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# NUCLEOPHILIC SUBSTITUTION REACTIONS OF 2,4,6-TRIS(TRINITROMETHYL)-1,3,5-TRIAZINE.

## 3*. REACTION OF 2,4,6-TRIS(TRINITROMETHYL)-1,3,5-TRIAZINE WITH AZIDES AND HYDRAZINE

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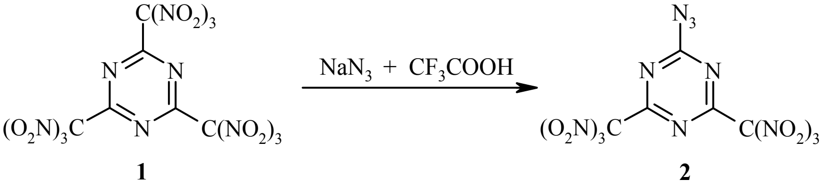
*As a result of nucleophilic substitution of the trinitromethyl groups in 2,4,6-tris(trinitromethyl)-1,3,5-triazine, the corresponding monoazido and diazido derivatives have been synthesized. The reaction of the starting triazine with hydrazine acetate in the presence of trifluoroacetic acid leads to 1-acetyl-2,2-bis[4,6-bis(trinitromethyl)-1,3,5-triazin-2-yl]hydrazine.*

**Keywords:** sodium azide, hydrazine, trimethylsilyl azide, 2,4,6-tris(trinitromethyl)-1,3,5-triazine, nucleophilic substitution.

We reported earlier on the synthesis of 2,4,6-tris(trinitromethyl)-1,3,5-triazine (**1**) [2, 3] and its reactions with such nucleophiles as alcohols, diols, ammonia, primary and secondary amines, hexamethyldisilazane [3, 4]. We showed that, depending on the experimental conditions, we can obtain the products of substitution of one, two, or three trinitromethyl groups.

Our results show that the chemical properties of triazine **1** are similar to those of cyanuric chloride, for which, in addition to reaction with alcohols and amines, reactions have also been described with sodium azide and hydrazine that lead to the corresponding azido and hydrazino derivatives [5]. No data on such triazine derivatives are available in the literature. Accordingly, in this work we have studied the possibilities for nucleophilic substitution of the trinitromethyl groups of triazine **1** in reactions with sodium azide and hydrazine.

The reaction of compound **1** with sodium azide leads to a mixture of mono-, di-, and trisubstitution products which are difficult to separate, regardless of the amount of azide used. When using a mixture of sodium azide and trifluoroacetic acid (this actually is a solution of hydrazoic acid in trifluoroacetic acid obtained *in situ*), we were able to carry out selective substitution of a single trinitromethyl group; in this case, the yield of 2-azido-4,6-bis(trinitromethyl)-1,3,5-triazine (**2**) was 75%:



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* For Communication 2, see [1].

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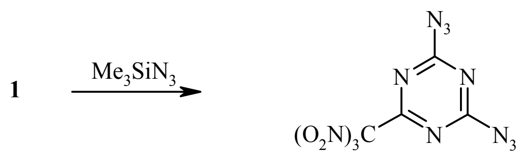
Compound **2** was isolated as a viscous oil that was prone to hydrolysis (decomposes on silica gel with evolution of nitroform).

