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Polynitronorbornanes, Bicyclooctanes, and Cyclohexanes[1]

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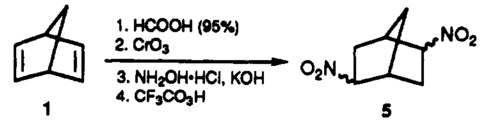
Strained polynitro organic compounds are potential energetic materials. Cyclic and polycyclic polynitro compounds and polycyclic polynitramines are important explosives. Cyclotrimethylenetrinitramine (RDX) has been an important explosive since World War II.[2] The higher homolog of cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetramine (HMX) has been one of the most important explosive and high-energy propellants since 1945. More recently polynitroadamantanes, polynitrocubanes, polynitrotrishomocubane, polynitropolycycloundecane, polynitropolycyclododecanes, polynitrocyclobutane, and their derivatives have been prepared as potential high-energy, high-density materials.[3] Recently we have reported[4] the synthesis of energetic amine nitroimides (R_3N^+–N^-–NO_2). Tetranitronorbornane is of particular interest as a high-energy material with a high nitro group to carbon ratio. The material is also expected to have a relatively high density. Preparation of polynitronorbornanes has not yet been explored in the literature. In addition to the synthesis of nitronorbornanes, we also extended our studies to the synthesis of polynitro derivatives of six-, five-, and four-membered ring systems.

Scheme I



2,5-Dinitronorbornane (5) was prepared as shown in Scheme I. Bicyclo[2.2.1]heptane-2,5-dione (3) was prepared from readily available bicyclo[2.2.1]hepta-2,5-diene (1) by an improvement of the reported procedure.[5] Formylation of the diene 1 with 90% HCOOH furnished 2,5-*exo, exo*-diformate ester 2 in 85% yield. Chromium trioxide oxidation of diformate ester 2 in acetone gave 2,5-dione 3 in 50% yield. Oximes 4, 7, 10, 13, and 16 were prepared according to literature methods.[6] Treatment of 3 with NH_2OH·HCl and KOH gave dioxime 4 in 71% yield as a white crystalline solid. Several methods for the oxidation of oximes to the corresponding nitro compounds were examined. Though several procedures are reported,[7] direct methods for conversion are scanty. Generally the nitro compounds are synthesized by the reduction of the oximes to amines and subsequent oxidation or oxidation by NBS followed by debromination.[8] In contrast we carried out direct oxidation of oximes to nitro compounds. The peroxytrifluoroacetic acid induced oxidation[9] of the dioxime 4 to the crystalline dinitro compound 5 proceeded in 52% yield. The oxidation of 4 was carried out by the dropwise addition of peroxytrifluoroacetic acid (made from 90% hydrogen peroxide and trifluoroacetic anhydride) in dry acetonitrile to a solution of 4 in acetonitrile containing sodium bicarbonate buffer maintained at a temperature of 75 °C. Rapid addition of the peroxide solution and a rise in temperature above 78 °C decreases the yield to 30%. By using disodium hydrogen phosphate as buffer, the yield increases to 65%. A transient yellow color is initially observed which gradually fades as more peracid is added. The NMR spectra of the product 5 suggests it to be a mixture of endo,endo (90%) and minor exo,exo (10%) isomers, and we do not see any exo,endo isomer by NMR. The endo,endo isomer was separated from the mixture by recrystallization from chloroform–hexane.[10] An alternative method based on the addition of sodium peroxide to trifluoroacetic acid followed by reaction with the oxime was also investigated but failed to give satisfactory results. Recently, we have also achieved convenient oxidation of oximes 4 and 7 to nitro compounds 5 and 8 with sodium perborate in glacial acetic acid.[11] The yield slightly improved with the sodium perborate method compared to the peroxytrifluoroacetic acid procedure.

