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SYNTHESIS OF *exo*-5-AZIDONORBORNENE AND *exo*-2,*exo*-5-DIAZIDONORBORNENE

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Abstract: Polar addition of HN_3 to norbornadiene (**1**) affords *exo*-5-azidonorbornene (**2**, 70%). Subsequent azidomercuration-demercuration of **2**, performed by using *in situ* generated $Hg(N_3)_2$ followed by reductive demercuration, proceeds stereospecifically to afford *exo*-2,*exo*-5-diazidonorbornane (**5**, 68% yield).

Azidoalkanes, and particularly diazidoalkanes of the type $C_nH_m(N_3)_2$, are of intense current interest as an important class of energetic fuel additives. Thus, addition of compounds of this type to hydrocarbon fuel mixtures generally leads to increased energy output and to improved overall combustion efficiency.[1-3] As part of a program that is concerned with the development of new high energy, high density fuel systems,[4] we have investigated the synthesis of *exo*-5-azidonorbornene (**2**) and its subsequent conversion to *exo*-2,*exo*-5-diazidonorbornane (**5**).

Polar addition of the elements of HN_3 to alkenes is often performed by using an "azidomercuration-demercuration" sequence that employs *in situ* generated $Hg(N_3)_2$ followed by reductive demercuration.[5,6] This reaction sequence when applied to norbornene affords *exo*-2-azidonorbornene in 75% yield.[6] More recently, a procedure has been described that employs hypervalent iodine containing reagents to prepare vicinal diazides from alkenes.[7]

The method utilized in the present study to prepare **2** and **5** is summarized in Scheme 1. Thus, polar addition of hydrazoic acid to norbornadiene (**1**) affords **2** in good yield. The stereochemistry of the C(5)-N_3 bond in **2** was established via

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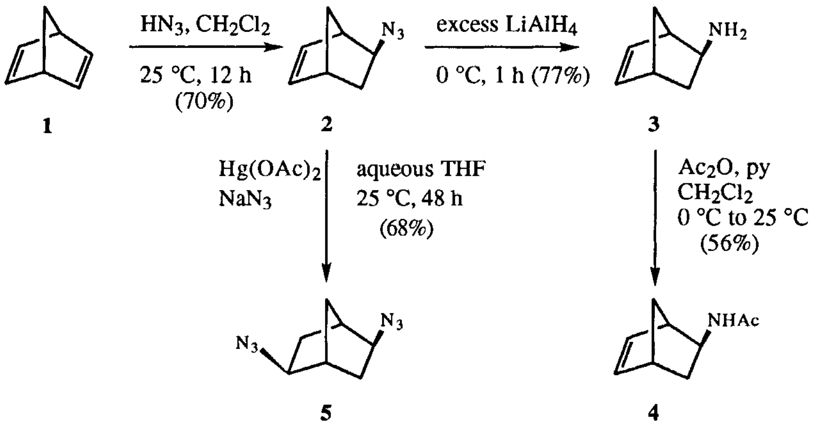
$LiAlH_4$ promoted reduction of azide **2** to the corresponding aminonorbornene, **3**. Compound **3** was characterized as the corresponding *N*-acetylamido derivative, **4**, the structure of which was established unequivocally via X-ray crystallographic methods.

Next, $Hg(OAc)_2$-NaN_3 was employed for *in situ* generation of $Hg(N_3)_2$.[6] This azide, when generated in the presence of **2**, afforded a single product, **5** (68% yield). The fact that this reaction proceeds stereospecifically to afford exclusively the *exo*-2,*exo*-5 diazido compound was established via NMR spectral analysis. Thus, the proton-noise decoupled ^{13}C NMR spectrum of **5** contains only four resonances; an attached proton test (APT) reveals the presence of two doublets and two triplets. Based upon these results, we conclude that **5** is twofold-symmetric.

Since only four signals are observed in the proton-noise decoupled ^{13}C NMR spectrum of **5**, we conclude that the twofold symmetry element in **5** must be a C_2 axis (rather than a mirror plane). Furthermore, since the chemical conversion of **2** into **4** established the *exo* stereochemistry of the C(5)-N_3 bond in **2**, it follows that the azido groups in **5** must possess the *exo*-2,exo-5 configuration, as shown in Scheme 1.

Scheme 1



Experimental Section

Melting points are uncorrected. Elemental microanalyses were performed by M-H-W Laboratories, Phoenix, AZ.

