Reactions of Benzotriazolo[2,1-*a*]benzotriazole Derivatives. 2. An Unusual Hydrolysis−Oxidation Reaction

Ganesan Subramanian, Joseph H. Boyer, and
Mark L. Trudell*

*Department of Chemistry, University of New Orleans,
New Orleans, Louisiana 70148*

William M. Koppes, Michael E. Sitzmann, and
Lori A. Nock

*Naval Surface Warfare Center, Indian Head Division,
Indian Head, Maryland 20640-5035*

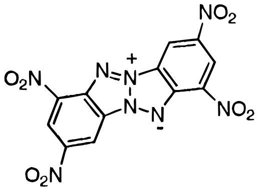
Richard Gilardi and Thomas P. Russell

Naval Research Laboratory, Washington, D. C. 20375-5341

Received October 23, 1995

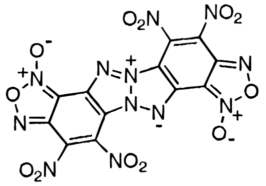
The insensitivity of the energetic material Tacot (**1**)[1] toward heat and impact has been the subject of recent investigations in these laboratories.[2] In an effort to improve upon the density (*d*) and the energetic properties (detonation velocity, *D*; detonation pressure, P_{CJ}) of **1** while exploiting the insensitivity of the material, the 4,5,11,12-tetranitro-14*H*-[1,2,5]oxadiazolo[3,4-*e*][1,2,5]oxadiazolo[3′,4′:4,5]benzotriazolo[2,1-*a*]benzotriazol-6-ium inner salt 1,8-dioxide **2** (TBBD) with molecular formula $C_{12}N_{12}O_{12}$ was envisaged as a new energetic material.[2] The computed high density and substantially improved computed energetic properties of **2** made it an attractive synthetic target.[3]

As part of the synthetic effort directed toward the synthesis of **2**, the dinitro derivative **3** (DBBD) has been prepared in three steps from **1**.[2] Further nitration of **3** to give the target compound **2** has been the subject of recent investigations. Although **2** has not been successfully isolated from the nitration reaction media, an unusual byproduct resulting from a hydrolysis−oxidation reaction of **3** was obtained. Herein we wish to report this unusual reaction associated with nitrated derivatives of **3**.



