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TRISUBSTITUTED 1,3,5-TRIAZINES.
4.* SYNTHESIS OF 2-NITROAMINO-4,6-BIS(TRINITROMETHYL)-1,3,5-TRIAZINE

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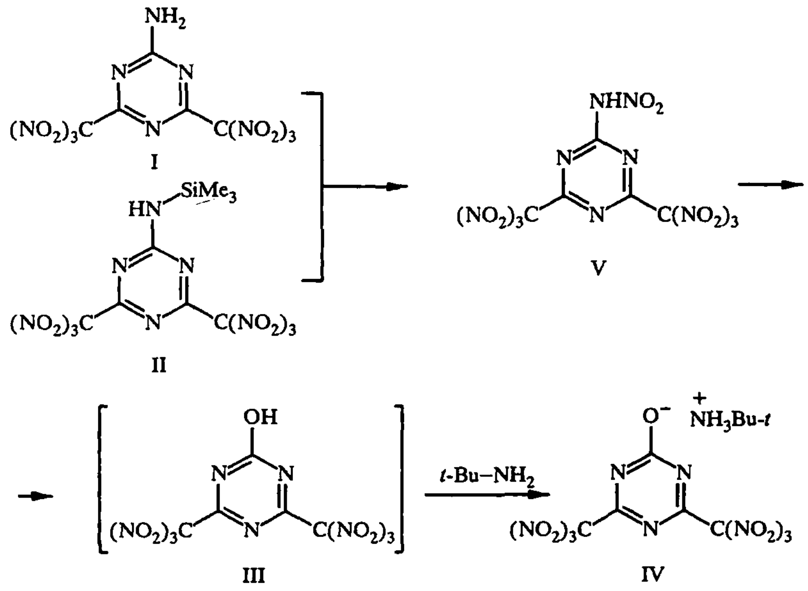
The nitration, at the amino group, of 2-amino-4,6-bis(trinitromethyl)-1,3,5-triazine and its derivatives has been studied.

Nitroamines manifest high reactivity and hence are of both scientific and practical interest [1]. In the 1,3,5-triazine series, *N*-nitroamines are known. Upon the nitration of 2,4,6-triaminotriazine (melamine) with a mixture of nitric acid and acetic anhydride, 2,4-bis(nitroamino)-6-hydroxy-1,3,5-triazine (dinitroammeline) is formed [2]. Triacetylmelamine under these conditions is converted to 4,6-dihydroxy-2-nitroamino-1,3,5-triazine; interaction with fuming nitric acid gives *N*-nitro-*N'*,*N''*-diacetylmelamine [3]. Also reported is 2,4,6-tris(methylnitroamino)-1,3,5-triazine [4].

In the work reported here, we investigated the nitration of 2-amino- and 2-trimethylsilylamino-4,6-bis(trinitromethyl)-1,3,5-triazines (I and II) under various conditions, with a series of nitrating agents. We had previously developed the method used in synthesizing these triazines [5, 6].



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*For Communication 3, see [1].

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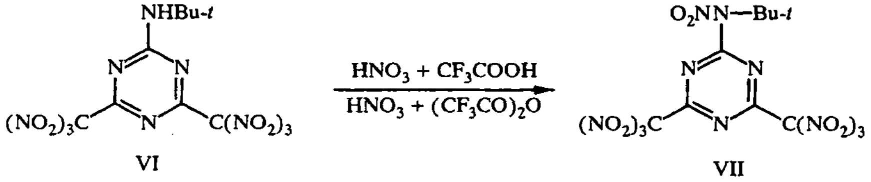
Numerous attempts at the direct *N*-nitration of compounds I and II were unsuccessful. The action of a mixture of nitric acid and acetic anhydride on the amine I resulted in recovery of the unchanged original substance, and the substituted amine II was converted into I under these conditions. When using mixtures of nitric acid with trifluoroacetic acid, trifluoroacetic anhydride, or sulfuric acid, and also when using nitronium borofluoride in acetonitrile or nitric acid ($d = 1.5$), we obtained only 2-hydroxy-4,6-bis(trinitromethyl)-1,3,5-triazine (III), isolated in the form of the *tert*-butylammonium salt (IV). It is highly probable that in the course of this reaction, the original compounds I and II are nitrated to form 2-nitroamino-4,6-bis(trinitromethyl)-1,3,5-triazine (V), which, under the action of the nitrogen oxides that are present in the nitrating agents, is converted to the unstable compound III.

