromethane, was practically not formed (traces of it were detected only in the case of HCl).* The reaction product of (Ia) with 2,4-(dinitrobenzene)-sulfenyl chloride is trinitromethyl 2,4-dinitrophenyl sulfide (II). The formation of $ClC(NO_2)_3$ is also not observed here. Fluorotrinitromethane is formed when (Ia) is reacted with $FClO_3$.

As a result, when (Ia) is reacted with various electrophilic reagents (A–B) the "electrophilic" portion (A) of the reagent adds to the carbon atom of (Ia) that is attached to the NO_2 groups, with the formation of the corresponding trinitromethyl derivatives. This makes it necessary to reexamine the hypothesis propounded in [1] regarding the reaction of (Ia) with electrophiles by the 1,3-addition scheme and propose a scheme where the "electrophilic" portion (A) of the reagent A–B attacks the carbon atom that bears the NO_2 group, with a simultaneous addition of the "nucleophilic" portion (B) to the carbon atom of the carbonyl group



(4)

This scheme is also supported by the fact that when (Ia) is reacted with N-chloropiperidine we isolated, along with $ClC(NO_2)_3$ (55% yield), also N-acetylpiperidine (III) (59% yield)



(5)

Another route is also possible for the formation of the trinitromethyl derivatives in the reactions of (Ia) with electrophilic reagents: all of these compounds could also be formed by the reaction of the electrophiles with the TNM anion. For example, it is possible to assume that the O-acetyl derivative is not the covalent compound (Ia), but rather that it exists in solution as the acylium salt of TNM, $CH_3CO^{\oplus}C(NO_2)_3^{\ominus}$. However, such an assumption is fairly improbable, since acylium salts are usually capable of giving only exceedingly strong acids. At first glance, the possibility of (Ia) converting to TNM, and its subsequent reaction with electrophiles, was also not excluded. However, a study of the ^{15}N NMR spectrum† of a freshly prepared solution of an enriched sample of (Ia) in CH_3CN at low temperatures refuted this assumption: signals, characteristic for the $C(NO_2)_3^{\ominus}$ (δ 28 ppm) and the free TNM (δ 34.2 ppm), were absent in the spectrum, as well as the signal of the primary decomposition product of (Ia), namely acetyl nitrate [1] (δ 66 ppm), and only two signals with δ 21.8 and 35.6 ppm were present, the first and more intense of which can be assigned to the nitrogen of the NO_2 group, while the second can be assigned to the nitrogen atom of the N-oxide of the O-acetyl derivative. Besides this, as was already mentioned in [1], TNM is absent in a solution of the freshly prepared (Ia), which was corroborated by us in each experiment, and also in its decomposition products.‡

The structure of (Ia) as not being the acylium salt of TNM is also corroborated by the UV spectroscopy data: although the UV spectrum of a solution of freshly prepared (Ia) in CH_3CN has a maximum in the 350 nm region, which is characteristic for the TNM anion, still the molar absorption coefficient (ε) in the

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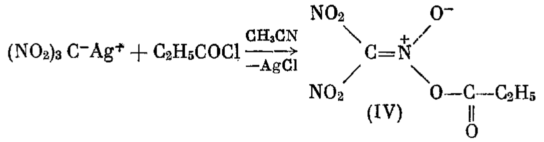
*It should be mentioned that $Cl\dot{C}(NO_2)_3$, as was shown in [1], can be formed in small amounts (up to 2-3%) when the Ag salt of TNM is treated with CH_3COCl, i.e., even in the step for the preparation of (Ia).

†Operating frequency = 6.07 MHz, and standard = $CH_3{}^{15}NO_2$.

‡The assumption that the TNM is formed from (Ia), and then is destroyed by the decomposition products of (Ia), should also be rejected, since when authentic TNM is added to a freshly prepared solution of (Ia) the amount of the former remains unchanged even after the complete decomposition of (Ia).

maximum is a total of ~600, whereas for the TNM anion it should be equal to 14,000.* The value of ε is retained when the solution of (Ia) is diluted with CH_3CN (the Beer law is obeyed), i.e., the ionization of (Ia) to the TNM anion fails to occur. As a result, it is possible to conclude that the trinitromethyl derivatives are formed only as the result of the reaction of (Ia) with electrophiles.