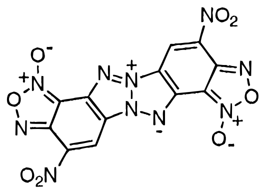
1

mp = 378 °C (dec)
d = 1.85 g/cm^3
D = 7.20 mm/μsec
P_{CJ} = 245 kbar



2

(TBBD; $C_{12}N_{12}O_{12}$)
d = 2.06 g/cm^3
D =8.03 mm/μsec
P_{CJ} = 319 kbar

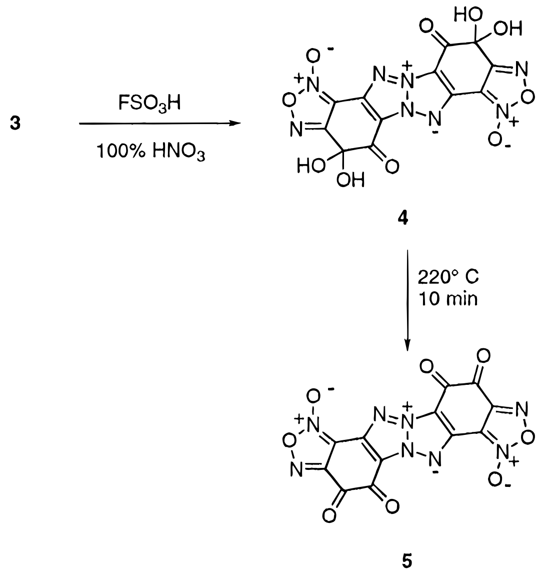


3

Results and Discussion

The synthesis of **2** was envisaged to proceed by electrophilic aromatic nitration of **3**. Treatment of **3** with normal nitration procedures were unsuccessful and gave only recovered starting material. Although there are several reagents available for nitration of deactivated aromatic systems, a number of successful nitrations have been reported in the literature using fluorosulfonic acid in 100% nitric acid.[4] Treatment of **3** with fluorosulfonic acid in 100% nitric acid at 70−80 °C for 2 h and after workup afforded a red crystalline material in 20% yield (Scheme 1). The structure of the product of this reaction was unequivocally identified by X-ray crystallography (Figure 1) as the hydrated form of the 5,12-dioxo-4,4,11,11-tetrahydroxy-14*H*-[1,2,5]oxadiazolo[3,4-*e*][1,2,5]oxadiazolo[3′,4′:4,5]benzotriazolo[2,1-*a*]benzotriazol-6-ium inner salt 1,8-dioxide (**4**) (DTBBD). The formation of **4** presumably results from the hydrolysis and subsequent oxidation of **3** in the fluorosulfonic acid/100% nitric acid media. Subsequent hydration of one of the carbonyls of each of the 1,2-diketone moieties then results in the observed product **4**.

Scheme 1



From the X-ray structure of **4** (Figure 1) there are several interesting features to note.[5] First, the basic ring system of **3** remained intact, despite the rigorous conditions of the nitration reaction. Both the furoxan ring and tetraazapentalene system were unaffected. Although nitrogen catenation usually has a destabilizing effect, clearly in this system the tetraazapentalene unit is a chemically and physically stable molecular substructure. Secondly, the 1,2-diketone moieties of **4** prefer to exist

---

(1) (a) Carboni, R. A.; Kauer, J. C.; Hatchard, W. R.; Harder, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 2618. (b) Carboni, R. A.; Kauer, J. C.; Hatchard, W. R.; Harder, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 2626. (c) Harder, R. J.; Carboni, R. A.; Castle, J. E. *J. Am. Chem. Soc.* **1967**, *89*, 2643. (d) E. I. du Pont de Nemours and Co., U.S. Patent 2,904,544 **1959**; *Chem. Abstr.* **1960**, *54*, 11062.

(2) Subramanian, G.; Boyer, J. H.; Buzatu, D.; Stevens, E. D.; Trudell, M. L. *J. Org. Chem.* **1995**, *60*, 6110.

(3) A program for the calculation of density (*d*), detonation velocity (*D*), and detonation pressure (P_{CJ}) was obtained from the Naval Weapons Center, China Lake, CA.

(4) Olah, G. A. Methods for Preparing Energetic Nitro-Compounds: Nitration with Superacid Systems, Nitronium Salts, and Related Complexes. In *Chemistry of Energetic Materials*; Olah, G. A., Squire, D. R., Eds; Academic Press, Inc.: New York, 1991; pp 139−204.

(5) The authors have deposited atomic coordinates for compound **4** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

