Synthesis of 2,4,6-Tris(trinitromethyl)-1,3,5-triazine

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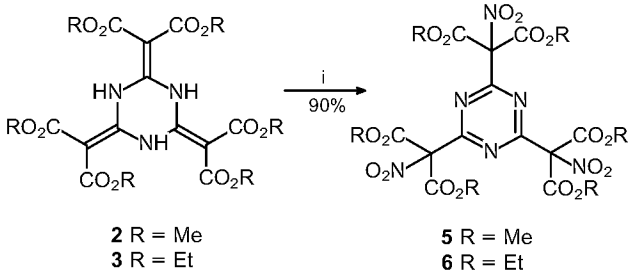
Destructive nitration of the carboxyl group to the trinitromethyl entity has been accomplished for the first time and 2,4,6-tris(trinitromethyl)-1,3,5-triazine, hitherto unknown, has been synthesized.

Destructive nitration of carboxyl and carbonyl derivatives is used as a method of polynitromethyl group formation in organic compounds. Thus, interaction between methyl malonate and nitric acid leads to methyl dinitroacetate,[1] and nitration of 1,1,1-trinitroalkylketones with a mixture of concentrated nitric and sulfuric acids affords hexanitroethane.[2] No compound containing the trinitromethyl group has, however, been synthesized from carboxyl derivatives.

To prepare 2,4,6-tris(trinitromethyl)-1,3,5-triazine **1**, the destructive nitration of 2,4,6-tris(dimethoxycarbonylmethylene)- and 2,4,6-tris(diethoxycarbonylmethylene)-1,3,5-hexahydrotriazines, **2** and **3** respectively, readily obtained from cyanuric chloride **4** and the pertinent malonic ester sodium salt,[3] was initially investigated.

The hydrolysis and nitration of **2** and **3** were intended to be carried out simultaneously by the use of a mixture of sulfuric and nitric acids. It was found, however, that the dicarboalkoxymethylene groups in compounds **2** and **3** did not transform into trinitromethyl groups under reaction conditions, but instead underwent exclusively mononitration to give 2,4,6-tris[(dimethoxycarbonyl)nitromethyl]- and 2,4,6-tris[(diethoxycarbonyl)nitromethyl]-1,3,5-triazines, **5** and **6**, respectively, Scheme 1.



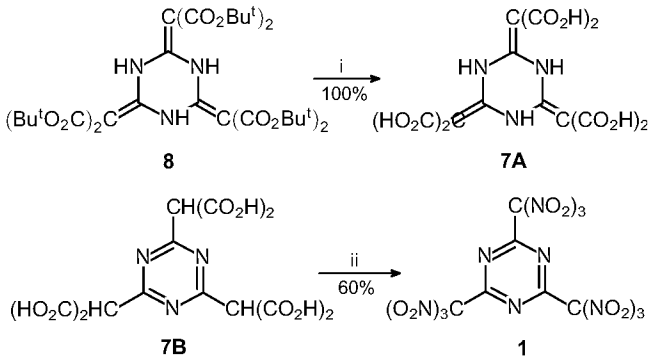
Scheme 1 *Reagents and conditions*: i, 1 mmol **2** or **3**, 1 ml HNO_3 (*d* 1.5), 2 ml H_2SO_4 (*d* 1.84), 3 ml $CHCl_3$, 0 °C, 40 min.

These results led us to the conclusion that an appropriate hexacarbonic acid **7**, not its esters, should be used to synthesize **1**.

The *tert*-butyl group is known to be removed by hydrolysis more readily than methyl and ethyl groups in esters and ethers.[4,5] 2,4,6-Tris(di-*tert*-butoxycarbonylmethylene)-1,3,5-hexahydrotriazine **8** was prepared in 50% yield from **4** and *tert*-butyl malonate sodium salt according to the procedure described in ref. 3. The hydrolysis of **8** was performed by trifluoroacetic acid. It is impossible to establish in which particular form, **A** or **B**, the acid **7** exists because of its insolubility in solvents used for taking NMR spectra.

The desired product **1** was obtained by nitration of **7** with a mixture of sulfuric and nitric acids, Scheme 2.