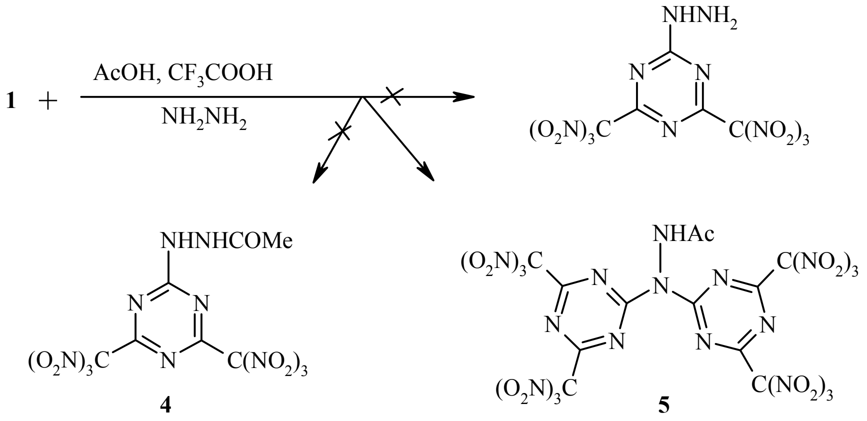
Selective substitution of two trinitromethyl groups occurs upon reaction of triazine **1** with trimethylsilyl azide; 2,4-diazido-6-trinitromethyl-1,3,5-triazine (**3**) is formed in 68% yield:



**3**

Diazidotriazine **3**, in contrast to monoazidotriazine **2**, is a solid and hydrolytically stable compound which sublimes at the melting point. Both compounds are sensitive to friction and shock, and working with them requires considerable caution. Their structure is supported by spectral data. Thus in the IR spectra, there are absorption bands from the azido groups in the 2100-2200 cm$^{-1}$ region and also from the triazine ring and the nitro groups in the 1400-1600 cm$^{-1}$ region; the number of signals and the chemical shifts of the carbon atoms in the $^{13}$C NMR spectra correspond to the proposed structures. It is interesting to note the presence of a qualitative correlation between the chemical shifts of the nitro groups in $^{14}$N NMR spectra and a tendency of the corresponding trinitromethyl-1,3,5-triazines toward hydrolysis. The decrease in the absolute values of the chemical shifts for the nitrogen nuclei of the $NO_2$ group is accompanied by a decrease in reactivity in the series of compounds **1** > **2** > **3**.

Triazine **1** vigorously decomposes when treated with hydrazine, hydrazine hydrate, and their solutions, while it does not react with hydrazine hydrochloride and hydrazine sulfate. The reaction of triazine **1** with commercial hydrazine acetate in the presence of trifluoroacetic acid leads to formation of a compound with a band in the IR spectrum from the carbonyl group (1720 cm$^{-1}$); in the 1H NMR spectrum, along with the downfield signal from the NH group at 9.91 ppm, there is a signal at 2.03 ppm, and the ratio of their intensities is 1:3 respectively; in the $^{13}$C NMR spectrum, along with signals from the triazine ring (167.89, 163.71, and 162.97 ppm) and the trinitromethyl groups that are nonequivalent due to hindered rotation (123.67 ppm and 123.55 ppm), we observe a multiplet at 169.21 ($J$ = 7.6 Hz) and a quartet at 20.57 ppm ($J$ = 129.0 Hz). These data allow us to hypothesize the presence of an $NHCOCH_3$ group and one or several triazine rings with two trinitromethyl groups in the product obtained (see structures **4** or **5**). The features of the NMR spectra (the ratio of the integrated intensities in the $^1$H NMR spectrum, the number of signals, and the lack of a spin–spin coupling constant $^3J_{CH}$ for NH–C(2) of the triazine in the $^{13}$C NMR spectrum) and the elemental analysis data are evidence in favor of structure **5**.



**4** **5**

## EXPERIMENTAL

The IR spectra were taken on a Specord UR-20. The $^1$H, $^{13}$C, $^{14}$N spectra were obtained on a Bruker AM-300 (300, 75, 21 MHz respectively), internal standard TMS. The melting points were determined on a Boetius heating stage with heating rate 4°C/min at the melting point.