0022-3263/96/1961-1898$12.00/0

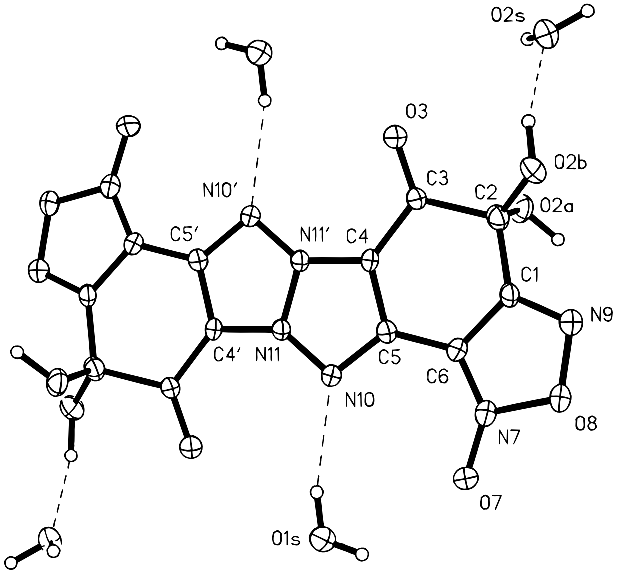


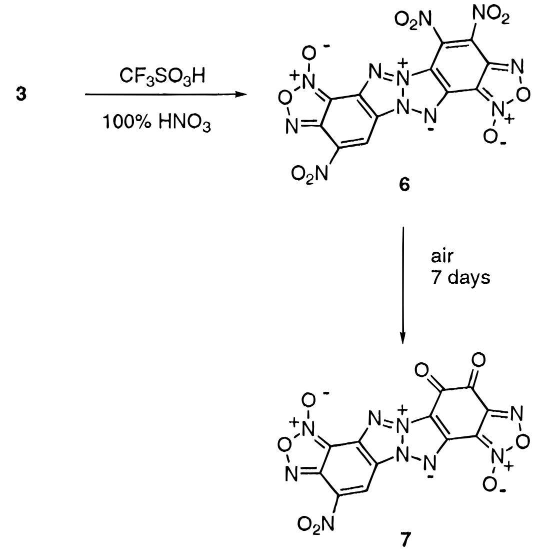
Figure 1. A drawing of the structure of **4** in its tetrahydrate crystal form, wherein **4** lies on an inversion center. Thermal-ellipsoid envelopes are shown at the 25% density level. **4** and its neighboring water molecules are approximately planar, with the exception of its axial hydroxyl groups, O2a and its symmetry-mate.

as a keto/*gem*-diol mixture. Although this has been reported in a similar system,[6] the keto/*gem*-diol equilibrium usually favors the 1,2-diketone. Finally, the density (d = 1.833 g/cm^3) of **4** was found to be unusually high for a hydrated material. This suggests that the hexacyclic system contributes significantly to the density of this and related compounds.

Compound **4** was converted into the tetraoxo derivative **5** by heating at 220 °C for 10 min (Scheme 1). The resultant yellow material **5** was obtained in quantitative yield. The material **4** prior to heating contained some CH_3CN as a stable solvent complex in addition to water. Upon heating, a 13% weight loss was observed corresponding to the loss of two molecules of water and one molecule of CH_3CN per molecule of **4**. TGA/FTIR analysis of **4** confirmed the sequential loss of water and CH_3CN in the amounts expected. The zero-hydrogen content tetraoxo derivative **5** was computed to have high density (d = 2.02 g/cm^3).[3] However, **5** was computed to have poor energetic properties (D and P_{CJ}) relative to **1**−**3**. Both **4** and **5** possessed good thermal stability and had significantly greater insensitivity to impact than **3**. However, both **4** and **5** could be detonated by hammer impact with **5** exhibiting greater sensitivity.

In order to avoid the problem of hydrolysis and oxidation encountered with the fluorosulfonic acid/100% nitric acid media, nitration of **3** with trifluoromethanesulfonic acid in 100% nitric acid was attempted (Scheme 2).[4] This furnished the trinitro derivative **6** in 40% yield. Further nitration of **6** under these reaction conditions was unsuccessful. High density and good energetic properties were computed for **6**.[3] The red material **6** was thermally stable up to 310 °C. However, the material was found to be air sensitive and was readily oxidized to the 1,2-diketone derivative **7** upon exposure to air over the course of a week.

Scheme 2



The lability of the 4,5-dinitro group toward nucleophilic displacement by water is consistent with the chemistry observed for 1,2,3,5-tetranitrobenzene and hexanitrobenzene which have been converted under hydrolysis conditions into picric acid and trinitrophloroglucinol, respectively.[7−9] Displacement of the 4,5-dinitro groups presumably results in the formation of an *o*-dihydroquinone species which then readily undergoes autooxidation to give **7**. Most likely, **4** was formed in similar fashion from **2** which was generated *in situ* during the nitration reaction.

In summary, we have found that further nitration of **3** leads to the formation of moisture sensitive nitration products which undergo further oxidation to give *o*-quinone-like species **4** and **7**. However, the tetraazapentalene subunit remained unaffected further demonstrating the robust nature of this heterocyclic system.

Experimental Section

All chemicals were purchased from Aldrich Chemical Co., Milwaukee, WI. Melting points and decomposition points are uncorrected. All compounds were homogeneous by TLC and NMR. Elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, TN, and Midwest Micro Lab, Indianapolis, IN. All reported compounds gave satisfactory carbon and hydrogen analysis. Due to the high nitrogen content and explosive nature of these compounds, microanalytical data for nitrogen was often outside the standard acceptable limit of ±0.4%. However, duplicate and triplicate analyses for nitrogen were usually within ±1% of calculated values and corresponded to the empirical formula of the compound. Crystals of **4** obtained from a saturated solution of acetone belong to triclinic space group $P(\text{-}1)$. Crystal Data: a = 5.587(1), b = 8.243(1), c = 10.369(2)Å, α = 85.61(1), β = 78.96(2), γ = 72.11(2)°, V = 445.9-(2)Å^3, Z = 1, D_x = 1.833 mg mm^{-3}, R = 0.0646, $wR2$ = 0.1452 for 854 unique observed reflections. Crystal packing, briefly: **4** stacks in parallel hydrogen-bonded almost-planar sheets, with adjacent sheets cross-linked by hydrogen bonds to and from the out-of-plane axial hydroxyl group. ***Caution*! Compounds 3−7 should be handled as potentially explosive materials!**