Oxidation of bicyclo[2.2.1]heptanone 2-oxime (7) with peroxytrifluoroacetic acid gave 60% 2-nitronorbornane (8), exhibiting proton and α-carbon NMR signals at $\delta(^1H)$ 4.4, 4.8 and $\delta(^{13}C)$ 84.9, 88.0, respectively, corresponding

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[1] Considered as Synthetic Methods and Reactions. Part 179. For part 178, see: Olah, G. A.; Wang, Q.; Li, X.-Y.; Prakash, G. K. S. *Synthesis*, submitted for publication.

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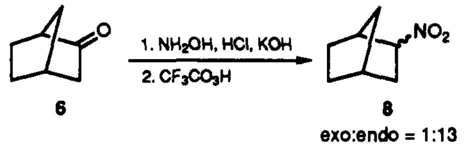
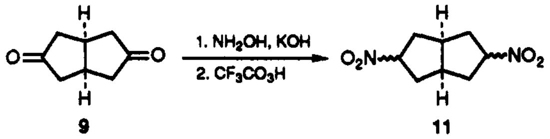
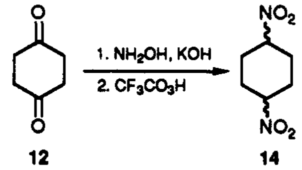
Scheme II



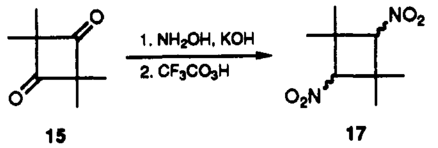
Scheme III



Scheme IV



Scheme V



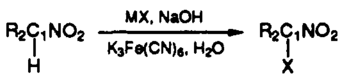
to the exo and endo isomers in 1:1.3 ratio (Scheme II). The overall yield slightly improved with sodium perborate.

Similar oxidation of bicyclo[3.3.0]octane 3,7-dioxime (**10**) with CF_3CO_3H gave the dinitro compound **11** in 60% yield. (Scheme III). The ^{13}C NMR signals at $\delta(^{13}C)$ 87.5, 86.6, 86.5, and 86.4 correspond to the syn and anti isomers in 1:1 ratio. The yield of **11** was further improved by using disodium hydrogen phosphate as a buffer instead of sodium bicarbonate. Isomeric mixture **11** was found unstable for prolonged periods of time at room temperature.

trans-1,4-Dinitrocyclohexane (**14**) was similarly prepared from dioxime **13** (Scheme IV). Initially the product was obtained as a mixture of cis and trans isomers and separation was achieved by three repeated recrystallizations from a 1:1 mixture of chloroform–hexane. The less soluble trans isomer was separated.[12]

Attempts to synthesize 1,3-dinitrotetramethylcyclobutane (**17**) by the oxidation of dioxime **16** with peroxytrifluoroacetic acid (Scheme V) gave a mixture of products of which **17** is only a minor product. Oxidation of **16** with sodium perborate also gave **17** in poor yield.

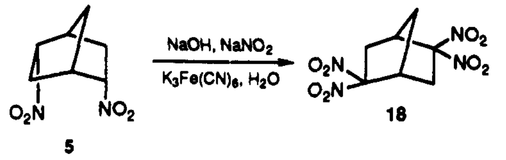
Electron-transfer substitution at saturated carbon atoms is well established.[13] Kornblum and co-workers have showed that nitroparaffin salts undergo oxidative substitution at the geminal position to give disubstituted compounds.[14]



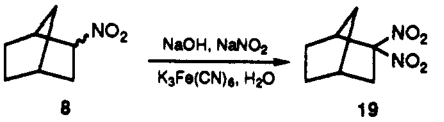
$$\underset{\displaystyle H}{R_2C_1NO_2} \xrightarrow[K_3Fe(CN)_6,\ H_2O]{MX,\ NaOH} \underset{\displaystyle X}{R_2C_1NO_2}$$