The structure of **1** was substantiated by elemental analysis, IR, ^{13}C and ^{14}N NMR spectroscopy as well as some chemical transformations. Thus 2,4,6-trimethoxy-1,3,5-triazine **9** and nitroform potassium salt **10** were formed from **1** and KOH or MeOK nearly quantitatively, Scheme 3.



Scheme 2 *Reagents and conditions*: i, 1 mmol **8**, 5 ml CF_3COOH, 0–5 °C, 30 min, **7** filtered; ii, 1 mmol **7**, 4 ml H_2SO_4 (*d* 1.84), 3 ml HNO_3 (*d* 1.5), 0–5 °C, kept 12 h at 18 °C.

Compound **1** is unstable in the air, and so is preferably stored as a solution in absolute CCl_4 at 5–10 °C. When an undried dioxane is added to the solution of **1** in absolute CCl_4, one trinitromethyl group is subjected to nucleophilic substitution by hydroxyl on account of the water present in the dioxane. The 2-hydroxy-4,6-bis(trinitromethyl)-1,3,5-triazine **11** formed was isolated as a stable complex **12** with dioxane in the ratio 2:1 mol, Scheme 4.

The structure of the complex **12** was determined by X-ray analysis of a single crystal† (Fig. 1). The triazine ring is planar,

† *Crystal data for* **12**: $C_5HN_9O_{13}{\cdot}0.5C_4H_8O_2$, triclinic, space group $P\bar{1}$, $a = 8.119(2)$, $b = 10.570(2)$, $c = 10.713(2)$ A, $\alpha = 75.64(2)$, $\beta = 73.73(2)$, $\gamma = 72.04(2)°$, $U = 826.7(3)$ A^3, $D_c = 1.764$ g cm^{-3}, $Z = 2$. The intensities of 2916 reflections (2060 observed): I_{hkl} were measured on a Syntex-P2$_1$ diffractometer [graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ A)] using the $\theta/2\theta$ scan technique ($2\theta \leqslant 50°$). The structure was solved by direct methods and refined by the full-matrix least-squares method, anisotropically for the non-hydrogen atoms. The final R_F was 0.067 for 1631 $F_{hkl} \geqslant 4\sigma$. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, see Notice to Authors, *Mendeleev Commun.*, 1995, issue 1.

1 M.p. 90–91 °C, ^{13}C NMR ($CDCl_3$): 164.525 (C=N) and 120.579 [$C(NO_2)_3$]; ^{14}N NMR ($CDCl_3$): −43.334 (NO_2): IR, ν/cm^{-1} (KBr pellets): 1600, 1565, 1520, 1420, 1300, 1250, 1145, 1100, 920, 835, 805, 750. **CAUTION!** Explosion hazardous.

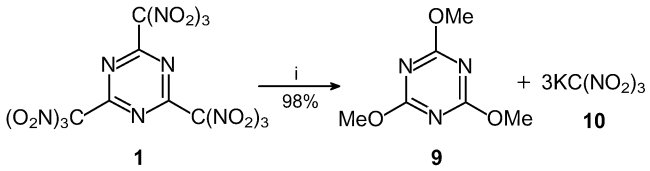
5 M.p. 90–91 °C; ^{13}C NMR ($CDCl_3$): 55.156 (Me), 99.358 (C *tert*), 158.997 (C=O), 169.012 (C=N); ^{14}N NMR ($CDCl_3$): −21.771 (NO_2).

6 M.p. 42–44 °C; ^1H NMR ($CDCl_3$): 1.23 t (18H, Me), 4.40 q (12H, CH_2); ^{13}C NMR ($CDCl_3$): 13.60 (Me), 65.22 (CH_2), 99.85 (C *tert*), 158.67 (C=O), 169.26 (C=N); ^{14}N NMR ($CDCl_3$): −20.984 (NO_2).

7 M.p. 120 °C (decomp.), unstable in storage; IR, ν/cm^{-1} (KBr pellets): 3400 (OH), 1600 (C=O), 1540 (C=C).

8 M.p. 203–205 °C (decomp.); ^1H NMR ($CDCl_3$): 1.500 s (54H, But), 12.935 s (3H, NH); ^{13}C NMR ($CDCl_3$): 166.951 (=CN), 145.670 (C=O), 85.738 (C=C), 80.985 (C–O), 26.163 (Me); ^{15}N NMR ($CDCl_3$): −277.318 (C–NH), $^1J_{N-H}$ 95.76 Hz, $^3J_{N-H}$ 2.40 Hz (NH form).

