1872 *J. Org. Chem.* **1997,** *62,* 1872−1874

Preparation and Characterization of *trans*-1,4-Diazido-1,4-dinitrocyclohexane and *exo*-2,5-Diazido-*endo*-2,5-dinitronorbornane: Stable Geminal Azido−Nitro Compounds

G. K. Surya Prakash,* John J. Struckhoff, Jr.,
Klaus Weber, Andre Schreiber, Robert Bau, and
George A. Olah*

Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661

Received October 29, 1996

Introduction

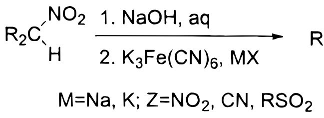
The development of methods for the synthesis of novel compounds that combine properties of high energy, high density, and high stability is a continuing effort in energetic materials research.[1] Cyclic nitramines such as cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX) have been in practical use since World War II.[2] Recent achievements in this field are highlighted by the synthesis of 1,3,3-trinitroazetidine (TNAZ)[3] , a four-membered cyclic nitramine containing geminal dinitromethylene unit, and condensations affording the hexaazaisowurtzitane skeleton and its subsequent conversion to the hexanitro derivative (HNIW).[4] In addition to work done on the synthesis of cyclic nitramines, recent efforts have focused on the development of methodologies to produce compounds containing novel functionalities of potential energetic interest, most notably the geminal dinitro group[5] and *mono-* and *gem*-difluoroamino groups.[6]

Bowman and co-workers found in a mechanistic investigation that oxidative addition of azide to the anions of secondary nitroalkanes proceeded to give the α-substituted azido−nitro compound.[7] They were able to prepare both 1-azido-1-nitrocyclohexane and 2-azido-2-nitropropane. However, these compounds were only isolable via distillation and were not amenable to other means of purification. Additionally, they state that longer reaction times and excess amounts of azide result in loss of the nitro group to give the secondary diazide. Wagner and Weber also encountered difficulty in attempts to synthesize 1-azido-1,1-dinitroethane electrochemically.[8] This compound showed propensity to displace a nitro group and form the highly unstable diazido derivative under electrochemical conditions. As part of our efforts to synthesize molecules of high nitrogen content, we have synthesized and fully characterized various carbon ring systems containing the *gem*-azido−nitro functionality.

Results and Discussion

As noted previously,[5] we have synthesized cyclic geminal dinitro compounds using methodology developed by Kornblum and co-workers for oxidative substitution of nitroparaffin salts.[9] We endeavored to use this same protocol for the synthesis of molecules containing geminal azido−nitro functionality. All starting secondary nitro compounds used in this study were prepared according to previously discussed methods,[5] and in all cases yields were comparable or slightly improved. 1,3,5-Trinitrobenzene (**1**) was reduced using sodium borohydride in aqueous methanol[10] to give 1,3,5-trinitrocyclohexane (**2**) as a mixture of isomers (Scheme 1).

Substitution at saturated carbons by means of electron-transfer reactions via radical anionic intermediates is long established.[11] Salts of secondary aliphatic nitro compounds readily undergo oxidative substitution to give the geminal substituted products.



$$R_2C(NO_2)H \xrightarrow[\text{2. } K_3Fe(CN)_6,\ MX]{\text{1. NaOH, aq}} R_2C(NO_2)Z$$

This method works well for the synthesis of α-substituted nitriles, sulfones, and even for the synthesis of *gem*-dinitro compounds. The great advantage of this method is that it relies on the use of the relatively inexpensive potassium ferricyanide as a one-electron oxidant versus other methods involving more expensive silver salts.[9]

We have been able to extend the use of this methodology of Kornblum for the synthesis of stable, isolable geminal azido−nitro compounds. For example, 1-azido-1-nitrocyclohexane (**4**) was prepared from nitrocyclohexane using sodium azide and potassium ferricyanide (Scheme 2).

Compound **4** was identified by its characteristic ^{13}C resonance at 103.1 ppm for C_1 and by its infrared absorption bands at 2212 and 1552 cm^{-1}, which is consistent with the data found by Bowman et al.[7] However, the oily product was not amenable to mass spectrometric analysis or purification by column chromatography. Spontaneous decomposition with evolution of gases resulted when **4** came in contact with silica gel, and the only product isolated was cyclohexanone. Despite the difficulties encountered in purification, we were encouraged by this result. We further investigated the utility of using this methodology on cyclic secondary di- and trinitro compounds to synthesize molecules with high nitrogen content. Similar to the above reaction, 1,4-

---

(1) Nielsen, A. T. Polycylic Amine Chemistry. In *Chemistry of Energetic Materials*; Olah, G. A. Squires, D. R., Eds.; Academic Press, Inc.: New York, 1991; pp 95−124.

