A Facile Two-Step Synthesis of 1,3,5-Trinitrobenzene

Jeffrey C. Bottaro,* Ripudaman Malhotra, Allen Dodge

Chemical Science and Technology Laboratory, SRI International, 333 Ravenswood Avenue, Menlo Park, CA 94025, USA
Fax +1(650)8594321; E-mail: Jeffrey.Bottaro@sri.com

Received 2 October 2003
This work is dedicated to the cherished memory of Tom Highsmith.

Abstract: Synthesis of 1,3,5-trinitrobenzene was achieved by converting phloroglucinol into its trioximes by reaction with aqueous hydroxylamine followed by oxidation of the trioxime product with 90% nitric acid.

Key words: 1,3,5-trinitrobenzene, cyclohexanetrione trioximes, phloroglucinol

The little-known explosive 1,3,5-trinitrobenzene (TNB) has not replaced TNT (2,4,6-trinitrotoluene) in spite of superior detonation velocity and pressure of TNB.1–3 The main reason for this is the economics; the most commonly cited synthesis of TNB involves oxidation of TNT to trinitrobenzoic acid followed by decarboxylation.3 Direct nitration of benzene requires such harsh conditions that yields are poor and purification of TNB is very difficult. Even the use of modern catalysts such as lanthanide nitrates does not alleviate this problem.4 Thus it stands that TNT successfully competes with TNB in what is a billion dollar annual market. We wish to report here a facile two-step synthesis of TNB starting from phloroglucinol. The only remaining technological impediment to its large-scale application is the absence of an economical dehydratation of HOAc or a trimerization of ketene to produce phloroglucinol. This challenge has a high probability of being met once it is defined in the appropriate setting.

Given the difficulties with the previous syntheses of trinitrobenzene, we examined an alternate approach; one in which a heteroatom is already at the 1-, 3-, and 5-positions. Phloroglucinol (1, 1,3,5, trihydroxybenzene) seemed to be a reasonable starting point. Furthermore, the fact that a small fraction of phloroglucinol exists as the keto tautomer, 1,3,5-cyclohexanetrione, means that it expected to give three peaks for each of these environments. The three peaks are not equal in intensity; the central peak is somewhat more intense. The spectrum also contains three almost equally intense peaks at 3.1, 3.3 and 3.5 ppm corresponding to the aliphatic protons. These strongly deshielded peaks were not visible when D2O was added to the sample, and thus they can be assigned to the oxime hydroxyls. The three peaks are not equal in intensity; the central peak is somewhat more intense. The spectrum also contains three almost equally intense peaks at 3.1, 3.3 and 3.5 ppm corresponding to the aliphatic protons. There is a weaker fourth peak at 3.3 ppm about 15% as intense as the others. There are two isomers of the trioxime, symmetric and unsymmetric. The symmetric isomer should show a single peak for the hydroxy and the remaining solution was dark brown. Infrared analysis (KBr pellet) showed bands at 3450 and 2900 cm–1 corresponding to O–H and C–H stretches, and at 1640 cm–1 for the C=N stretch. The 1H NMR of the product in DMSO showed three peaks between 10.7 and 10.8 ppm. These strong acids, but its dissolution in sulfuric and methanesulfonic acids is very exothermic and can lead to charred products. However, we found trioximes 2, to be completely soluble in mixtures of THF and water. Purification of the trioxime was achieved by dissolving the crude product in a mixture of THF and water, and then evaporating the THF at reduced pressure in a rotary evaporator. The solid thus obtained was markedly lighter in color and the remaining solution was dark brown. Infrared analysis (KBr pellet) showed bands at 3450 and 2900 cm–1 corresponding to O–H and C–H stretches, and at 1640 cm–1 for the C=N stretch. The 3H NMR of the product in DMSO showed three peaks between 10.7 and 10.8 ppm. These strongly deshielded peaks were not visible when D2O was added to the sample, and thus they can be assigned to the oxime hydroxyls. The three peaks are not equal in intensity; the central peak is somewhat more intense. The spectrum also contains three almost equally intense peaks at 3.1, 3.3 and 3.5 ppm corresponding to the aliphatic protons. There is a weaker fourth peak at 3.3 ppm about 15% as intense as the others. There are two isomers of the trioxime, symmetric and unsymmetric. The symmetric isomer should show a single peak for the hydroxy and the aliphatic protons, whereas the unsymmetric isomer is expected to give three peaks for each of these environments. The NMR spectrum is consistent with a mixture containing 95% of the unsymmetric isomer. Tokura et al. raised the question of isomerization of cyclohexanetrione oximes to 1,3,5-benzenetrihydroxylaminol. The NMR data presented here, in particular, the results of exchange

SYNTHESIS 2004, No. 4, pp 0499–0500
Advanced online publication: 09.02.2004
DOI: 10.1055/s-2004-815958; Art ID: M04303SS
© Georg Thieme Verlag Stuttgart · New York
with D₂O, argue against the presence of the isomerized structure.