M = Na, K; X = NO_2 CN, RSO_2

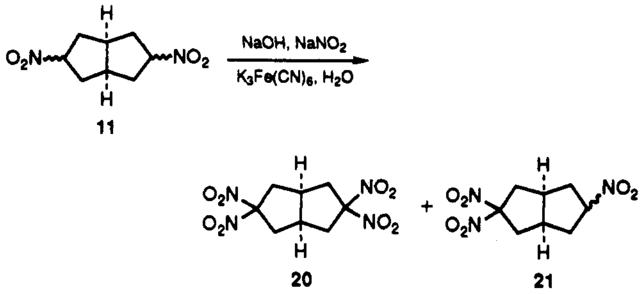
Scheme VI



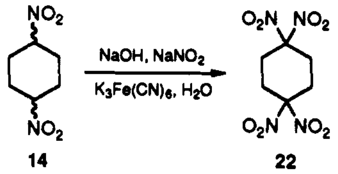
Scheme VII



Scheme VIII



Scheme IX



Kornblum's method has been used for synthesis of *gem*-dinitro compounds in our systems. The dinitro compound **5** when treated with aqueous sodium hydroxide forms a greenish yellow color, apparently due to the formation of dianions of **5**. Oxidative nitration of the dianions of 2,5-dinitrobicyclo[2.2.1]heptane (**5**) with potassium ferricyanide in the presence of sodium nitrite at 0 °C to ambient temperature gave 2,2,5,5-tetranitrobicyclo[2.2.1]heptane (**18**) in 83% yield. (Scheme VI). The structure of **18** was confirmed by proton and carbon NMR and single-crystal X-ray diffraction (vide infra). **18** is thermally stable upto its melting point of 194 °C and can be stored for long periods of time without decomposition.

Similar oxidative nitration of **8** gave 2,2-dinitrobicyclo[2.2.1]heptane (**19**) in 81% yield respectively (Scheme VII).

Further studies were carried out to introduce additional nitro groups into the cyclopentane and cyclohexane skeletons. When **11** was treated with aqueous NaOH solution at room temperature for 20 h a burgandy-colored solution of dianion of **11** was formed. Reaction of the disodium salt of 3,7-dinitro derivative **11** with potassium ferricyanide and sodium nitrite gave a mixture of 3,3,3,7-tetranitrobicyclo[3.3.0]octane (**20**) and 3,3,7-trinitrobicyclo[3.3.0]octane (**21**) as the major and minor products, respectively, from which **20** was isolated in 76% yield by column chromotography. (Scheme VIII). No attempt was made to isolate the minor product **21**.

Finally, the similar oxidative nitration of **14** gave 1,1,4,4-tetranitrocyclohexane **22** in 80% yield (Scheme IX).

The newly synthesized *gem*-polynitro derivatives of norbornane, bicyclo[3.3.0]octane, and cyclohexane represent stable, high-density energetic compounds of sub-

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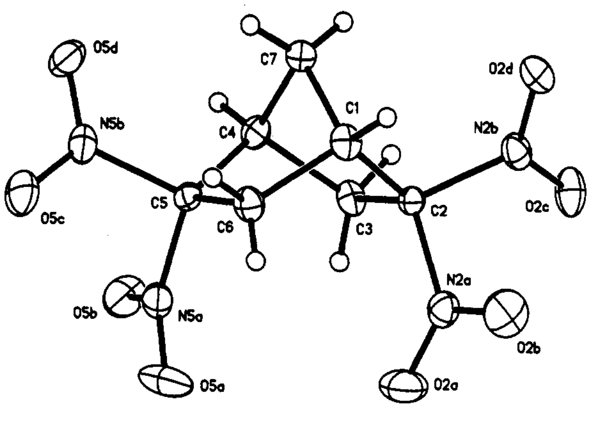

Figure 1. The molecular structure and numbering scheme for 18. The figure was drawn using experimentally determined coordinates and thermal ellipsoids represented at the 20% probability level.