12 M.p. 150–152 °C (decomp.); ^1H NMR ($CDCl_3$): 3.62 s (8H, CH_2), 12.01 br.s (1H, OH); ^{13}C NMR ($CDCl_3$): 170.985 s (=COH), 164.197 s (C=N), 121.415 s [$C(NO_2)_3$], 66.696 t (CH_2); ^{14}N NMR ($CDCl_3$): −40.0613 (NO_2), $\gamma_{\frac{1}{2}} = 4.5$ Hz.



Scheme 3 *Reagents and conditions*: i, 1 mmol **1**, 3 mmol KOH or MeOK, 5 ml abs. MeOH, 18 °C, 2 h.

the trinitromethyl groups have a propeller-like conformation and are oriented identically relative to the triazine plane. The intramolecular distances N(1)...N(11) 2.770(7), N(2)...N(13) 2.645(7), N(2)...N(22) 2.738(7) and N(3)...N(23) 2.709(7) Å are shorter than the two-fold Van-der-Waals radius (3.00 Å). The dioxane molecule in the chair conformation occupies the centrosymmetric position in the crystal.

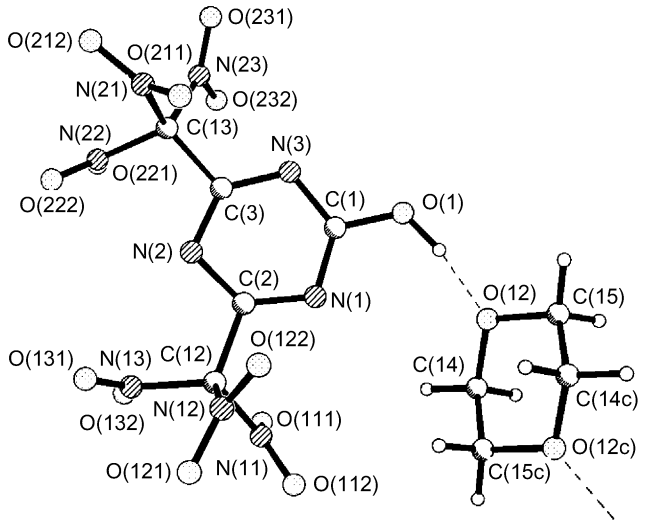
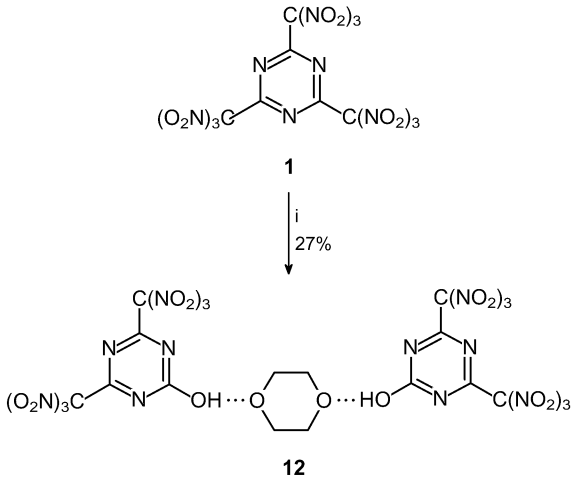


Fig. 1 Molecular structure of **12**. (The second molecule **11** has a position symmetric relative to dioxane). The main bond lengths/Å: C_{cycle}–N_{cycle} 1.302–1.346 [mean 1.325(8)], C_{cycle}–C_{sp^3} 1.519, 1.527 [mean 1.523(9)], C_{sp^3}–N_{nitro} 1.510–1.550 [mean 1.528(9)], N–O 1.110–1.210 [mean 1.17(1)], C(1)–O(1) 1.298(8). H-Bond parameters: O(1)...O(12) 2.502(8), O(1)...H 0.98, H...O(12) 1.55, angle O(1)–H...O(12) 169°.



Scheme 4 *Reagents and conditions*: i, 1 mmol **1** in 10 ml abs. CCl_4, 5 ml dioxane, 18 °C, 1 h.

All new compounds prepared have satisfactory elemental analysis data and have been characterised by ^{1}H, ^{13}C and $^{14/15}N$ NMR spectroscopy.

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