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3,4-DIAZABENZVALENE, THE AZOALKANE PRECURSOR TO TETRAHEDRANE. SYNTHESIS AND REACTIVITY.

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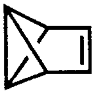
Abstract: The title diazene **1** has been synthesized and shown to decompose thermally to cyclobutadiene over a surprisingly small barrier.

Cyclic 1,2-diazenes (azoalkanes) have been shown to be of great value in the synthesis of reactive and strained molecules.[2] A variety of such structures has been prepared, but the tricyclic compound, 3,4-diazatricylo[3.1.0.0^{2,6}]hex-3-ene (**1**, 3,4-diazabenzvalene), has yet to be described. This molecule is of considerable interest, both in relation to its own inherent strain (*ca.* 77 kcal/mol, the value estimated for benzvalene,[3] **2**) and reactivity, and as a potential precursor to tetrahedrane[4] (**3**). We describe herein the synthesis and spectroscopic characterization of **1** and a study of its thermal decomposition and photochemical behavior above -150° C.

1



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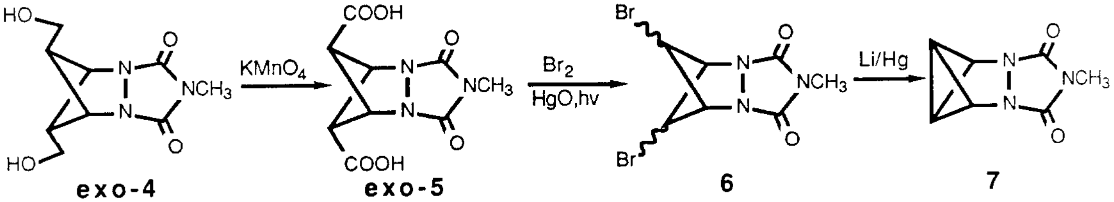
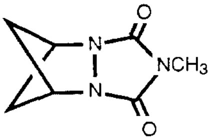
3

The synthesis of **1** begins with the diol, **4** which has been synthesized previously in this laboratory.[5] The diacid, **5**, was formed in 55% yield by oxidation with potassium permanganate in water. This was followed by a modified Hunsdiecker reaction.[6] Refluxing **5** in the presence of bromine and mercuric oxide with magnesium sulfate in methylene chloride while irradiating with a 67 watt incandescent light bulb afforded a mixture of three isomers of the dibromide, **6**, in 44% yield. The dibromide mixture was reductively coupled using 2% lithium amalgam in THF, giving **7** as a white, crystalline product in 70% yield. Urazoles **6** and **7** were purified using flash column chromatography on silica with a petroleum ether/ethyl acetate eluent system, and were fully characterized by ^{1}H and ^{13}C NMR, G.C./M.S., and, in the case of **7**, exact mass measurements.[7]



exo-4 **exo-5** **6** **7**

The ^1H NMR spectrum ($CDCl_3$) of **7** contains the characteristic *N*-methyl peak at δ 2.97 and two coupled triplets ($J = 1.71$ Hz) at δ 2.84 and δ 4.60 which were assigned to the bicyclobutane ring protons. The chemical shifts and small H – H coupling constants are similar to those of the related urazole[8] **8** and the analogous ketone,[9] **9**. The strained character of the bicyclobutane ring in **7** is reflected in the large ^{13}C-^1H coupling constants ($J = 223.02, 195.14$ Hz).



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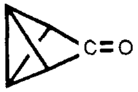

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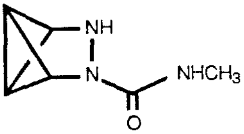

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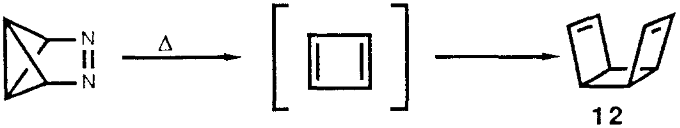
11

Hydrolysis of the urazole ring in **7** was accomplished with potassium hydroxide in isopropanol. The resulting semicarbazide, **10**, exhibited the characteristic *N*-methyl doublet and inequivalence of the C_2 and C_5 ring protons in the ^1H NMR spectrum. Oxidation of the semicarbazide to the diazene was accomplished using nickel peroxide[5] in methylene chloride/dimethyl ether at -78° C. Cold filtration of the heterogeneous mixture followed by distillation of the solvent at -78° C completed the synthesis of **1**.

The ^1H NMR spectrum of **1** in methylene chloride[10] exhibits two coupled triplets ($J = 1.22$ Hz) at δ 3.87 and δ 4.91. The signal at δ 4.91 corresponds to the C_2 and C_5 positions and may be compared to that found for the similar proton in **11** (δ 4.80).[8] The C_1 and C_6 protons show a similar shift to those of benzvalene (**2**) (δ 3.53).[3] The UV spectrum of **1** (diethyl ether) is highly structured with an intense 0,0 band (λ_{max} 310 nm) and two smaller peaks (304, 300). The spectral shape seen is similar to that for **11** and is consistent with the rigid structure of **1**.[8] The λ_{max} is at shorter wavelength than that seen for **11** and most other cyclic diazenes. This observation can be attributed to a more favorable interaction between the π^* orbital of the diazene and the a_2 orbital of the bicyclobutane system, which results in a higher energy n-π^* transition for diazabenzvalene when compared to **11**.[3,11]

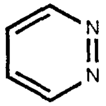
Diazene **1** decays thermally to produce syn-tricyclooctadiene, **12**, presumably via cyclobutadiene (eq 1).[10,12] At -60° C, this process has a half-life of 22 minutes, implying a surprisingly small barrier. For comparison, the closely related diazene **11** decomposes with $\log A = 15.5$, $E_a = 34.4$ kcal/mol, giving it a similar half-life at 133° C.[13] Thus, conversion of **11** to **1** lowers E_a by *ca.* 16 kcal/mol (assuming similar $\log A$ values). The thermal decomposition of **11** has been shown to proceed via one-bond cleavage, producing an intermediate diazenyl biradical.[13] Replacing the cyclobutane ring of **11** by a bicyclobutane to produce **1** does lead to a substantial increase in strain. However, this additional strain is also present in the deazetation transition state, if **1** and **11** decompose by the same mechanism. Using the best estimates for the strain energies of the compounds involved,[14] we conclude that the increase in strain on going from bicyclobutane to **1** is comparable to, or perhaps even *less* than that for going from cyclobutane to **11**. Thus, the release of strain upon C – N cleavage is not significantly greater in **1** *vs* **11**.