We also studied the acylation of the Ag salt of TNM using C_2H_5COCl (in an equimolar ratio); here, the same as in the case of other acyl halides [1], only O-acylation† is observed, with the formation of the O-propionyl derivative of TNM (IV)

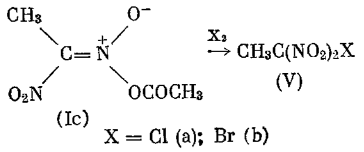


(6)

Compound (IV), the same as (Ia), is stable in solution only at low temperatures; $(C_2H_5CO)_2O$ and nitrogen oxides were identified (based on the GLC data, TNM is absent) in its decomposition products. A maximum is observed at 350 nm in the UV spectrum of (IV) (in CH_3CN solution) (ε = 1000, which remains constant on dilution). Similar to (Ia), when (IV) is treated with water it is quantitatively hydrolyzed to TNM, while on bromination it gives bromotrinitromethane (60% yield)

$$BrC(NO_2)_3 \xleftarrow{Br_2} (IV) \xrightarrow{H_2O} HC(NO_2)_3 \qquad (7)$$

The O-acyl derivatives of the gem-dinitroalkanes behave in the same manner as the O-acyl derivatives of TNM in the reactions with electrophilic reagents. Thus, for example, the O-acetyl derivative of 1,1-dinitroethane (Ic), which is formed by the reaction of the Ag salt of dinitroethane with an equimolar amount of CH_3COCl (in dimethoxyethane) [2], when reacted with either chlorine or bromine (at 0°) is respectively converted to either 1-chloro-1,1-dinitroethane (Va) in ~5% yield,‡ or 1-bromo-1,1-dinitroethane (Vb) in ~30% yield



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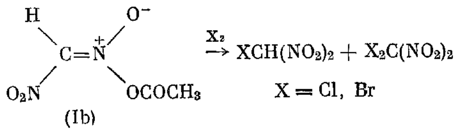
As was already mentioned [3], the chlorination of the O-acetyl derivative of dinitromethane (Ib) in dimethoxyethane leads to a mixture of the chloro- and dichloronitromethanes. An analogous mixture of products is obtained when the reaction is run in CH_2Cl_2. The bromination of (Ib) in dimethoxyethane gives a mixture of $Br_2C(NO_2)_2$ and $BrCH(NO_2)_2$, whereas only dibromodinitromethane is formed in CH_2Cl_2



(9)

EXPERIMENTAL METHOD**

Absolute solvents were used (the amount of water was less than 0.005-0.01%). The acetyl chloride was distilled twice over $POCl_3$, while the propionyl chloride was distilled without any additive, after which both of the acyl halides were distilled over CaH_2 (to remove traces of HCl). The preparation of the other starting materials was described in [1-3]. All of the yields based on the GLC were calculated without employing correction factors.

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*The absorption in the 350 nm region cannot be assigned to the unreacted TNM anion, since a quantitative yield of AgCl is always observed when (Ia) is prepared from the Ag salt of TNM and CH_3COCl; in addition, when a substantial excess of CH_3COCl (up to 40%) is used in this reaction, i.e., under conditions where even a small amount of unreacted TNM anion cannot authentically remain, the value of ε (~600) for (Ia) at 350 nm is retained constant.

†The absence of C-acylation products in the reaction mixture was established in conventional manner (see [2]).

‡As was mentioned in [2], chlorodinitroethane is not formed when (Ic) is chlorinated at −30°.

**Carried out with the assistance of T. P. Pan'shina.

Preparation of O-Acetyl Derivative of Trinitromethane (Ia). With stirring and cooling (–20°), to a freshly prepared solution of 0.02 mole of the Ag salt of TNM in 85 ml of CH_3CN was added in drops a solution of 1.75 g of CH_3COCl in 3 ml of CH_3CN, after which the mixture was stirred at –20 to –15° for 1 h, the AgCl precipitate was filtered (theoretical amount), and the filtrate was immediately used in subsequent reactions.

Reaction of (Ia) with Electrophiles. a) The reaction with chlorine was run as described in [1]; the yield of $ClC(NO_2)_3$ was 60%.

b) Reaction with bromine. With stirring and cooling (–5°), to a solution of 0.02 mole of (Ia) in CH_3CN was added a solution of 3.12 g of Br_2 in 3 ml of CH_3CN. The mixture was stirred at this temperature for another hour and then allowed to stand at 0° for a day. The solvent was removed under reduced pressure, and the residue was distilled to give the following fractions: 1 g with bp 27-30° (18-20 mm), and 3.05 g with bp 37-42° (4-5 mm). Based on the GLC data, the first fraction contains acetic anhydride and a small amount of $ClC(NO_2)_3$, while the second fraction is mainly bromotrinitromethane, yield ~2.8 g (~61%).

c) Reaction with iodine. With stirring, to a solution of 0.02 mole of (Ia) in CH_3CN at –20° was added a solution of 1.25 g of iodine in 10 ml of CH_3CN, after which the mixture was stirred at –15° for 30 min and then allowed to stand at 0° for a day. The solution became nearly colorless. The solvent was removed in vacuo, and the residue was dissolved in 50 ml of ether and shaken with 10 ml of 20% $AgNO_3$ solution (to remove the unreacted I_2),* then with water, and dried over $MgSO_4$. After removal of the ether the residue was dissolved by heating in 10 ml of hexane and then cooled to –70°. The obtained semicrystalline mass was pressed on a porous plate. We obtained 0.15 g (8%) of iodotrinitromethane with mp 55° [5].

