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O-α-NITROALKYL OXIMES OF 1,5-DISUBSTITUTED 1,1,5,5-TETRANITRO-
PENTAN-3-ONES

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There is limited information on the autocondensation of the salts of nitro compounds [1-4]. The reaction of the salts of gem-dinitroalkanes (1,1-dinitroethane and 1,1-dinitropropane) with acylating agents leads to the products of autocondensation of the initial nitroalkanes — the α,α-dinitroalkyl esters of nitrolic acids [2, 4]

\[ 2[R\text{C(NO}_2\text{)}_2]^-M^+ \rightarrow R\text{C} = \text{NOC(NO}_2\text{)}_2R \]

The following conversion was described in the series of the salts of secondary nitroalkanes [5]:

\[ 2(\text{PhC} = \text{NOC(NO}_2\text{)Ph}) \text{Ag}^+ \rightarrow \text{PhC} = \text{NOC(NO}_2\text{)Ph} \]

The action of strong acids on the salts of secondary polynitroalkanes and the corresponding nitronic acids was investigated in the present work. It was found that the O-α-nitroalkyl nitro-substituted oximes are formed on the treatment of the salts of 1,5-disubstituted 1,1,3,5,5-pentanitropentanes with concentrated sulfuric or trifluoroacetic acid

\[ 2R_2\text{C} = \text{NO}_2^+ \text{BH}^+ \rightarrow 2R_2\text{C} = \text{NO}_2 \text{H} \rightarrow R_2\text{C} = \text{NOC(NO}_2\text{)R} \]

\[ R = \text{CH}_3\text{CF(NO}_2\text{)C}_2\text{H}_2\text{, (I); CH}_3\text{C(NO}_2\text{)CH}_2\text{C}_2\text{H}_2\text{ (II); CH}_2\text{C(NO}_2\text{)CH}_2\text{CH}(\text{III). B} = \text{NH}_3, \text{C}_2\text{H}_5\text{N.} \]

The reaction proceeds via the formation of nitronic acids, and (II) was obtained previously [6] from 1,1,1,5,5,5,-hexanitropentane-3-nitronic acid by heating in CF3COOH.

We utilized the nitronic acid described in [7], and also synthesized 2,2,6,6-tetranitroheptane-4-nitronic acid (IV), with the aim of investigating the general character of the formation of O-substituted oximes of polynitroketones from nitronic acids

\[ [\text{MeC(NO}_2\text{)CH}_2\text{]}_2\text{C} = \text{NO}_2^+ \text{K}^+ \frac{\text{CF}_3\text{COOH}}{\varphi} \rightarrow [\text{MeC(NO}_2\text{)CH}_2\text{]}_2\text{C} = \text{NOOH} \]

The formation of the O-substituted oximes of 1,5-substituted 1,1,5,5-tetranitropentane-3-ones proceeds by heating the nitronic acids with CF3COOH; a higher yield (87.4%) was obtained for (II) by utilizing trifluoroacetic anhydride.

The O-substituted oximes synthesized are colorless crystals with mp 64-65°C (I), 144-146°C (with decomposition) (II), and 146-147°C (with decomposition) (III). They have good solubility in chloroalkanes and benzene, are stable in acidic media, and decompose when subjected to oxidation by KMnO4.

The structure of (I)-(III) was confirmed by the data of the IR and PMR spectra. The weak bands at 1000, 1175 cm⁻¹ (I), 920, 1115, and 1195 (II), and 1145 cm⁻¹ (III), which are characteristic [8] of O-substituted oximes but somewhat displaced under the influence of the


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nitro groups, appear in the IR spectra of the O-substituted oximes of 1,5-substituted 1,1,5,5-tetranitropentanones by comparison with the initial alkanes or nitronic acids. The C=N bond is not expressed in the spectra of (II) and (III), but is presented with a band at 1690 cm^{-1} in (I).

In the PMR spectra of (I)-(III),

\[
\begin{align*}
&\text{(NO}_2\text{)}_2\text{CXCH}_2
\begin{array}{c}
\text{C}=\text{N} \rightarrow \text{O} \\
&\text{CH}_2\text{CX(NO}_2\text{)}_2
\end{array}
\begin{array}{c}
\text{(NO}_2\text{)}_2\text{CXCH}_2
\end{array}
\end{align*}
\]

X = F (I), NO₂ (II), Me(III)

the four methylene groups are clearly shown in all cases (cf. the Experimental section). Two of the methylene groups (1 and 2), with the magnetically equivalent geminal protons, are non-equivalent (in connection with the different orientation relative to the O atom of the oxime grouping); whereas the two others (3 and 4), equivalent in pairs, have magnetic nonequivalence of the geminal protons (due to the presence of three different substituents at the neighboring atom of C). The number of the lines is doubled in the spectrum of (I) by comparison with (II) on account of the spin–spin interaction with the ^{19}F nucleus. Three signals of the methyl groups, with the ratio of intensities 1:1:2, are observed in the spectrum of (III) besides the signals of the methylene protons, i.e., the nonequivalence, determined by the position relative to the C=N bond, is also shown.