(2) Urbanski, T. *Chemistry and Technology of Explosives*; Pergamon Press: Oxford, 1967; Vol. III, Chapter IV.

(3) (a) Archibald, T. G.; Gilardi, R.; Baum, K.; George, C. *J. Org. Chem.* **1990**, *55*, 2920. (b) Katritzky, A. R.; Cundy, D. J.; Chen, J. *J. Heterocycl. Chem.* **1994**, *31*, 271. (c) Marchand, A. P.; Rajagopal, D.; Bott, S. G.; Archibald, T. G. *J. Org. Chem.* **1995**, *60*, 4943. (d) Axenrod, T.; Watnick, C.; Yazdekhasti, H.; Dave, P. R. *J. Org. Chem.* **1995**, *60*, 1959.

(4) (a) Nielsen, A. T.; Nissan, R.; Vanderah, D. J.; Coon, C.; Gilardi, R.; George, C. F.; Flippen-Andersen, J. L. *J. Org. Chem.* **1990**, *55*, 1459. (b) Miller, R. S. Research on New Energetic Materials. In *Decomposition, Combustion, and Detonation Chemistry of Energetic Materials*; Brill, T. B., Russell, T. P., Tao, W. C., Wardle, R. B., Eds.; Materials Research Society: Pittsburgh, PA, 1996; Vol. 418, p 3−14.

(5) Olah, G. A.; Ramaiah, P.; Prakash, G. K. S.; Gilardi, R. *J. Org. Chem.* **1993**, *58*, 764.

(6) See ref 4b.

(7) (a) Al-Khalil, S. I.; Bowman, W. R.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 1* **1986**, 555. (b)Al-Khalil, S. I.; Bowman, W. R. *Tetrahedron Lett.* **1982**, *23*, 4513.

(8) Wagner, R.; Weber, J. Personal communication from efforts carried out at Rocketdyne, Inc., in 1984−85.

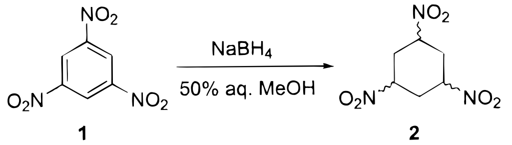
(9) Kornblum, N.; Singh, H. K.; Kelly, W. J. *J. Org. Chem.* **1983**, *48*, 332 and references therein.

(10) (a) Severin, T.; Schmitz, R. *Chem. Ber.* **1962**, *95*(6), 1417. (b) Atroshchenko, Yu.M.; Nasonov, S. N.; Gitis, S. S.; Kaminskii, A. Ya.; Mel'nikov, A. I.; Shakhkel'dyan, I. V. *Zh. Org. Khim.* **1994**, *30*, 675.

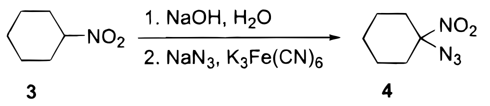
(11) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734.

S0022-3263(96)02026-9 CCC: $14.00

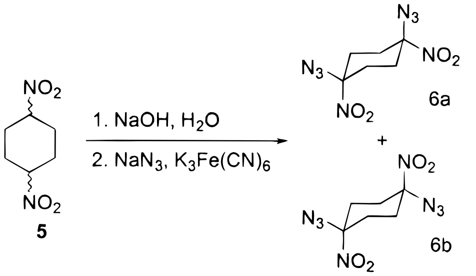
Scheme 1



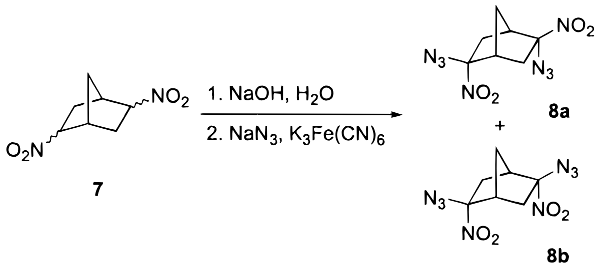
Scheme 2



Scheme 3



Scheme 4



dinitrocylcohexane (**5**) undergoes oxidative azidation to give 1,4-diazido-1,4-dinitrocyclohexane (**6a** and **6b**) in 85% overall yield as a mixture of *cis* and *trans* isomers (see Scheme 3).