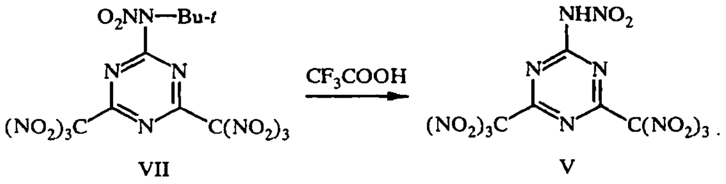
On the assumption that the main reason for the failure of direct nitration of the triazines I and II is the instability of the nitroamine V under the selected conditions, we resorted to intermediate protection of the nitroamino group. As the initial compound we used 2-*tert*-butylamino-4,6-bis(trinitromethyl)1,3,5-triazine (VI). Its nitration by a mixture of nitric and trifluoroacetic acids or a mixture of nitric acid and trifluoroacetic anhydride gave good yields of 2-*tert*-butylnitroamino-4,6-bis(trinitromethyl)-1,3,5-triazine (VII).



The structure of compound VII was confirmed by physicochemical methods and by elemental analysis. Its IR spectrum contains absorption bands of the NO_2 group and the triazine ring, with no bands that are characteristic for the NH group; also, the upfield signal of the proton of this group is also absent in the ^1H NMR spectrum.

The ^{13}C NMR spectrum does not contradict the structure VII, and it contains characteristic signals of the carbon atoms of the triazine ring (162.72 and 161.81 ppm), trinitromethyl groups (121.58), the quaternary carbon atom (67.78), and methyl groups (27.33). In the ^{14}N NMR spectrum we observed two signals with different intensities, from nitrogen atoms of the nitro groups, at -40.39 ppm for $C(NO_2)_3$, and -41.13 ppm for $N–NO_2$.

Upon refluxing the triazine VII in trifluoroacetic acid, the *tert*-butyl protective group is removed, and the nitroamino V is formed with a yield of 56%.



The structure of compound V was confirmed by spectrometric methods and elemental analysis. The IR spectrum contains absorption bands of NH and NO_2 groups, and also of the triazine ring. In the ^1H NMR spectrum, there is an isolated singlet signal from the proton of the NH group (5.17 ppm). In the ^{13}C NMR spectrum, there are signals from the triazine ring carbon atoms (164.06 and 162.34 ppm) and from the carbon atoms of the trinitromethyl groups (121.28 ppm). In the ^{14}N NMR spectrum, the signals from the nitrogen atoms of the trinitromethyl groupings are shifted downfield (-45.56 ppm) in comparison with the analogous signals of the triazine VII; and for the $N–NO_2$ group, this shift is greater (-64.00 ppm).

EXPERIMENTAL

The IR spectra were taken on a Specord instrument in KBr tablets. The ^1H, ^{13}C, and ^{14}N NMR spectra were obtained on a Bruker AM-300 instrument (300, 75.5, and 21.67 MHz, respectively), internal standard TMS.

Melting points were determined on a Boeitus heating stage, with a heating rate of 4°C/min at the melting point.

The synthesis of the 2-amino-4,6-bis(trinitromethyl)-1,3,5-triazine I was described in [4], and the synthesis of the 2-trimethylsilylamino- and *tert*-butylamino-4,6-bis(trinitromethyl)-1,3,5-triazines II and VI was described in [5].