Conversion of oximes into gem-dinitro products by Ponzio reactions and its variants has been reviewed by Honey et al. Aksenrod et al. have reported on the oxidative nitrolysis of oximes to give gem-dinitro products by nitric acid. However, instead of producing 1,1,3,3,5,5-hexanitrocyclohexane, we found that reaction of trioximes 2 in 90% nitric acid produced 1,3,5-trinitrobenzene (3) (Scheme 1). Evidently, the loss of HONO from adjacent carbons to give the aromatic product was extremely favorable. The reactions were very vigorous and accompanied by evolution of gases. For safe operation it was necessary to cool the reactions in an ice bath and also moderate them with a solvent. Addition of small aliquots of the trioximes to cooled nitric acid was preferred over the addition of nitric acid. The former mode limits the amount of material that can be oxidized. When dry powder of the trioxime is added, a small burst of reaction can be observed when the powder hits the liquid. Addition of a suspension of the trioximes in CH₂Cl₂ to nitric acid proceeded more smoothly, and was the preferred method. 1,3,5-Trinitrobenzene could be detected in the reaction mixture by TLC almost immediately after completion of the addition. A second product of slightly lower polarity was also observed. At longer reaction times or upon warming the reaction mixture to about 55 °C, the second product was converted to TNB. By using preparative TLC, we were able to isolate a small amount (about 30 mg) of this second product. Whereas in dilute solution this second product was colorless, it developed a green tint upon concentrating. Its IR spectrum was very similar to that of TNB, except for an additional band at 1325 cm⁻¹. The development of green tint and the IR data are consistent with the presence of nitroso group, and we suspect that this compound has one or two nitroso groups, which are subsequently oxidized to the nitro groups.

1,3,5-Cyclohexanetrione Trioximes; General Procedure
Phloroglucinol dihydrate (8.11 g; 0.050 mol) was taken in a 500 mL Erlenmeyer flask. To it was added a 50% by weight aq solution of hydroxyamine (29.2 g; 0.44 mol). Phloroglucinol dissolved in the aqueous medium and over a period of about 3 min to give a clear yellow solution. The solution was let stand at r.t. After 1 h a thin layer of solid had separated and the solution had turned noticeably darker. The solution was gently agitated to break up the crystals and allowed to stand for 2 h. The solution turned dark brown and a copious quantity of solids had separated. The solids were filtered, washed with water and dried (yield: 7.59 g; 88%). The product was analyzed by TLC on silica gel (toluene–i-PrOH, 1:1). A strong spot was detected upon exposure to I₂ vapors at an Rₜ of 0.85. This spot was close to that of phloroglucinol (Rₜ 0.9), but it was not UV active like the starting material. TLC also showed a few other spots near the origin. Purification was achieved by dissolving about 2.0 g of the crude product in THF–water (1:1, 50 mL) mixture, and then evaporating THF in a rotary evaporator. The resulting solid (1.65 g) was light brown, and gave a single spot by TLC.

1,3,5-Trinitrobenzene; Typical Procedure
Approximately 8.0 g concd HNO₃ (90%) under Ar were taken in a 25 mL 3-necked round-bottom flask and cooled in an ice bath. In a separate flask, the trioximes of 1,3,5-cyclohexanetrione (171 mg, 1.0 mmol) were suspended in about CH₂Cl₂ (2 mL). About 100 µL aliquots of the suspension were slowly added to the cooled stirring HNO₃. Immediately following each addition there was evolution of fumes of nitrogen oxides, which were swept away by Ar. Sufficient time was allowed for the fuming to subside (about 15 s) before the next aliquot was added. After all of the trioximes had been added, the flask was fitted with a reflux condenser and transferred to a bath held at 55 °C. After 3 h the contents of the flask were poured into water (100 mL), and extracted with EtOAc (50 mL). The EtOAc extract was washed sequentially with water, NaHCO₃ solution, and brine, dried over anhyd Na₂SO₄, and then flash chromatographed over silica gel; yield: 109 mg (50%). The IR spectrum of the product was identical with that of authentic 1,3,5-trinitrobenzene and showed the band due to aromatic C–H stretch at 3150 cm –¹ and a pair of bands due to the NO₂ group at 1340 and 1560 cm–¹. The ¹H NMR spectrum showed a single peak at 9.2 ppm. The progress of the oxidation reaction was monitored by TLC on silica, with toluene as the eluant. A small aliquot of the reaction mixture was diluted with water and extracted with EtOAc. TLC of the EtOAc extract showed two fast moving spots (Rₜ 0.95, 0.88), both UV active, along with a spot near the origin. TLC of an authentic sample of 1,3,5-trinitrobenzene showed a spot with an Rₜ 0.88.

References