Brief Communications

A new method for the synthesis of 2,4-diazido-6-trinitromethyl-1,3,5-triazine

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A new method for the synthesis of 2,4-diazido-6-trinitromethyl-1,3,5-triazine was elaborated. The method makes it possible to exclude the work with unstable 2,4,6-tris(trinitromethyl)-1,3,5-triazine.

Key words: di-*tert*-butyl-[2-(4,6-dihydrazinyl-1,3,5-triazin-2-yl)]nitromalonate, di-*tert*-butyl-[2-(4,6-diazido-1,3,5-triazin-2-yl)]nitromalonate, 2,4-diazido-6-(nitromethyl)-1,3,5-triazine, 2,4-diazido-6-(trinitromethyl)-1,3,5-triazine, nitration, trinitromethyl group.

We have previously[1] performed the selective substitution of two trinitromethyl groups by azido groups in 2,4,6-tris(trinitromethyl)-1,3,5-triazine (**1**) by the reaction of this compound with trimethylsilylazide. Thus obtained 2,4-diazido-6-trinitromethyl-1,3,5-triazine (**2**) is a thermally and hydrolytically stable substance with the high positive enthalpy of formation (191 kcal mol^{-1}, calculated by the data[2] of the ICT thermochemical database) and is interesting for the synthesis of various energy-rich 1,3,5-triazine derivatives. A drawback of this method of synthesis is the necessity to work with chemically unstable 2,4,6-tris(trinitromethyl)-1,3,5-triazine.

In the present study, we report the synthesis of triazine **2** *via* the alternative scheme excluding the participation of compound **1**. At the first stage, dihydrazide **3** was diazotizated with sodium nitrite in acetic acid (the synthesis of dihydrazide **3** has earlier been described[3]). The removal of the *tert*-butoxycarbonyl protecting group (Boc protection) in the synthesized di-*tert*-butyl-[2-(4,6-diazido-1,3,5-triazin-2-yl)]nitromalonate (**4**) by trifluoroacetic acid gave 2,4-diazido-6-nitromethyl-1,3,5-triazine (**5**) in high (96%) yield. The nitration of the latter with a sulfuric—nitric mixture gave the target 2,4-diazido-6-trinitromethyl-1,3,5-triazine in good (68%) yield (Scheme 1).

The structures of the synthesized compounds were proved by a complex of physicochemical methods and confirmed by the elemental analysis data. Note that there are single examples in the literature for the nitration of the nitromethyl group to the trinitromethyl group for both aromatic and heteroaromatic compounds.[4] As a rule, the nitration of the corresponding oximes,[5] nitrile oxides,[6] compounds with activated methyl groups,[7—9] and dinitromethyl compounds,[10] trinitromethylation of aromatic compounds with tetranitromethane,[11] or (only in the case

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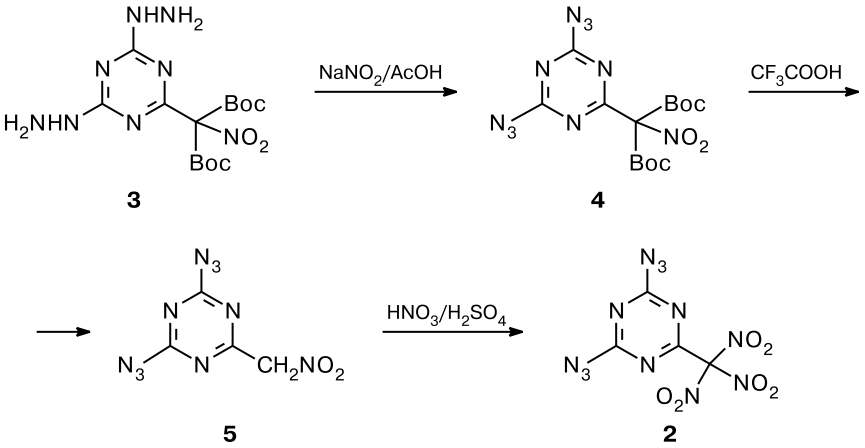
Scheme 1



3 **4** **5** **2**

of 1,3,5-triazine) trinitromethylation with nitroform salts[12] are used for the introduction of trinitromethyl groups. Several examples for the nitration of methyl groups to trinitromethyl groups by the action of N_2O_4 or a sulfuric—nitric mixture in aromatic and heteroaromatic compounds are also known.[13—16]

Experimental

IR spectra were recorded on a Specord UR-20 instrument in KBr pellets. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM-300 instrument (^{1}H, 300 MHz; ^{13}C, 75.5 MHz) using Me_4Si as an internal standard and $CDCl_3$ as a solvent. Melting points were determined on a Boetius heating stage with a heating rate of 4 °C min^{-1} near the melting point.