***exo*-5-Azidonorborn-2-ene (2).** To a solution of HN_3 in CH_2Cl_2 (20 mL of a 1.7 N solution, 34 mmol HN_3) at room temperature was added norbornadiene (**1**, 1.2 mL, 1.0 g, 11 mmol), and the resulting mixture was stirred overnight at room temperature. The reaction mixture was diluted with water (20 mL), and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed sequentially with 20% aqueous $NaHCO_3$ (25 mL), water (25 mL), and brine (25 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue, a yellow oil, was purified via flash chomatography on silica gel by eluting with hexane. Pure **2** (1.03 g, 70%) was thereby obtained as a colorless oil: bp 36-38 °C (8 torr). IR (film) 2960 (m), 2870 (w), 2094 (vs), 1460 (w), 1333 (w), 1254 (w), 1090 (w), 979 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.45 (dt, J = 12.1, 2.9 Hz, 1 H), 1.50–1.65 (m, 3 H), 2.90 (br s, 2 H), 3.48 (dd, J = 6.4, 3.1 Hz, 1 H), 5.98 (dd, J = 6.1, 3.0 Hz, 1 H), 6.21 (dd, J = 5.9, 2.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 33.54 (t), 41.02 (d), 45.91 (t), 47.57 (d), 61.47 (d), 133.3 (d), 140.4 (d). Neat **2** slowly polymerizes when allowed to stand overnight at room temperature. Thus, **2** was used in the next synthetic step immediately as obtained upon isolation from the chromatography column.

***exo*-5-Aminonorborn-2-ene (3).** A saturated solution of $LiAlH_4$ in dry Et_2O (20 mL, excess) was cooled to 0 °C via application of an external ice-water bath. To this cooled solution was added dropwise with stirring **2** (130 mg, 0.96 mmol). The resulting mixture was stirred at 0-3 °C for 1 h, at which time the external cold bath was removed and the reaction mixture was allowed to warm slowly to ambient temperature. Water (20 mL) was added dropwise to quench the reaction, and the resulting aqueous suspension was extracted with Et_2O (2 x 10 mL). The combined ether layers were washed with water (20 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with Et_2O. Pure **3** (81 mg, 77%) was thereby obtained as a colorless oil; IR (film) 3304 (m), 3055 (m), 2960 (vs), 2860 (s), 1639 (s), 1539 (s), 1444 (m), 1370 (m), 1328 (m), 1100 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.04 (dt, J = 11.8, 3.4 Hz, 1 H), 1.40–1.68 (m, 5 H), 2.49 (s, 1 H), 2.80 (s, 1 H), 2.89 (dd, J = 7.5, 2.6 Hz, 1 H), 6.06 (dd, J = 15.7, 5.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 37.03 (t), 41.23 (d), 44.86 (t), 50.86 (d), 51.93 (d), 135.1 (d), 138.1 (d). Compound **3** was further characterized via the corresponding acetamide, **4** (*vide infra*).

***exo*-5-*N*-Acetylamidonorborn-2-ene (4).** A solution of **3** (450 mg, 4.13 mmol) and pyridine (1.30 g, 16.5 mmol) in $CHCl_3$ (10 mL) was cooled to 0 °C via application of an external ice-water bath. To this cooled solution was added dropwise with stirring Ac_2O (440 mg, 4.3 mmol). The reaction mixture was stirred at 0 °C for 0.5 h after all of the Ac_2O had been added. The cold bath then was removed, and the reaction mixture was allowed to warm slowly to ambient temperature while stirring during 1 h. The resulting mixture was washed sequentially with saturated aqueous $NaHCO_3$ (20 mL) and water (10 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was recrystallized from $CHCl_3$-hexane, thereby affording pure **4** (350 mg, 56%) as colorless needles: mp 112-113 °C; IR (film) 3417 (m), 2954 (m), 1726 (vs), 1438 (m), 1338 (w), 1244 (m), 1169 (w), 1031 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.18 (dt, J = 12.3, 3.3 Hz, 1 H) 1.39-1.55 (m, 1 H), 1.65–1.80 (m, 2 H), 1.98 (s, 3 H), 2.79 (s, 1 H), 2.88 (s, 1 H), 3.76 (dt, J = 7.7, 2.6 Hz, 1 H), 5.62 (br s, 1 H), 6.10 (dd, J = 13.0, 5.7 Hz, 1 H), 6.12 (dd, J = 12.9, 5.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.53 (q), 35.29 (t), 40.92 (d), 45.95 (t), 47.85 (d), 49.94 (d), 134.7 (d), 138.6 (d), 169.7 (s). Anal. Calcd for $C_9H_{13}NO$: C, 71.49, H, 8.67. Found: C, 71.67; H, 8.67. The structure of **4** was established unequivocally via application of X-ray crystallographic methods (*vide infra*).