d) Reaction with N_2O_4. With stirring and cooling (–15 to –10°), to a solution of 0.02 mole of (Ia) in CH_3CN was added a solution of 5 ml of N_2O_4 in 5 ml of CH_3CN, after which the mixture was kept at –10° for 1 h and then allowed to stand at 0° for a day. Then the solution was evaporated in vacuo to half volume, poured into 150 ml of water, and extracted with 100 ml of ether. The ether extract was washed with water and dried over $CaCl_2$. Removal of the ether gave 0.6 g of residue, which, based, on the GLC data, contained ~60% tetranitromethane, yield ~9%.

e) Reaction with ICl. With stirring, to a solution of 0.02 mole of (Ia) in CH_3CN at –10° was added a solution of 1.2 g of ICl in 3 ml of CH_3CN. The mixture was stirred at –10° for 2 h, and then at 0° for 1 h. The solvent was removed in vacuo, and the residue was dissolved in 100 ml of ether, shaken with 20 ml of 20% $AgNO_3$ solution, then several times with water, and dried over $MgSO_4$. After distilling off the ether, the residual oil was dissolved in 10 ml of hot hexane and then cooled in Dry Ice. We obtained 0.35 g (17%) of iodonitromethane with mp 54-55°.

f) Reaction with HCl. With stirring and cooling (–15°), dry HCl was passed into a solution of 0.02 mole of (Ia) in CH_3CN for 30 min, after which the mixture was allowed to stand at 0° for a day. The solvent was removed in vacuo, and the residue was distilled at 62-65° (30 mm). We obtained 2.3 g of a fraction, which (based on the GLC) contains ~95% of $HC(NO_2)_3$ (76% yield) and ~5% of $ClC(NO_2)_3$ (~2.5% yield).

g) Reaction with 2,4-(dinitrobenzene)sulfenyl chloride. With stirring and cooling (–15°), to a solution of 0.02 mole of (Ia) in CH_3CN was added a solution of 4.7 g of 2,4-(dinitrobenzene)sulfenyl chloride [6] in 10 ml of dimethoxyethane. The mixture was stirred at –15° for 1 h, and then it was allowed to stand at 0° for 2 days. The solvent was removed in vacuo, and the residue was pressed on a porous plate. The crystals that were separated here (0.45 g) represented unreacted sulfenyl chloride. The oil-impregnated plate was repeatedly extracted with $CHCl_3$, and the chloroform extracts were combined and evaporated in vacuo. The residue was treated with 50 ml of a boiling hexane–$CHCl_3$ mixture (2 : 1), the insoluble tarry mass was separated, and the solution was cooled in Dry Ice with vigorous stirring. The obtained crystals were separated and washed with a little hexane. We obtained 0.85 g (30%) of trinitromethyl 2,4-dinitrophenyl sulfide (II), with mp 68-69° (from hexane–$CHCl_3$, 2 : 1). The compound was identical with an authentic sample [7] (mixed melting point, TLC data).

h) Reaction with $FClO_3$. With stirring and cooling (0°), a stream of dry $FClO_3$ was passed into a solution of 0.02 mole of (Ia) for 4 h. Then the mixture was kept at 0° for a day, after which it was poured into cold water (500 ml) extracted with ether (100 ml). The ether solution was repeatedly washed with water, 5% $NaHCO_3$ solution, again with water (until the wash waters were colorless), and dried over $CaCl_2$. The ether

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*In the control experiment, it was shown that $IC(NO_2)_3$ does not react with $AgNO_3$ under analogous conditions.

was carefully distilled off at atmospheric pressure. Based on the GLC data, the residue contains fluorotrinitromethane (~5% yield) and $ClC(NO_2)_3$ (~2.5% yield).

i) Reaction with N-chloropiperidine. With stirring and cooling (0°), to a solution of 0.02 mole of (Ia) in CH_3CN was added 2.4 g of N-chloropiperidine [8] dropwise, after which the mixture was stirred for another 2 h, and then allowed to stand at 0° for a day. The solvent was removed in vacuo, and the residue was distilled. We obtained 2.05 g (55%) of chlorotrinitromethane with bp 51-54° (25 mm), and 1.5 g (59%) of N-acetylpiperidine* (III), bp 69-70° (2 mm).

