REACTION OF O-ACYL DERIVATIVES OF POLYNITROALKANES
WITH ELECTROPHILIC REAGENTS

V. I. Erashko, B. G. Sankov, S. A. Shevelev, and A. A. Fainzil'berg

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 bromotrinomethanes [1], while the chlorination of the O-acetyl derivative of dinitromethane (Ib) led to the chloro-derivatives of dinitromethane [3]:

\[
\begin{align*}
R\overset{\text{NO}_2}{} + RC\left(\text{NO}_2\right)\overset{\text{OCOCH}_3}{} & \quad \xrightarrow{\text{AgCl}} \quad R\overset{\text{NO}_2}{} \overset{\text{OCOR'}}{} \quad (I) \quad \overset{\text{AgCl}}{} \\
R=\text{NO}_2, \ R'=\text{CH}_3(a); \ R=\text{H}, \ R'=\text{CH}_3(b); \ R=\text{CH}_3, \ R'=\text{CH}_3(c)
\end{align*}
\]

In the present paper we studied the reaction of (I) with a broader gamut of electrophilic reagents (halogens, ICl, N_2O_4, HCl, FCIO_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\(^\circ\) and a concentration of \(~0.2\) mole/liter; (Ia) remains unchanged for \(~2-3\) h when the temperature is raised up to 0\(^\circ\), while at 20\(^\circ\) 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\(^\circ\).

The corresponding halotrinomethanes, 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:

\[
\begin{align*}
\text{H}_2\text{O} & \quad \xrightarrow{} \quad \text{HC(NO}_2)_3 \\
X & \quad \xrightarrow{} \quad \text{XC(NO}_2)_3 (X=\text{Cl, Br, I}) \\
\text{NO}_4 & \quad \xrightarrow{} \quad \text{C(NO}_2)_4 \\
\text{ICl} & \quad \xrightarrow{} \quad \text{IC(NO}_2)_3 \\
\text{HCl} & \quad \xrightarrow{} \quad \text{HC(NO}_2)_3 \\
\text{2,4(NO}_2)_3\text{PhCl} & \quad \xrightarrow{} \quad \text{O}_2\text{N-S-C(NO}_2)_3 \\
\text{PCIO}_3 & \quad \xrightarrow{} \quad \text{FC(NO}_2)_3
\end{align*}
\]

*See [4] for preliminary communication.
Tetranitromethane is formed when (Ia) is treated with N₂O₄. Another possible route for the formation of C(NO₂)₄, namely the reaction of N₂O₄ with the (CH₃CO)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 (Cl₂ and Br₂) 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 N₂O₄ molecules) the "nucleophilic" ("anionoid") and "electrophilic" ("cationoid") portions were different. Only iodotnitromethane 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(NO₂)₃ is also not observed here. Fluorotnitromethane is formed when (Ia) is reacted with FCIO₃.

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 NO₂ 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 NO₂ group, with a simultaneous addition of the "nucleophilic" portion (B) to the carbon atom of the carbonyl group

\[
\begin{align*}
\text{(Ia)} & \xrightarrow{A-B} \text{A} + \text{B} \\
\text{NO}_2 & \quad \text{O}^+ \quad \text{O}^- \\
\text{C} = \text{N} & \quad \text{OCCOCH₃} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

(4)

This scheme is also supported by the fact that when (Ia) is reacted with N-chloropiperidine we isolated, along with ClC(NO₂)₃ (55% yield), also N-acetylpiperidine (III) (59% yield)

\[
\begin{align*}
(\text{Ia}) + \text{Cl} & \xrightarrow{-N} \text{ClC(NO₂)₃} + \text{CH₃C} - \text{N} \\
\text{O} & \quad \text{(III)}
\end{align*}
\]

(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, CH₃CO⁺C(NO₂)₃. 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 ¹⁵N NMR spectrum† of a freshly prepared solution of an enriched sample of (Ia) in CH₃CN at low temperatures refuted this assumption; signals, characteristic for the C(NO₂)₃ (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 NO₂ 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 CH₃CN has a maximum in the 350 nm region, which is characteristic for the TNM anion, still the molar absorption coefficient (ε) in the

*It should be mentioned that ClC(NO₂)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 CH₃COCl, i.e., even in the step for the preparation of (Ia).

†Operating frequency = 6.07 MHz, and standard = CH₃¹⁵NO₂.

‡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).