12

(1)

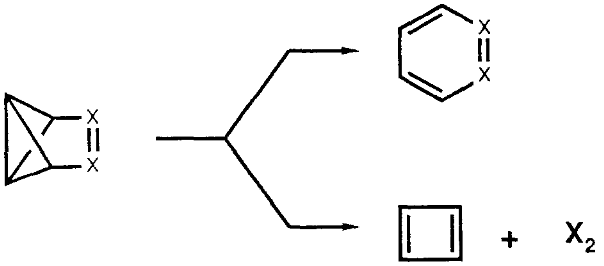
An alternative explanation of the difference between **1** and **11** would be a change in mechanism. Diazene **1** can undergo a direct, concerted, $[_{\sigma}2_s + _{\sigma}2_a + _{\sigma}2_a]$ conversion to cyclobutadiene plus N_2. There is ample precedent for dramatic rate accelerations of diazene decompositions upon introduction of a strained σ bond that can divert the reaction from a biradical path to a concerted six-electron process.[2a,17] While the orientation of the strained bond in **1** is different than in previous cases, the cyclic array shown seems quite feasible.



13

It is interesting to compare the thermal decompositions of benzvalene (**2**) and **1** (Scheme). Both can rearrange to an aromatic product (benzene or pyridazine (**13**)), in a reaction that is highly exothermic, but still possesses a substantial barrier.[3] Only for diazene **1**, however, is the fragmentation to cyclobutadiene exothermic. This is, of course, a consequence of the much greater thermodynamic stability of N_2 *vs* acetylene.

SCHEME



ΔH° (kcal/mol)	
X=CH	X=N
-67.5	-65.1
+67.0	-31.6

The photochemical behavior of **1** has been studied using several solvents at varying temperatures.[10] Photolysis of **1** at -196° C followed by ^1H NMR at -150° C (propane-d_8) or at -100° C (diethylether-d_{10}) resulted in cyclobutadiene dimer. Photolysis of **1** in a 1:3 mixture of $CDCl_2F$:$CDClF_2$[18] at -196° C followed by ^1H NMR at -150° produced both **13** and **12**, (*ca.* 1:1).

In all our studies of the chemistry of **1** to date, no direct evidence of tetrahedrane has been found. There have been several recent theoretical studies,[19] both ab initio and semi-empirical in nature, on the stability of tetrahedrane. These have concluded that tetrahedrane does lie in a potential energy well. If we assume that tetrahedrane is a product of the photolysis of **1**, and if we assume a *log A* of 15 for the thermal decomposition of tetrahedrane, then an upper limit of 10 kcal/mol is imposed upon this process by the -150° NMR experiments.

It appears that if tetrahedrane is a viable product from the photolysis of **1**, the characterization will depend on low temperature matrix isolation techniques. We are currently investigating the photolytic properties of **1** in inert gas matrices at 10 K, using FT-IR to characterize the resulting products.

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(7) **6**: ^{1}H NMR ($CDCl_3$) **exo,exo**; δ 3.05 (s, 3 H), 4.23 (t, 2 H, J = 1.71 Hz), 4.92 (t, 2 H, J = 1.71 Hz), **endo,exo**; δ 3.05 (s, 3 H), 4.25 (s, 1 H), 4.87 (d, 2 H, J = 1.71 Hz), 5.31 (t, 1 H, J = 1.71 Hz), **endo, endo**; δ 3.10 (s, 3 H), 4.15 (s, 2 H), 4.79 (s, 2 H); ^{13}C NMR ($CDCl_3$) **exo,exo**; δ 26.58, 39.87, 67.57, 158.11, **exo,endo**; 26.64, 47.49, 47.81, 68.76, 158.10, **endo,endo**; 26.64, 48.42, 67.75, 158.20; M.S., three M^+ peaks corresponding to the bromine isotope effect in a dibromide were found at *M*/e 323, 325, and 327 with ratios of 1.05:2.12:1.00 in a sample containing a mixture of the three isomers. **7**: Mp 116-116.5° C; ^{13}C NMR ($CDCl_3$) δ 7.51, 25.97, 52.35, 161.86; Exact mass calcd: 165.0538, found: 165.0539.

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(10) All ^{1}H NMR solutions contained varying amounts of unreacted and rearranged semicarbazide which could not be separated from **1**. However, the thermal behavior of **1** is unaffected by the impurities. Similarly, both the thermal and photochemical behavior of **1** are unchanged by the addition of 2,6-lutidine, indicating that acid catalysis is not involved.

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(14) Strain energies were calculated as follows: 77 kcal/mol as an upper limit for **1**, based on the observations of Kao[15] that polycyclic diazenes have strain energies that are slightly less than the analogous alkene (**2**, in this case); 47.3 kcal/mol for **11** calculated using the molecular mechanics model of Kao[15]; and Wiberg's[16] values for cyclobutane and bicyclobutane (26.5 and 63.9 kcal/mol, repectively).

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