stantial interest. Four of these polynitro compounds were subjected to X-ray crystallographic analysis. The ORTEP diagram for 18 is shown in Figure 1. The results for 19, 20, and 22 are illustrated in Figures 2–4 in the supplementary material. Statistically, crystallographic determinations of the structures of *gem*-dinitro groupings have shown no strongly preferred torsional conformation, but the dihedral angle between the adjacent planar nitro groups tends to be near 90°; the six independent dihedral angles of this type found herein range from 72.5 to 89.4° (with both extremes found in 20). The most symmetric arrangement is seen (Figure 4, supplementary material) in 22, which contains a strict inversion center at the center of its chair-shaped cyclohexane ring and, in addition, an approximate mirror plane passing through C1, C4, and the four N atoms. The equatorial nitro groups are twisted less than 5° from this plane, while the axial nitro groups are essentially perpendicular to this plane. Two of the compounds analyzed, 19 and, to a minor extent, 20, show the "double images" (see Figure 2 in the supplementary material) characteristic of a molecular stacking fault (usually described as "disorder") of a type seen in crystals of acepleiadylene[15] and perfluorotricyclo[3.3.0.0^{2,6}]octane.[16] In the analysis of 19 and 20, several crystals, grown from more than one solvent, were examined. Results were identical, indicating that the disorder is truly characteristic of the material and was not due to a peculiar crystal-growth condition.

Experimental Section

Melting points were not corrected. NMR spectra were recorded in $CDCl_3$ and CD_3COCD_3 solutions at 200 and 300 MHz. FT-IR spectra were obtained either as KBr pellets or neat films on NaCl plates. Mass spectra were measured with a Finnigan MAT Model INCOS 50 GC–MS instrument. The procedure for the preparation compounds 4, 5, 8, 10, and 11 are given in the supplementary material.

2,2,5,5-Tetranitrobicyclo[2.2.1]heptane (18). To a solution of NaOH (0.35 g, 8.7 mmol) in water (10 mL) was added as a solid 5 (1.33 g, 7.1 mmol) at 20 °C under N_2. The mixture was stirred for 4 h, and a yellow solution was obtained. This solution was mixed with CH_2Cl_2 (25 mL), and the mixture was cooled to 0 °C. To this mixture was added solution of $NaNO_2$ (5 g, 72 mmol) in water (12 mL) followed by a solution of $K_3Fe(CN)_6$ (13 g, 40 mmol) in water (25 mL) over 30 min. The resulting reaction mixture was kept at 0 °C for 3 h, brought to rt, and stirred overnight. Subsequently, the mixture was poured into water and extracted with CH_2Cl_2 (2 × 25 mL). The CH_2Cl_2 layer was washed with water and saturated brine, dried ($MgSO_4$), and evaporated. Recrystallization from ethyl acetate yielded 1.63 g (83%) of white crystals: mp 194 °C; ^1H NMR (CD_3COCD_3) δ 3.87 (m, 2 H, bridged head H), 3.37 (dd, $J = 6$ and 17.1 Hz (gem), 2 H, endo, H_3, H_6), 2.90 (dm, $J = 17.1$ Hz (gem), 2 H, exo, H_3, H_6), 2.47 (m, 2 H, H_7); ^{13}C NMR (CD_3COCD_3) δ 124.4, 47.3, 39.4, 35.9; IR (KBr) 1590, 1445, 1372, 1319 cm^{-1}; MS (EI) *m/e* (rel intensity) 183 (M − 93, 2.19), 112 (16.62), 79 (70.92), 65 (99.56), 53 (49.78), 39 (100). Anal. Calcd for $C_7H_8N_4O_8$: C, 30.44; H, 2.92; N, 20.27. Found: C, 30.62; H, 2.89; N, 20.20. Density: 1.71 mg·mm^{-3}.

