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TRISUBSTITUTED 1,3,5-TRIAZINES.

3.* SYNTHESIS OF SUBSTITUTED 2,4,6-TRIS(HYDROXYIMINOMETHYL)-1,3,5-TRIAZINES

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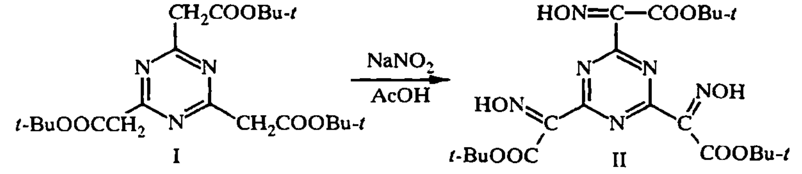
Previously undescribed substituted 2,4,6-tris(hydroxyiminomethyl)-1,3,5-triazines, including 2,4,6-(1,3,5-triazinetriyl)trinitrolic acid, have been synthesized.

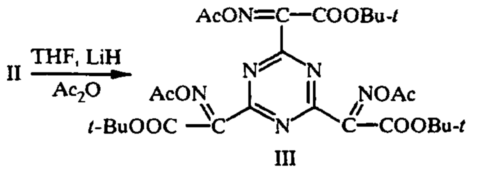
We had reported previously [1] on the preparation of 2,4,6-tris(*tert*-butoxycarbonylmethyl)-1,3,5-triazine (I), a compound containing activated methylene groups. We initiated our investigation of the chemical properties of this triazine by a study of the nitration reaction, with the aim of synthesizing the corresponding nitro derivatives, ultimately 2,4,6-tris(dinitromethyl)-1,3,5-triazine. However, we found that under the conditions of nitration (HNO_3, HNO_3/H_2SO_4, HNO_3/CF_3COOH), the compound I decomposes completely.

At the same time, the nitrosation of the triazine I with sodium nitrite in acetic acid proceeds quite smoothly, and the trioxime II is obtained in good yields.



The structure of the trazine II was confirmed by ^1H and ^{13}C NMR and IR spectroscopy; however, the elemental analyses deviated from the calculated values, apparently because of the acetic acid still present in the compound—which we were not able to remove either by holding the product II under vacuum or by recrystallization.

Final confirmation of the structure of II was provided by its conversion to the tris-O-acyl derivative (III) by the action of acetic anhydride in the presence of lithium hydride:



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*For Communication 2, see [1].

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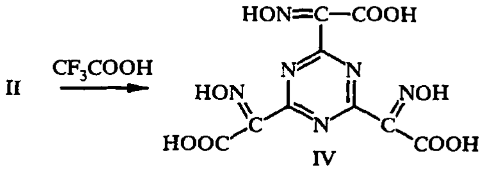
One of the methods used to obtain nitro compounds is the oxidation of oximes [2]. We investigated the possibility of using this method to synthesize from compound II certain valuable products, namely the nitro derivatives of the triazine I.

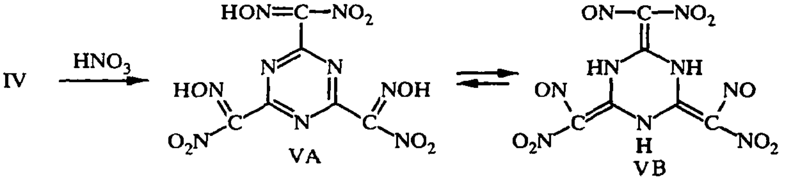
Oxidation of the trioxime II by nitric acid or by a mixture of nitric acid and acetic anhydride resulted only in decomposition of the trioxime. The same as in the reaction with the triazine I, this result is apparently related to the presence of the *tert*-butoxyl group, which is labile with respect to acid hydrolysis and is rapidly oxidized under the influence of nitric acid. This is responsible for the observed evolution of gas, formation of nitrogen oxides, and subsequent complete decomposition.

In order to convince ourselves that this hypothesis was correct, we investigated the oxidation of the tricarboxylic acid IV, obtained by saponifying the triazine II with trifluoroacetic acid.



The structure of compound IV was confirmed by ^1H and ^{13}C NMR spectrometry. The same as in the case of the triazine II, this compound contains traces of the acid (CF_3COOH), which, however, do not interfere with the nitration reaction.

Attempts to carry out the nitration of the acid IV with 100% nitric acid or its mixture with acetic anhydride were unsuccessful. The use of 68-70% nitric acid leads to the formation of 2,4,6-(1,3,5-triazinetriyl)trinitrolic acid (V).



In principle, compound V may exist in two tautomeric forms A and B, with the latter preferred for further oxidation, since the nitroso groups are oxidized more readily than the oxime groups. The structure of compound V was confirmed by ^1H, ^{13}C, and ^{14}N NMR spectrometry. The ^1H NMR spectrum, containing one signal with a chemical shift of 12.93 ppm, is characteristic for the forms of both VA and VB (hexahydrotriazine structure [III]). However, the ^{13}C and ^{14}N NMR spectra provide evidence in favor of only the triazine structure VA [3, 4].