Recrystallization from warm ethyl acetate yielded solely the stable *trans* isomer as crystalline white needles that decomposed above its melting point of 138 °C. The structure of **6b** was confirmed by proton and carbon NMR, as well as by single-crystal X-ray diffraction analysis (*vide infra*).

Similarly, 2,5-dinitronorbornane (**7**) was oxidatively converted to 2,5-diazido-2,5-dinitronorbornane (**8a** and **8b**) in 72% yield as a mixture of *exo*-2-azido-*endo*-5-azido (**8a**) and *exo*-2-azido-*exo*-5-azido (**8b**) isomers (Scheme 4).

It is important to note that no evidence was found for a product with the *endo*-2-azido-*endo*-5-azido arrangement, presumably due to the hindered nature of the *endo* face of the norbornane skeleton. Recrystallization, again from warm ethyl acetate, yielded pure **8b**, which was fully characterized by ^{1}H and ^{13}C NMR and X-ray crystallography (*vide infra*). This compound has a melting point of 94−96 °C, and it decomposes upon further heating above 100 °C.

Further work on oxidative azidation of other ring systems, however, proved to be less successful. When the dianion of **9** was treated with sodium azide and potassium ferricyanide, NMR showed ^{13}C resonances between 108 and 110 ppm, indicative of the formation of the geminal azido−nitro species (Scheme 5).

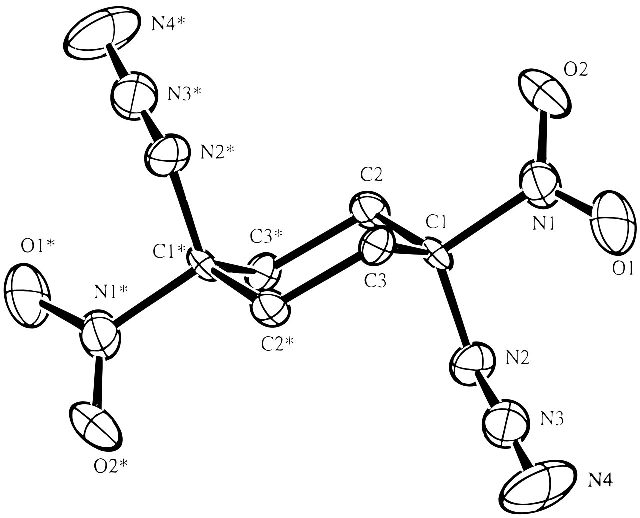
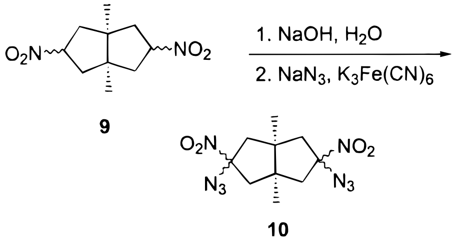


Figure 1. Molecular plot of *trans*-1,4-diazido-1,4-dinitrocyclohexane (**6b**). A crystallographic center of symmetry is situated in the middle of the molecule.

Scheme 5



However, no isolation of any of the isomeric products via recrystallization was achieved as they proved to be unstable.[12] Additionally, 1,3-dinitrotetramethycyclobutane proved unreactive under these conditions, and no *gem*-azido−nitro products were found. This is consistent with prior work done in our group in attempts to synthesize the geminal dinitro compound.[5] Finally, treatment of isomeric trinitrocyclohexane **2** with aqueous sodium hydroxide resulted in a black solution that was not amenable to this present methodology.

Both *trans*-1,4-diazido-1,4-dinitrocyclohexane (**6b**) and *exo*-2,5-diazido-2,5-*endo*-dinitronorbornane (**8b**) represent new, stable energetic compounds of substantial interest. It is important to note that we found no evidence for further displacement of a nitro group when using excess amounts of sodium azide in the preparation or even when reactions were stirred overnight. Recrystallization was found to be the only suitable method for isolation in pure form. The pure crystalline compounds (**6b** and **8b**) were used in single-crystal X-ray diffraction structure determinations.