***exo*-2, *exo*-5 -Diazidonorbornane (5).** To solution of NaN_3 (1.40 g, 21.5 mmol) in 50% aqueous THF (25 mL) and $Hg(OAc)_2$ (2.0 g, 6.3 mmol) at room temperature was added dropwise with stirring a solution of **2** (700 mg, 5.2 mmol) in HN_3-CH_2Cl_2 solution (15 mL of a 1.7 N solution of HN_3 in CH_2Cl_2, 1.09 g, 25.5 mmol). The resulting mixture was stirred at room temperature for 48 h. To the reaction mixture was added 15% aqueous KOH (13 mL) followed by dropwise addition of a solution of $NaBH_4$ (500 mg, 13.5 mmol) in 15% aqueous KOH (13 mL). The resulting mixture was stirred for 2 h after the addition of the reducing agent had been completed. The reaction mixture then was extracted with Et_2O (3 x 20 mL). The combined ethereal extracts were washed with water (100 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo*. The residue, a yellow oil, was purified by column chromatography on silica gel by using hexane as eluent. The first chromatography fraction afforded unreacted **2** (190 mg, 21%). Subsequently, pure **5** (420 mg, 68%) was obtained as a colorless oil which decomposes explosively when heated above 200 °C; IR (film) 2953 (s),

Table 1. X-ray structure data for **4**.

Compound	**4**
Formula	$C_9H_{13}NO$
Size (mm)	.21 x .22 x .68
Space Group	P1
a (Å)	9.385 (2)
b (Å)	9.570 (3)
c (Å)	10.499 (1)
α (°)	89.59 (2)
β (°)	74.04 (1)
γ (°)	83.51 (2)
V (Å^3)	900.5 (3)
Z	4
D_c (g-cm^{-3})	1.116
μ (cm^{-1})	0.67
ω–2θ ($2\theta_{max}$)	44
Total refl.	2191
Unique refl.	2191
R_{int}	- -
$I \geq 3\sigma(I)$	599
Parameters	109
R, wR	0.127, 0.110
$(\Delta/\sigma)_{max}$	<0.01
ρ_{min}; ρ_{max}	0.30; -0.28

2096 (vs), 2088 (vs), 1340 (m), 1248 (s), 1042 (w), 969 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.45–1.65 (m, 6 H), 2.35-2.42 (m, 2 H), 3.46 (dd, *J* = 6.9, 3.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 32.10 (t), 34.37 (t), 41.15 (d), 63.00 (d). Anal. Calcd for $C_7H_{10}N_6$: C, 47.18, H, 5.66; N, 47.17. Found: C, 47.39; H, 5.75; N, 47.39.

X-ray Structural Analysis of 4. Data were collected on an Enraf-Nonius CAD-4 diffractometer by using the ω–2θ scan technique, Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Standard procedures used in our laboratory for this purpose have been described previously.[8] Pertinent X-ray data are given in Table 1.[9] Data were correected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods (i.e., SIR[10]), and the model was refined by using full-matrix least-squares techniques. Hydrogen atoms were included in the model in idealized positions [U(H) = 1.3 B_{eq}(C)]. All computations other than those specified were performed by using MolEN.[11] Scattering factors were taken from the usual sources.[12]

The poor crystal quality (in both morphology and scattering strength) are evident from the high residuals (Table 1). Both the low number of observed reflections and the large thermal parameters are indicative of some disorder within the crystal. However, this disorder could not be resolved on the basis of the X-ray data collected. Nevertheless, the data as obtained are sufficient to permit unequivocal assignment of the gross geometry of **4**.

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References

1. Lee, A.; Jiang, Y. J.; Zhu, D. L.; Law, C. K. *AIAA Journal* **1992**, *30*, 1298.

2. Lee, A.; Law, C. K.; Randolph, A. L. *Combustion and Flame* **1988**, *71*, 123.

3. Moriarty, R. M. "Alkyl Azides, Diazides, Haloazides and Bridged Polycyclic Diazides", *Report,* 1991, Order No. AD-A236 202, 34 pp. Avail. NTIS. From *Gov. Rep. Announce. Index (U. S.)* **1991**, *91* (19), Abstr. No. 151,679; see: *Chem. Abstr.* **1992**, *116*, 255,155k.

4. Marchand, A. P.; Deshpande, M. N.; Reddy, G. M.; Watson, W. H.; Nagl, A. *Preprints, ACS Division of Fuel Chemistry,* Papers Presented at the 198th ACS National Meeting, Miami Beach, FL, September 10-15, 1989; American Chemical Society: Washington, D. C.; 1989, pp. 946-954.

5. Sokolov, V. I.; Reutov, O. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, 1632; see: *Chem. Abstr.* **1968**, *68*, 49704a.

6. Heathcock, C. H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 134.

7. Moriarty, R. M.; Khosrowshahi, J. S. *Tetrahedron Lett.* **1986**, *27*, 2809.

8. Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.*, **1993**, *115*, 4971.

9. Tables of positional parameters and their estimated standard deviations, general displacement parameter expressions, bond distances, bond angles, and torsion angles for **4** are available upon request from the Director of the

Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CV2 1EW, U. K. Requests should be accompanied by the full literature citation for this article.

10. Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Crystallogr.*, 1989, **22**, 389.

11. *MolEN, An Interactive Structure Solution Program.* Enraf-Nonius: Delft, The Netherlands, 1990.

12. Cromer , D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Vol. IV, Kynoch Press:Birmingham, 1974, Table 2.

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