DTBBD (4). Under an atmosphere of nitrogen, fluorosulfonic acid (1.35 g, 0.80 mL, 13.5 mmol) was placed in a round bottom

---

(6) Gridunova, G. V.; Shklouer, V. E.; Struchkov, S.; Yu, T.; Linko, R. V.; Poplanskii, A. N.; Andrievskii, A. M. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1990**, 575.

(7) Urbanski, T. *Chemistry and Technology of Explosives*, Pergamon Press: Oxford, 1964; pp 258−259.

(8) Nielson, A. T.; Atkins, R. L.; Norris, W. P. *J. Org. Chem.* **1979**, *44*, 1181.

(9) Nielson, A. T.; Atkins, R. L.; Norris, W. P.; Coon, C. L.; Sitzmann, M. E. *J. Org. Chem.* **1980**, *45*, 2341.

flask (25 mL) equipped with magnetic stirrer and nitrogen inlet tube. Nitric acid (100%, 1.19 g, 0.80 mL, 19 mmol) was added in one portion at 25 °C. After 5 min, dry nitromethane (5 mL) was added over a period of 10 min with stirring. The dinitro derivative **3**^{2} (350 mg, 0.85 mmol) was added in one portion. The temperature was maintained at 80−90 °C for 2 h, nitromethane was removed under vacuum, and the mixture was cooled and added to ice−water (150 mL) to bring about the precipitation of **4**. The material was recrystallized from acetonitrile, triturated with boiling ether for 15 min, cooled, filtered, and dried to give **4** as a red microcrystalline solid: 84 mg (20%), mp 340−341 °C dec. During the measurement of the melting point an irreversible color change from red to yellow was observed at 180−185 °C. IR (KBr) 3480 (OH), 1725 (C=O), 1678 (C=N), 1467, 1378, 1322, 1044, 967, 897 cm^{-1}. ^{13}C NMR (DMSO-d_6): 166.65, 163.57, 149.41, 137.51, 113.91, 103.10. Anal. Calcd for $C_{12}H_4N_8O_{10}$: C, 34.30; H, 0.96; N, 26.65; O, 38.09. Found: C, 33.93; H, 0.96; N, 25.27; O, 36.92.

4,5,11,12-Tetraoxo-14*H*-[1,2,5]oxadiazolo[3,4-*e*][1,2,5]-oxadiazolo[3′,4′:4,5]benzotriazolo[2,1-*a*]benzotriazol-6-ium Inner Salt 1,8-Dioxide (5). The compound **4** (199 mg, 0.47 mmol) was heated at 220 °C for 10 min (an irreversible color change from red to yellow was observed). This afforded **5** as a yellow solid in quantitative yield: 178 mg (99%), mp 330 °C dec. IR (KBr) 1729 (C=O), 1675 (C=N), 1467, 1383, 1329, 1049, 971, 671 cm^{-1}. Anal. Calcd for $C_{12}N_8O_8$: C, 37.53; N, 29.16. Found: C, 37.26; N, 28.81.