2,2-Dinitrobicyclo[2.2.1]heptane (19) was obtained similarly in 81% yield by the reaction of 8: mp 110 °C; ^1H NMR ($CDCl_3$) δ 3.35 (m, 1 H, bridged head, H_1), 2.90 (dd, $J = 3.6$, 15.4 Hz (gem), endo, H_3, 1 H), 2.52 (m, 1 H, bridged head, H_4), 2.28 (dm, $J = 15.4$ Hz (gem), 1 H, exo, H_3), 1.60–1.84 (m, 4 H, H_5, H_6), 1.10–1.40 (m, 2 H, H_7); ^{13}C NMR ($CDCl_3$) δ 126.2, 46.6, 41.6, 39.6, 36.0, 26.2, 23.4; IR (KBr) 1562, 1371 cm^{-1}; MS (EI) *m/e* (rel intensity) 140 (M − 46, 2.03), 109 (23), 91 (55.12), 81 (83.0), 66 (100), 53 (42.09), 39 (94.70). Anal. Calcd for $C_7H_130N_2O_4$: C, 45.16; H, 5.41; N, 15.05. Found: C, 45.46; H, 5.57; N, 15.02. Density: 1.45 mg·mm^{-3}.

3,3,7,7-Tetranitro-*cis*-bicyclo[3.3.0]octane (20). This procedure is the same as for 18 and furnished a mixture of tetranitro 20 and trinitro 21. Column chromatography and recrystallization of this mixture from chloroform gave 2.64 g (76%) of 20 as a colorless solid: mp 188 °C; ^1H NMR (CD_3COCD_3) δ 3.35 (br m, 2 H, H_1, H_5), 3.15 (m, 8 H, H_2, H_4, H_6, H_8); ^{13}C NMR (CD_3COCD_3) δ 127.7, 41.9, 40.8; IR (KBr) 1561, 1456, 1369, 1334 cm^{-1}; mass spectrum (EI) *m/e* (rel intensity) 198 (M − 92, 13.37), 168 (9.00), 103 (46.02), 91 (49.87), 77 (100), 65 (48.33). Anal. Calcd for $C_8H_{10}N_4O_8$: C, 33.11; H, 3.47; N, 19.31. Found: C, 33.02; H, 3.57; N, 19.13. Density: 1.63 mg·mm^{-3}.

1,1,4,4-Tetranitrocyclohexane (22). The compound was obtained similarly from 14[11] in 86% yield: mp 201 °C; ^1H NMR (CD_3COCD_3) δ 2.99–3.12 (m, 8 H, 4 CH_2); ^{13}C NMR (CD_3COCD_3) δ 117.5, 29.8, 29.2; IR (KBr) 1578, 1388 cm^{-1}; MS (EI) *m/e* (rel intensity) 171 (M − 93, 37.73), 95 (18.88), 77 (100), 67 (48.38), 53 (63.47), 39 (94.60). Anal. Calcd for $C_6H_8N_4O_8$: C, 27.28; H, 3.05; N, 21.21. Found: C, 27.67; H, 3.07; N, 20.85. Density: 1.72 mg·mm^{-3}.

Single-Crystal X-ray Diffraction Analyses of 18–20 and 22. Crystallographic data for four compounds are presented in the supplementary material. The diffraction experiments share several aspects. All were performed at the Naval Research Laboratory on one of two automated Siemans diffractometers equipped with incident-beam graphite monochromators. Unit cell parameters were calculated from a least-squares fit of the coordinates of 25 centered reflections. Three check reflections were collected after every 97 observations to check for deterioration or instability (not found in any of these compounds). All data were collected in the $\theta/2\theta$ scan mode, with scan width $[\theta(K_{\alpha 1}) - 0.5]$ to $[\theta(K_{\alpha 2}) + 0.5]°$. All structures were solved, using direct methods, and refined, using full-matrix least-squares methods, with the aid of the SHELXTL[17] system of programs.

Acknowledgment. Support of our work by the Office of Naval Research, Mechanics Division, is gratefully acknowledged.

Supplementary Material Available: Detailed procedures for the synthesis of compounds 4, 5, 8, 10, and 11, tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and ORTEP diagrams for 19, 20, and 22 (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[16] Karle, I. L.; Karle, J.; Owen, T. B.; Hoard, J. L. *Acta Crystallogr.* **1965**, *18*, 345.

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