***tert*-Butylammonium salt of 2-hydroxy-4,6-bis(trinitromethyl)-1,3,5-triazine (IV).** To a solution of 394 mg (1 mmole) of the triazine I or 466 mg (1 mmole) of the triazine II in 4 ml of $(CF_3CO)_2O$, at 0°C, 0.5 ml of HNO_3 (d = 1.5) was added. The reaction mixture was stirred 1 h at 18-20°C, then evaporated in a rotary evaporator. The residue was extracted with chloroform, and the extract was washed with a minimum amount of cold water (5 ml), after which 1 ml of *tert*-butylamine was added. The precipitated product was filtered off, dried on the filter, and recrystallized from a 1:1 mixture of chloroform and ethyl acetate. Obtained 230 mg (50%) of the triazine IV, mp 150°C (decomp.). IR spectrum: 3210, 3165, 3050, 2975, 2900, 2810, 1690, 1575, 1530, 1440, 1400, 1380, 1350, 1275, 1225, 1115, 765, 755 cm^{-1}. ^{13}C NMR spectrum, in $(CD_3)_2CO$: 164.98; 163.34 (—C=N); 121.90 ($C(NO_2)_3$); 51.58 ($\underline{C}(CH_3)_3$); 29.53 ppm (CH_3). ^{14}N NMR spectrum, in $(CD_3)_2CO$: -35.47 ($\Delta\nu_{1/2}$ = 4.5 Hz, NO_2); - 324.29 ppm (br. s, $+NH_3C_4H_9$-*tert*). Found, %: C 23.26; H 2.69; N 29.73. $C_9H_{12}N_{10}O_{13}$. Calculated, %: C 23.09; H 2.58; N 29.91.

2-(*tert*-Butylnitroamino)-4,6-bis(trinitromethyl)-1,3,5-triazine (VII). To a solution of 720 mg (1.6 mmoles) of the triazine VI in 3 ml of $(CF_3CO)_2O$ or CF_3COOH, at 0°C, 1.5 ml of HNO_3 (d = 1.5) was added, the solution was stirred 1 h at 18-20°C, and then 5-6 ml of cold water was added. The resulting precipitate was filtered off, washed with 2 ml of CF_3COOH chilled to 0°C, and dried on the filter in a flow of dry nitrogen or argon. Obtained 670 mg (84%) of the triazine VII, mp 92°C. By extraction of the filtrate (along with the acid used to wash the precipitate) with $CHCl_3$, the yield of the product VII can be brought up to the quantitative level. IR spectrum: 1605, 1575, 1570, 1550, 1495, 1480, 1430, 1350, 1260, 1240, 1150, 1090, 1010, 960, 910 cm^{-1}. PMR spectrum, in $CDCl_3$: 1.70 ppm (9H, s, $3CH_3$). ^{13}C NMR spectrum, in $CDCl_3$: 162.72; 161.81 (—C=N); 121.58 ($C(NO_2)_3$); 67.78 ($\underline{C}(CH_3)_3$); 27.33 ppm (CH_3) . ^{14}N NMR spectrum, in $CDCl_3$: -40.39 (NO_2 in $C(NO_3)_3$); -41.13 ppm (N—NO_2). Found, %: C 21.98; H 1.54; N 31.31. $C_9H_9N_{11}O_{14}$. Calculated, %: C 21.83; H 1.83; N 31.11.

2-Nitroamino-4,6-bis(trinitromethyl)-1,3,5-triazine (V). A solution of 670 mg (1.35 mmoles) of the triazine VII in 5 ml of trifluoroacetic acid was refluxed 15 min and then cooled; the crystals were filtered off, washed with chilled CF_3COOH (2 ml), and dried on the filter in a flow of dry nitrogen or argon. Obtained 0.59 g (56%) of the product V, mp 69-70°C (decomp.). PMR spectrum, in $CDCl_3$: 5.17 ppm (1H, s, NH). ^{13}C NMR spectrum, in $CDCl_3$: 164.06; 162.34 (—C=N); 121.28 ($C(NO_2)_3$). ^{14}N NMR spectrum, in $CDCl_3$: -45.56 (s, $\Delta\nu_{1/2}$ = 2.25 Hz, NO_2 in $C(NO_2)_3$); -64.00 ppm (br. s, N—NO_2). Found, %: C 14.08; H 0.10; N 34.93. $C_5H_1N_{11}O_{14}$. Calculated, %: C 13.68; H 0.22; N 35.09.

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