**EXPERIMENTAL**

The pyridinium and ammonium salts of 1,1,1,3,5,5,5-heptanitro- and 1,5-difluoro-1,1,3,5,5-pentanitropentane were obtained according to [9]. The potassium salt of 2,2,4,6,6-pentanitroheptane was obtained according to [10]. We obtained 1,1,1,5,5,5-hexanitropentane-3-nitronic acid according to [7].

The PMR spectra were taken on an OIKhF (Academy of Sciences of the USSR) spectrometer with a cryogenic magnet (294 MHz) from TMS. The IR spectra were taken on a UR-20 instrument.

**0-Bis(2-fluoro-2'-2'-dinitroethyl)nitromethyl Bis(2'-fluoro-2',2'-dinitroethyl)carboxime (I).** To 100 ml of conc. H₂SO₄ at 0°C was added, with stirring, a suspension of 4.1 g (0.01 mole) of the pyridinium salt of 1,5-difluoro-1,1,3,5,5-pentanitropentane in 40 ml of CCl₄. The mixture was extracted with 50 ml of CH₂Cl₂ after 5 min. The extract was washed with conc. H₂SO₄ and concentrated in vacuo. The residue was crystallized from dry CHCl₃. The yield of (I) was 2 g (61%); it had mp 64-65°C. Found: C 18.9; H 1.3; N 21.5; F 11.8%; mol. wt. 650 (in benzene). C₁₀H₆N₁₀O₁₉F₄. Calculated: C 18.53; H 1.24; N 21.61; F 11.72%; mol. wt. 648.2. IR spectrum (ν, cm^{-1}): 818 medium, 852 medium, 940 weak, 1000 weak, 1075 weak, 1090 medium, 1150 weak, 1190 weak, 1270 medium, 1315 strong, 1340 medium, 1375 medium, 1412 medium, 1600 strong, 1620 strong, 1690 weak, 2380 medium, 2960 weak, 2980 weak, and 3020 weak. PMR spectrum (in MeCN, δ, ppm; J, Hz): 4.254 doublet (2H, CH₂, JHF = 16.5), 4.065 doublet (2H, CH₂, JHF = 18.3), and 4.245 doublet (4H, CH₂, the AB part of the spectrum of type ABX, X = ^{19}F, Δν = 62.2 Hz, Jg = 16.9, JAX = 19.1, JBX = 11.5).

**0-Bis(2,2,2-trinitroethyl)nitromethyl Bis(2',2',2'-trinitroethyl)carboxime (II).** A. To 100 ml of conc. H₂SO₄ at 0°C was added, with stirring, a suspension of 4.0 g (0.01 mole) of the ammonium salt of 1,1,1,3,5,5,5-heptanitropentane in 40 ml of CCl₄. The solid product was filtered off after 4 min. It was pressed out on the filter and then placed in a flask equipped with a reflux condenser. We added 150 ml of CCl₄ and boiled until the complete solution of the product was effected. The organic layer was separated and slowly cooled. The crystals were filtered off and dried. The yield of (II) was 2.65 g (70%); the temperature of decomposition was 144-146°C. Found: C 15.7; H 1.0; N 26.3%; mol. wt. 756 (in benzene). C₁₀H₈N₄O₂₇. Calculated: C 15.88; H 1.07; N 25.93%; mol. wt. 756.26. IR spectrum (ν, cm^{-1}): 792 medium, 811 strong, 845 medium, 865 medium, 920 weak, 972 strong/weak, 1065 weak, 1115 weak, 1160 weak, 1299 strong, 1372 medium, 1415 medium, 1599 strong, 1602 strong, 2380 medium, 2920 weak, 2980 medium, 3000 medium, and 3016 medium. PMR spectrum (in CH₂Cl₂, δ, ppm): 4.374 singlet (2H, CH₂), 4.100 singlet (2H, CH₂), and 4.277 (4H, CH₂, the spectrum of the type ABX, X = ^{19}F, Δν = 62.2 Hz, Jg = 16.9, JAX = 19.1, JBX = 11.5).