**Synthesis of 2,4,6-tris(trinitromethyl)-1,3,5-triazine 1** is described in [3].

**2-Azido-4,6-bis(trinitromethyl)-1,3,5-triazine (2).** A mixture of $NaN_3$ (0.975 g, 15 mmol), trifluoroacetic acid (5 ml), and methylene chloride (10 ml) were added at room temperature with stirring to a solution of triazine **1** (2.01 g, 4 mmol) in $CCl_4$ (20 ml). The reaction mass was stirred for 30 min, washed with water (100 ml), and dried with calcined $Na_2SO_4$ (100 ml); the solvents were evaporated off and 1.26 g (75%) of compound **2** was obtained as a viscous oil. IR spectrum (thin film), ν, cm$^{-1}$: 2150, 1620, 1580, 1550, 1430, 1450, 1350, 1300, 1270, 1180, 1150, 1100, 1090, 980, 890, 800, 780. $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 172.33 (N–C=N); 164.11 (C–$\underline{C}$=N); 121.30 ($C(NO_2)_3$). $^{14}$N NMR spectrum ($CDCl_3$), δ, ppm: -41.01 ($NO_2$), $\Delta\nu_{1/2}$ (peak width at half height) 1.62 Hz; -151.05 ($N_3$). Found, %: N 39.55. $C_5N_{12}O_{12}$. Calculated, %: N 40.00.

**2,4-Diazido-6-trinitromethyl-1,3,5-triazine (3).** Trimethylsilyl azide (1.38 g, 12 mmol) was added at room temperature with stirring to a solution of triazine **1** (2.01 g, 4 mmol) in $CCl_4$ (20 ml). The reaction mass was stirred for 30 min, washed with water (5 × 20 ml), dried with calcined $Na_2SO_4$, and filtered through a thin layer of silica gel; the filtrate was evaporated off and 0.85 g (68%) of product **3** was obtained as a viscous liquid which crystallized upon standing; mp 96-97°C (heptane). IR spectrum (KBr), ν, cm$^{-1}$: 2900, 2185, 2160, 1625, 1590, 1510, 1450, 1385, 1370, 1320, 1280, 1150, 980, 890, 840, 790. $^{13}$C NMR spectrum ($CDCl_3$), δ, ppm: 171.91 (N–C=N); 163.91 (C–$\underline{C}$=N); 122.19 ($C(NO_2)_3$). $^{14}$N NMR spectrum, ($CDCl_3$), δ, ppm: -39.14 ($NO_2$); -149.37 ($N_3$). Found, %: N 53.18. $C_4N_{12}O_6$. Calculated, %: N 53.85.

**1-Acetyl-2,2-bis[4,6-bis(trinitromethyl)-1,3,5-triazin-2-yl]hydrazine (5).** Hydrazine acetate (0.92 g) in a mixture of trifluoroacetic acid (5 ml), $CH_2Cl_2$ (10 ml) and dry dioxane (5 ml) was added at room temperature with stirring to a solution of triazine **1** (2.01 g, 4 mmol) in $CCl_4$ (20 ml). The reaction mass was stirred for 30 min, washed with water (5 × 20 ml), dried with calcined $Na_2SO_4$, filtered through a thin layer of silica gel; the filtrate was evaporated off and 1.16 g (73%) of compound **5** was obtained; mp 151-152°C ($CCl_4$). IR spectrum (KBr), ν, cm$^{-1}$: 3390, 3200, 3100, 2990, 1720, 1600, 1560, 1450, 1350, 1300, 1240, 1140, 1100, 1020, 1000, 980, 910, 900, 800. $^1$H NMR spectrum (acetone-d$_6$), δ, ppm: 2.03 (3H, s, $CH_3$); 9.91 (1H, s, NH). $^{13}$C NMR spectrum (acetone-d$_6$), δ, ppm, *J* (Hz): 169.21 (m, $^3J = 7.6$, $CH_3\underline{C}ONH$); 167.89 (s, N–$\underline{C}$=N); 163.71 and 162.97 (s, C–$\underline{C}$=N); 123.67 and 123.55 (s, $C(NO_2)_3$); 20.57 (q, $^1J = 129.0$, $CH_3$). $^{14}$N NMR spectrum (acetone-d$_6$), δ, ppm: -38.06 ($NO_2$). Found, %: C 17.40; H 1.20; N 33.72. $C_{12}H_4N_{20}O_{25}$. Calculated, %: C 17.40; H 0.49; N 33.82.

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