Di-*tert*-butyl(4,6-diazido-1,3,5-triazin-2-yl)-2-nitromalonate (4). Sodium nitrite (220 mg, 1.4-fold excess) was added to a solution of di-*tert*-butyl(4,6-dihydrazinyl-1,3,5-triazin-2-yl)-2-nitromalonate (490 mg, 1.22 mmol) in acetic acid (5 mL) on cooling in an ice bath and with stirring. The mixture was stirred for 30 min and poured into water. The organics was extracted with methylene chloride, washed with water several times, dried with calcined Na_2SO_4, and passed through a thin layer of silica gel. The solvent was evaporated, and compound **4** was obtained as colorless crystals in a yield of 429 mg (83%), m.p. 112—113 °C. IR, ν/cm^{-1}: 3000, 2983, 2944, 2915, 2890, 2190, 2160, 2137, 1754, 1742, 1571, 1545, 1432, 1385, 1365, 1344, 1280, 1241, 1223, 1200, 1151, 1079, 1012, 971, 891, 850, 832, 801, 750, 732, 701, 634. ^{1}H NMR, δ: 1.57 (s, 18 H, 6 Me). ^{13}C NMR, δ: 171.23, 170.68 (CN, triazine); 157.83 (COO); 100.37 (CNO_2); 86.71 (C quatern.); 27.51 (Me). Found (%): C, 39.84; H, 4.36; N, 32.86. $C_{14}H_{18}N_{10}O_6$. Calculated (%): C, 39.81; H, 4.30; N, 33.16.

2,4-Diazido-6-(nitromethyl)-1,3,5-triazine (5). Triazine **4** (429 mg, 1.01 mmol) was dissolved with stirring in trifluoroacetic acid (1.5 mL). The solution was stirred for 1 h, evaporated to dryness at ~20 °C, extracted with methylene chloride, and passed through a thin layer of silica gel. The solvent was evaporated, and colorless crystals of triazine **5** were obtained in a yield of 215 mg (96%), m.p. 66—67 °C. IR, ν/cm^{-1}: 3042, 2981, 2928, 2861, 2201, 2171, 2141, 2125, 1563, 1537, 1483, 1434, 1401, 1380, 1347, 1301, 1221, 1195, 1151, 1012, 981, 812, 791 (sh), 670, 552. ^{1}H NMR, δ: 5.57 (s, 2 H, CH_2). ^{13}C NMR, δ: 171.46, 170.56 (CN, triazine); 79.29 (C—NO_2). Found (%): C, 21.66; H, 1.10; N, 62.60. $C_4H_2N_{10}O_2$. Calculated (%): C, 21.63; H, 0.91; N, 63.06.

2,4-Diazido-6-(trinitromethyl)-1,3,5-triazine (2). 2,4-Diazido-6-nitromethyl-1,3,5-triazine (107 mg, 0.48 mmol) was added to nitric acid (3 mL, density ≥1.5 g cm^{-3}) preliminarily cooled in an ice bath, and then concentrated H_2SO_4 (3 mL) was carefully added. The mixture was stirred for 3 h at ~20 °C and poured into ice. The precipitate that formed was filtered off and washed with water (3×10 mL). Compound **2** was obtained as colorless crystals in a yield of 100 mg (68%), m.p. 97—98 °C (sublimation above 80 °C, *cf.* Ref. 1: m.p. 96—97 °C). IR, ν/cm^{-1}: 2250, 2183, 2153, 2095, 1584, 1577, 1460, 1367, 1283, 1252, 1159, 992, 899, 832, 796, 752, 670, 601, 549. ^{13}C NMR, δ: 171.97, 163.87 (CN, triazine); 122.24 ($C(NO_2)_3$). Found (%): C, 15.59; N, 53.72. $C_4N_{12}O_6$. Calculated (%): C, 15.39; N, 53.85.

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