Synthesis of 1,3,5-trinitrosobenzene

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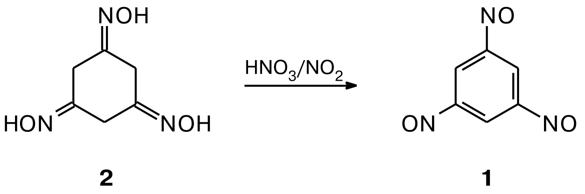
Mononitrosoarenes are well-known compounds, dinitrosoarenes are significantly less familiar, while trinitrosoarenes have not been described at all. This communication reports the synthesis of the first representative of trinitrosoarenes, namely, 1,3,5-trinitrosobenzene (**1**). This compound was obtained in 30—35% yield by oxidation of the known cyclohexane-1,3,5-trione trioxime (**2**) (see Ref. 1) with 30—35% HNO_3 in the presence of catalytic amounts (~0.1%) of nitrogen oxides (Scheme 1).

Scheme 1



In dilute 30—35% nitric acid free of nitrogen oxides, trioxime **2** easily dissolves to give a brown solution but is not oxidized into nitroso compound **1**. Oxidation can be initiated by adding a small amount of $NaNO_2$ as a source of nitrogen oxides.

The IR spectrum of trinitrosobenzene **1** (Bruker Vector-22, KBr pellets) (Fig. 1) shows an intense band at 1272 cm^{-1} characteristic of *trans*-dimeric nitrosoarenes,[2] which suggests its structure with *trans*-dimerized nitroso groups. Because of this, compound **1** is relatively stable and comparable in properties with polymeric *p*-dinitrosobenzene having a similar *trans*-structure.[3,4]

The mass spectrum of completely sublimed trinitrosobenzene **1** (Finnigan MAT-212, EI, 70 eV) shows peaks with m/z (I_{rel} (%)): 165.1 $[M]^+$ (59), 135 $[M - NO]^+$ (42), 105.1 $[M - NO - NO]^+$ (8), and 75.1 $[M - NO - NO - NO]^+$ (100).

Fragmentation of the molecular ion of compound **1** occurs with the loss of three NO groups, which is characteristic of nitrosoarenes[2] (Scheme 2).

As expected, the oxidation of trinitrosobenzene **1** yields 1,3,5-trinitrobenzene.[2] 1,3,5-Trinitrobenzene was also synthesized by the oxidation of trioxime **2** with 90%

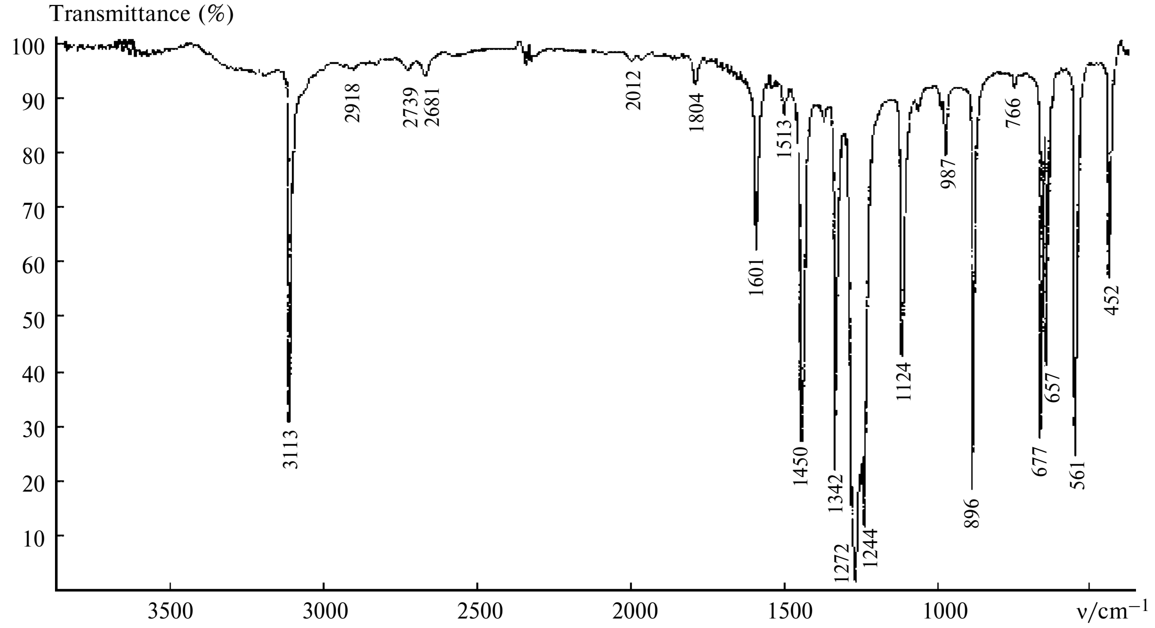


Fig. 1. IR spectrum of 1,3,5-trinitrosobenzene (**1**).

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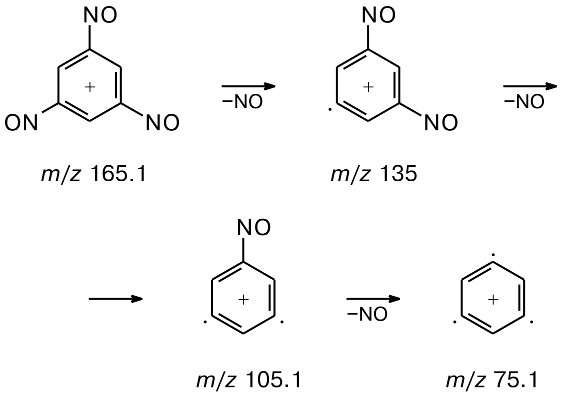
Scheme 2



HNO_3,[5] but no intermediate nitroso compound **1** was detected or isolated.

Nitroso compound **1** is virtually insoluble in organic solvents at room temperature. Yet it is soluble at 100 °C in toluene or xylene, giving an unstable green solution.

1,3,5-Trinitrosobenzene (1). Nitric acid (98%, 16 mL) containing 0.2—0.4% nitrogen oxides was added to ice (50 g) and then trioxime **2** (1.0 g) was added at 12—15 °C to the vigorously stirred 35% HNO_3 obtained. The light foam of product **1** that formed almost immediately after dissolution of oxime **2** was filtered off, washed with water to a neutral reaction and acetone, and dried. The yield of compound **1** (a light turquoise powder) was 0.32 g (34%), m.p. 170 °C (decomp.). No resinification of the reaction mixture was observed. Found (%): C, 43.90; H, 1.65; N, 25.20. $C_6H_3N_3O_3$. Calculated (%): C, 43.65; H, 1.83; N, 25.45.

1,3,5-Trinitrobenzene. 1,3,5-Trinitrosobenzene (**1**) (1 g) was added to 98% HNO_3 (20 mL) and the reaction mixture was heated at 80 °C for 2 to 3 min and then diluted with water (100 mL). The yield of 1,3,5-trinitrobenzene was 0.9 g (70%), m.p. 121—122 °C. The compound obtained is identical with an authentic sample (IR and ^{1}H NMR spectroscopic and TLC data).

The mechanism of formation of 1,3,5-trinitrosobenzene upon oxidation of cyclohexane-1,3,5-trione trioxime with dilute nitric acid in the presence of nitrogen oxides calls for a further investigation involving other compounds of this class.

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