4,5,11-Trinitro-14*H*-[1,2,5]oxadiazolo[3,4-*e*][1,2,5]-oxadiazolo[3′,4′:4,5]benzotriazolo[2,1-*a*]benzotriazol-6-ium Inner Salt 1,8-Dioxide (6). Nitric acid (100%, 380 mg, 0.25 mL, 6 mmol) was added dropwise with stirring to trifluoromethanesulfonic acid (1.80 g, 1.01 mL, 12 mmol) under nitrogen in a flask (25 mL) equipped with a magnetic stirrer, nitrogen inlet tube, and a dropping funnel. A colorless crystalline solid separated[10] and after 10 min, **3**^{2} (410 mg, 1 mmol) was added in one portion. The temperature of the oil-bath was raised and maintained at 70−80 °C for 2 h. The mixture was cooled and poured into ice−water (150 mL). The precipitate was collected, dried, and triturated with acetonitrile to give **6** as a red solid: 180 mg (40%), mp 310−315 °C dec. IR (KBr) 1655 (C=N), 1560, 1534 and 1322 (NO$_2$) cm^{-1}. ^{1}H NMR (DMSO-d_6): 9.67 (s). ^{13}C NMR (DMSO-d_6): 151.07, 140.02, 138.20, 133.02, 131.00, 126.00, 122.22, 118.26, 112.00, 108.32, 104.07, 102.02. Anal. Calcd for $C_{12}H_1N_{11}O_{10}$: C, 31.40; H, 0.22; N, 33.55. Found: C, 31.70; H, 0.36; N, 32.60.

4,5-Dioxo-11-nitro-14*H*-[1,2,5]oxadiazolo[3,4-*e*][1,2,5]-oxadiazolo[3′,4′:4,5]benzotriazolo[2,1-*a*]benzotriazol-6-ium Inner Salt 1,8-Dioxide (7). The compound **5** (100 mg) was placed in a vial and was kept open to the air for seven days. There was a color change from light maroon to dark brown. The compound was reprecipitated with acetonitrile and dried under vacuum to give **7** as a yellow solid: 50 mg (50%), mp 300 °C dec. IR (KBr) 1734, 1654, 1314, 1174 cm^{-1}. ^{1}H NMR (DMSO-d_6): 9.72 (s). ^{13}C NMR (DMSO-d_6): 168.00, 164.73, 150.80, 145.86, 137.97, 136.08, 132.70, 121.08, 114.97, 114.86, 106.69, 104.46. Anal Calcd for $C_{12}H_1N_9O_8$: C, 36.12; H, 0.26; N, 31.57; O, 32.06. Found: C, 36.29; H, 0.42; N, 30.01; O, 32.06.

Acknowledgment. We are grateful to the Office of Naval Research (N00014−90−J−1661) and Program Officer Dr. Richard S. Miller for the financial support of this work. We also wish to thank Ms. Lu Espina for her assistance in the preparation of this manuscript.

JO951889I

---

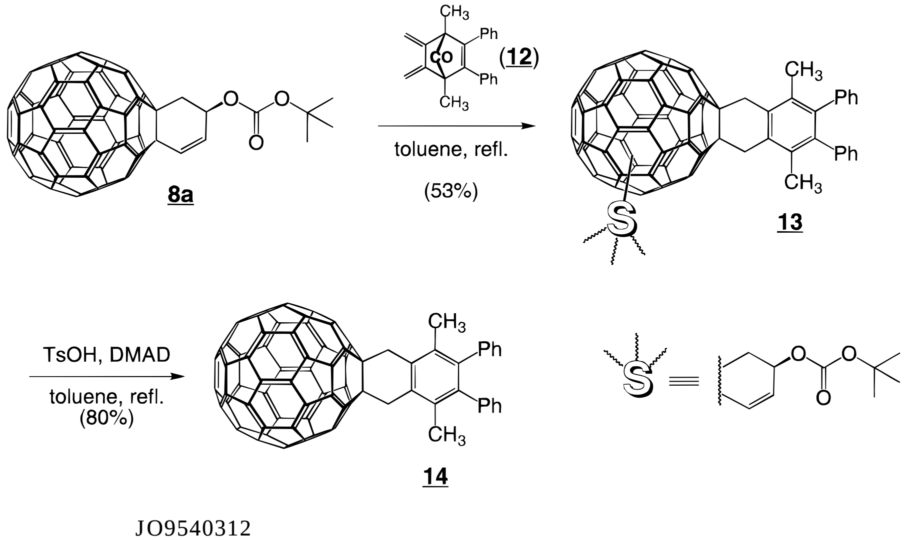
(10) Coon, C. L.; Blucher, W. G.; Hill, M. E. *J. Org. Chem.* **1973**, *38*, 4243.

Additions and Corrections

Vol. 60, 1995

Yi-Zhong An, George A. Ellis, Argimiro L. Viado, and Yves Rubin*. A Methodology for the Reversible Solubilization of Fullerenes.

Page 6357. Corrected Scheme 8 is shown below.



JO9540312