The triazine V is distinguished by low thermal stability. Attempts to oxidize its oxime groups were unsuccessful; whether we used as the oxidant $K_2Cr_2O_7$, CrO_3, or $KMnO_4$ in acetic acid at room temperature, we did not obtain the desired nitro derivatives. At a slightly higher reaction temperature, we observed decomposition of the original substance.

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 Boetius heating stage with a heating rate of 4°C/min at the melting point.

The synthesis of the 2,4,6-tris(*tert*-butoxycarbonylmethyl)-1,3,5-triazine (I) was described in [1].

2,4,6-Tris[(1-hydroxyimino-1-*tert*-butoxycarbonyl)methyl]-1,3,5-triazine (II). To a solution of 6.35 g (15 mmoles) of the triazine I in 120 ml of glacial acetic acid, cooled to 15°C, a solution of 6.35 g (92 mmoles) of sodium nitrite in a minimum amount of water was added while stirring (with larger quantities of water, the reaction stops in the dioximation stage); the solution was added at a rate such that the red color appearing when the $NaNO_2$ is added disappears until the next portion of nitrite is added. The stirring was continued an additional 2 h at 18-20°C; then 75 ml of distilled water was added, and the solution was held ~16 h at room temperature. The reaction mixture was diluted with 500 ml of distilled water; the precipitate was filtered off, washed repeatedly with water, and dried on the filter. Obtained 8.5 g (87%) of the triazine II (containing acetic acid as an impurity), mp 183°C (decomp.). IR spectrum: 3400, 2960, 2900, 1750, 1700, 1620, 1520, 1470, 1400, 1370, 1300, 1250, 1150, 1070, 1050, 900 cm^{-1}. PMR spectrum, in $(CD_3)_2CO$: 1.56 (27H, s, $9CH_3$); 11.00 (3H, br. s, 3OH); 1.99 ppm (3H, s, CH_3 in CH_3COOH). Ratio ~9.5:1 corresponds to ratio of number of protons in triazine II to number of protons in CH_3COOH (1 mole of CH_3COOH per mole of triazine II). ^{13}C NMR spectrum, in $(CD_3)_2CO$: 168.06 (C=N); 161.53 (COO); 149.78 (C=NOH); 84.37 [$\underline{C}(CH_3)_3$]; 28.59 ppm (CH_3). CH_3COOH: 177.87 (COOH); 22.71 ppm (CH_3).

2,4,6-Tris[(1-acetoximino-1-*tert*-butoxycarbonyl)methyl]-1,3,5-triazine (III). To 1.02 g (2 mmoles) of the triazine II in 5 ml of absolute tetrahydrofuran, 1 ml (11 mmoles) of freshly distilled acetic anhydride was added. The reaction mass was stirred 2 h and then diluted with 20 ml of water. The resulting precipitate was filtered off, washed with water (2×50 ml), dried on the filter, and recrystallized from heptane. Obtained 0.91 g (71%) of the triazine III, mp 149-151°C (decomp.). IR spectrum: 2960, 2920, 1800, 1750, 1640, 1510, 1350, 1290, 1250, 1170, 1140, 1090, 1050, 1000, 950, 900 cm^{-1}. Found, %: C 50.72; H 5.90; N 13.27. $C_{27}H_{36}N_6O_{12}$. Calculated, %: C 50.94; H5.70; N 13.20.

2,4,6-Tris[(1-hydroxyimino-1-carboxy)methyl]-1,3,5-triazine (IV). To 30 ml of trifluoroacetic acid, 4.0 g (7 mmoles) of the triazine II (containing an equimolar quantity of CH_3COOH) was added, and the mixture was stirred 40 min. The resulting precipitate was filtered off, washed with 5 ml of CF_3COOH and then 10 ml of dry chloroform, and dried on the filter. Obtained 2.4 g (100%) of the triazine IV, mp 162°C (decomp.). The product contained an admixture of trifluoroacetic acid. PMR spectrum, in DMSO-d_6): 9.72 (3H, br. s, 3COOH); 13.31 ppm (3H, br. s, 3NOH). ^{13}C NMR spectrum, in (DMSO-d_6): 167.26 (s, C=N); 163.29 (s, COOH); 150.51 (s, C=NOH); 159 ppm (CF_3).

2,4,6-(1,3,5-Triazinetriyl)trinitrolic acid (V). To 10 ml of 68% nitric acid, while stirring at 0°C, 1.03 g (3 mmoles) of the triazine IV was added. After a certain time, violent evolution of gas began, along with the formation of a precipitate. The stirring was continued for another 20 min after the gas evolution had ceased. The precipitate was filtered off, washed with 50% CF_3COOH (2×5 ml), then with CF_3COOH chilled to 0°C (2 ml), after which the precipitate was dried on the filter in a flow of dry nitrogen or argon. Obtained 76 g (73%) of the triazine V, mp 68°C (decomp.). PMR spectrum, in CD_3CN: 12.92 ppm (3H, br.s, 3NOH). ^{13}C NMR spectrum, in CD_3CN: 163.94 (s, C=N); 150.16 ppm (s, C=NOH). ^{14}N NMR spectrum, in CD_3CN: -17.67 (NO_2); -137.88 ppm (NOH). The substance can be stored for about one day in a refrigerator or in a solution of dry acetonitrile. Upon heating above 68°C, it decomposes with the apparent formation of a polymeric compound with mp >250°C, insoluble in organic solvents.

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