Compound **6b** crystallizes in the monoclinic space group $P2_1/n$, with $a = 5.988(2)$ Å, $b = 13.791(2)$ Å, $c = 6.616(2)$ Å, $\beta = 105.81(2)°$, $Z = 2$. Data were collected at −100 °C on a Siemens P4/RA X-ray diffractometer with Cu Kα radiation up to a 2θ maximum of 102.5°. The structure was solved with direct methods and refined to a final agreement factor of R = 5.3%. The molecule, shown in Figure 1, is situated on a crystallographic center of symmetry. The two azide groups are axial, and the nitro groups are equatorial. The bond between the carbon of the ring and the nitrogen of the azide group is

---

[12] A 15 mg sample used for NMR analysis in DMSO-d_6 built up considerable pressure, and gas evolved when the cap of the tube was removed after analysis.

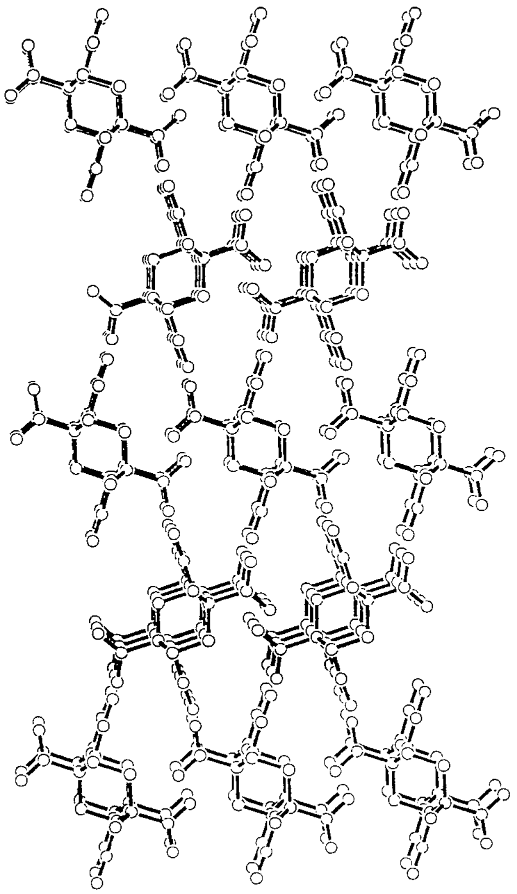


Figure 2. Packing diagram of **6b** in the crystalline state, showing interactions between the azide and nitro groups of adjacent molecules.

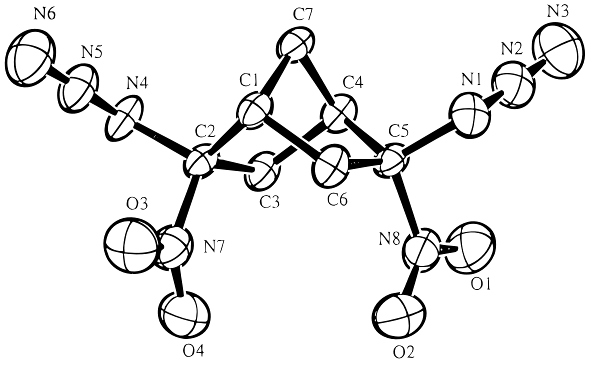


Figure 3. Molecular plot of *exo*-2,5-diazido-*endo*-2,5-dinitronitronorbornane (**8b**). A noncrystallographic 2-fold rotation axis is present vertically through atom C_7.

distinctly bent [$C_1-N_2-N_3 = 114.8(4)°$], consistent with sp^2 hybridization, while the $N_2-N_3-N_4$ angle is linear [171.5(5)°] as expected. Figure 2 shows a portion of the intermolecular packing in the crystal, which features some interactions between azido and nitro groups of neighboring molecules.

Compound **8b** crystallizes in the triclinic space group $P1$ with $a = 6.554(3)$ Å, $b = 7.030(5)$ Å, $c = 13.568(5)$ Å, $\alpha = 78.37(4)°$, $\beta = 80.85(3)°$, $\gamma = 67.94(4)°$, $Z = 2$. Data were collected as described above at room temperature and the structure refined to a final R factor of 6.7%. The structure, shown in Figure 3, shows a noncrystallographic 2-fold rotation axis passing through the bridgehead atom (C_7), bisecting the angle $C_1-C_7-C_4$. As in the case of compound **6b**, the azide ligands are bent at the point of attachment to the carbon framework [$C_2-N_4-N_5 = 114.9(5)°$, $C_5-N_1-N_2 = 115.0(5)°$], but the azide groups themselves are linear [$N_1-N_2-N_3 = 171.5(6)°$, $N_4-N_5-N_6 = 171.7(7)°$].[13]