Preparation of O-Propionyl Derivative of Trinitromethane (IV). With stirring and cooling (–5°), to a freshly prepared solution of 0.02 mole of the Ag salt of TNM in 85 ml of CH_3CN was added dropwise a solution of 2.05 g of C_2H_5COCl in 3 ml of CH_3CN, after which the mixture was stirred at –5 to 0° for 1 h, cooled to –25°, the AgCl precipitate was filtered (98% yield), and the obtained solution was immediately used in subsequent reactions.

Reaction of (IV) with Bromine. With stirring and cooling (–5 to 0°), to a solution of 0.02 mole of (IV) in CH_3CN was added a solution of 3.2 g of Br_2 in 2 ml of CH_3CN. The mixture was stirred at this temperature for another hour, and then it was allowed to stand at 0° for a day. The solvent was removed under reduced pressure, and the residue was distilled. We obtained 3.4 g (60%) of bromotrinitromethane with bp 70-80° (35 mm), contaminated with a small amount of chlorotrinitromethane (~3% yield).

Reaction of O-Acetyl Derivative of Dinitromethane (Ib) with Electrophiles. a) Reaction with chlorine. With stirring and cooling (–20 to –10°), to a suspension of 4.26 g of the Ag salt of dinitromethane in 70 ml of CH_2Cl_2 was added 1.65 g of CH_3COCl. The mixture was stirred for another 30 min at this temperature,† after which a stream of dry Cl_2 was passed into it for 30 min. Then the reaction mixture was allowed to warm up to 20°, and the AgCl precipitate was filtered. The filtrate was evaporated in vacuo, and the residue was distilled at 10 mm. We obtained 0.56 g of a mixture, which, based on the GLC data, contained 51% of $Cl_2C(NO_2)_2$ (~8% yield), and 29% of $ClCH(NO_2)_2$ (5.7% yield).

b) Reaction with bromine. To a solution of (Ib) in CH_2Cl_2, obtained in the same manner as described above, was added a solution of 3.12 g of Br_2 in 10 ml of CH_2Cl_2. The mixture was stirred for another 15 min at –10°, and then allowed to stand at 0° for a day. The AgCl precipitate was filtered, and the solvent was removed at a pressure of ~100 mm. Based on the GLC data, the residue contained $Br_2C(NO_2)_2$ and $BrCH(NO_2)_2$ was absent. Then the residue was dissolved in 100 ml of CH_2Cl_2, washed with 5% $NaHCO_3$ solution (4 × 30 ml), then with water, and dried over $MgSO_4$. The solvent was removed in vacuo. Based on the GLC data, the residue (0.6 g) contained 86% of dibromodinitromethane (~10% yield).

When the reaction was run in dimethoxyethane under analogous conditions a mixture was obtained that, based on the GLC data, contained $Br_2C(NO_2)_2$ (~17% yield) and $BrCH(NO_2)_2$ (~3% yield).

Reaction of O-Acetyl Derivative of 1,1-Dinitroethane (Ic) with Electrophiles. a) Reaction with chlorine. With stirring and cooling (–20 to –10°), to a suspension of 8.6 g of the Ag salt of 1,1-dinitroethane in 60 ml of dimethoxyethane was added 3 g of CH_3COCl. The mixture was stirred at –10° for another hour,‡ cooled to –30° and the passage of Cl_2 was started, with a gradual elevation of the temperature up to 0°, after which the Cl_2 was passed for another 2 h, and the mixture was allowed to stand at 0° for a day. The AgCl precipitate was filtered, and the filtrate was evaporated in vacuo. The residue was dissolved in ether, washed several times with water, and dried over $MgSO_4$. The ether was evaporated, and the residue (1.2 g), based on the GLC data, was found to contain 20% of 1-chloro-1,1-dinitroethane** (~5% yield).

b) Reaction with bromine. With stirring and cooling (–30°), to a solution of (Ic), obtained in a similar manner from 9.5 g of the Ag salt of 1,1-dinitroethane and 3.3 g of CH_3COCl, was added a solution of 6.7 g of Br_2 in 10 ml of dimethoxyethane. Then the temperature was gradually raised up to 0° and the mixture was kept for a day. The AgCl precipitate was separated, and the filtrate was worked up as described above. Based on the GLC data, the yield of 1-bromo-1,1-dinitroethane was ~27%.

The ^{15}N NMR spectrum of (Ia) was taken by M. Myagi, for which the authors express their gratitude to him.

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*The compound was identified by comparison with an authentic specimen, which was obtained from piperidine and CH_3COCl [9].

†The Ag salt did not react completely here [3].

‡The Ag salt did not react completely here [2].

**Dinitroethane, which can be formed in the decomposition of (Ic) [2], does not halogenate under these conditions.

CONCLUSIONS

The O-acyl derivatives of polynitroalkanes (trinitromethane, dinitromethane and 1,1-dinitroethane) react with various electrophilic reagents to give the corresponding trinitro- and dinitromethyl derivatives.

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