Experimental Section

NMR spectra were recorded in $CDCl_3$, DMSO-d_6, or CD_2Cl_2 at 200 or 300 MHz. FT-IR spectra were obtained either as KBr pellets or as neat films on NaCl plates. Melting points were not corrected. Starting materials were obtained from Aldrich and used without purification, except for **1**, which was purchased from Tokyo Kasei Kogyo Co. All secondary nitro compounds were prepared from the corresponding oximes according to previously reported methods.[5]

Caution: Outside of the difficulties encountered with **10**, all other isolated materials were stable. All reactions were performed behind a safety shield in the dark, and all isolated compounds were stored in a freezer. Both isolated crystalline compounds **6b** and **8b** were subjected to a hammer test on 20−30 mg samples wrapped in aluminum foil and showed no reaction. **However, working with azides is inherently dangerous and full safety precautions must be taken. Additionally, the biological toxicity of this geminal functional grouping is unknown, but should be regarded as substantial.**

Preparation of *trans*-1,4-Diazido-1,4-dinitrocyclohexane (6b). 1,4-Dinitrocyclohexane (**5**), 0.52 g, was added to a solution of NaOH (0.24 g, 2 equiv) in 12 mL of water and stirred under argon for 5.5 h (until all solid had dissolved). This solution was then added dropwise under argon to a solution of $K_3Fe(CN)_6$ (9.83 g, 10 equiv) and NaN_3 (3.89 g, 20 equiv) in 50 mL of water and 15 mL of CH_2Cl_2 at ice temperature that was protected from light. The solution was stirred at this temperature for 3 h and then stirred at room temperature overnight. The reaction was poured into a separatory funnel, and the organic layer was drawn off. Solid NaCl was added to the aqueous layer, and it was extracted with 3 × 30 mL of CH_2Cl_2. The extracts were combined and dried with $MgSO_4$, and the solvent was removed under reduced pressure to yield 0.65 g (85.0%) of a yellow/white solid. NMR of the crude material indicated a 60:40 mixture of trans:cis isomers, of which the *trans* isomer (**6b**) could be separated by recrystallization from warm (50 °C) ethyl acetate, forming fine white needles: mp 138 °C dec; ^1H NMR (benzene-d_6) δ 1.38 (d, 4H, $J = 9.4$ Hz), 1.72 (d, 4H, $J = 9.4$ Hz); ^{13}C NMR (DMSO-d_6) δ 29.06 (t), 100.58 (s); IR (KBr) 2127 (vs), 1543 (vs) cm^{-1}. Anal. Calcd for $C_6H_8N_8O_4$: C, 28.13; H, 3.15; N, 43.74. Found: C, 28.18; H, 2.97, N, 43.91. Density: 1.62 mg/mm^3 (from X-ray measurement).

Preparation of *trans*-2,5-Diazido-2,5-dinitrobicyclo[2.2.1]heptane (8b). This product was obtained in a similar manner to **6** in 72% yield. Recrystallization could be achieved from warm ethyl acetate to yield **8b**, which has a mp of 94−96 °C: ^1H NMR (CD_2Cl_2) δ 3.06 (dt, 2H, H_1 and H_4), 2.49 (dt, 2H, H_3 endo, H_6 endo, $J_{endo-exo} = 16.1$ Hz), 2.16 (m, 2H, H_7), 2.06 (ddd, 2H, H_3 exo, H_6 exo, $J_{exo-endo} = 16.1$ Hz, $J_{3-4} = 5.86$ Hz); ^{13}C NMR (CD_2Cl_2) δ 34.48, 37.45, 46.13, 106.63; IR (KBr) 2122 (vs), 1559 (vs) cm^{-1}. Anal. Calcd for $C_7H_8N_8O_4$: C, 31.35; H, 3.01; N, 41.78. Found: C, 31.58, H, 3.10, N, 42.44. Density: 1.58 mg/mm^3 (from X-ray measurement).

Acknowledgment. Support for our work by the Office of Naval Research (Program Manager: Richard S. Miller) is gratefully acknowledged. A.S. wishes to thank the Feodor Lynen Foundation for financial support.

JO9620268

---

(13) The author has deposited atomic coordinates for this structure 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, UK.