

NEW HIGHLY STRAINED BRIDGEHEAD IMINES, 2-AZAADAMANT-1-ENE  
AND 4-AZAPROTOADAMANT-3-ENE

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**Summary** An azaanalog of adamantene, 2-azaadamant-1-ene (1) and 4-azaprotadamant-3-ene (7) were generated in the nonstatistical ratio via photolysis of 3-azidonoradamantane (2). The highly strained 1 and 7 could not be isolable but were trapped by MeOH. Acidolysis of 2 was also reported, and discussed in comparison with the photolysis.

The synthesis and chemistry of anti-Bredt's olefins have received considerable attention over the years<sup>1</sup>. In particular, adamantene as an extremely distorted bridgehead olefin has been extensively investigated<sup>2</sup>. However, there are only a few studies on bridgehead imines which are expected to be highly reactive also because of the structural characteristics similar to bridgehead olefins. 2-Azaadamant-1-ene (1), an azaanalog of adamantene has not been recorded yet to the best of our knowledge<sup>3</sup>. We report here facile generation of 1 and 4-azaprotadamant-3-ene (7)<sup>4</sup> as highly strained new bridgehead imines by photolysis of 3-azidonoradamantane (2) (Scheme I).

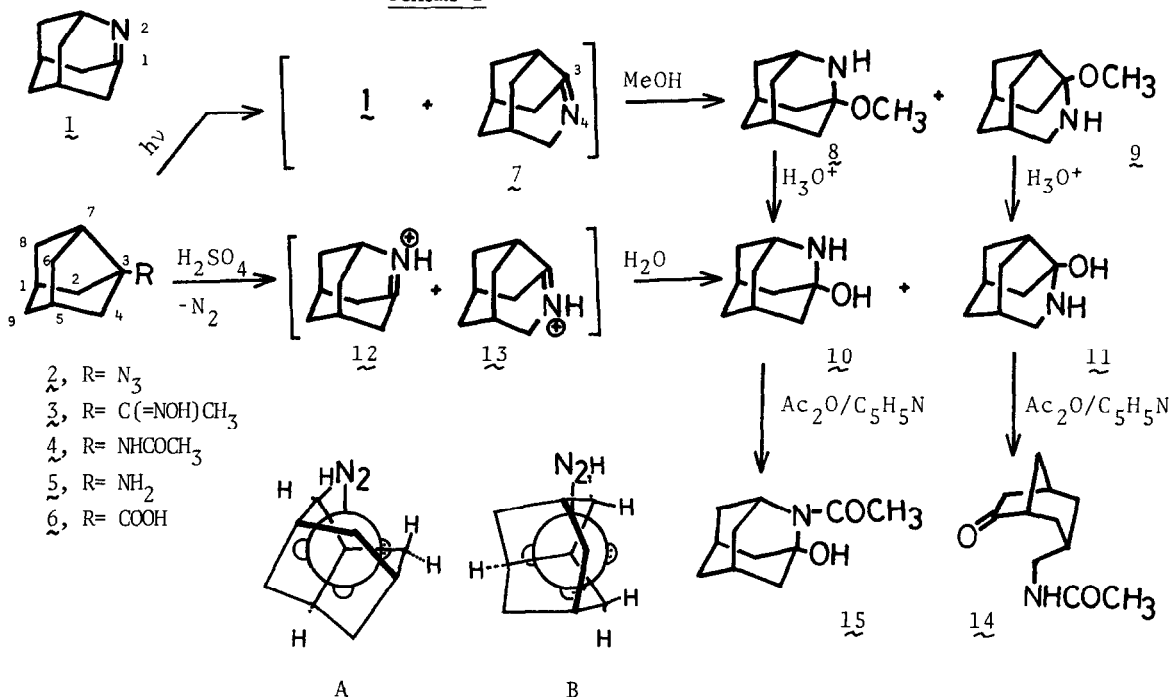
The required azide 2 was readily obtained from the known 3-noradamantyl methyl ketone oxime (3)<sup>5</sup> or 3-noradamantanecarboxylic acid (6)<sup>5</sup> as follows. Treatment of 3 with tosyl chloride-pyridine gave amide 4 (70%), mp 131-133 °C,<sup>6</sup> which was converted to amine 5, mp 173-175 °C, on hydrolysis (78%). The amine 5 was also obtained from 6 via Curtius degradation. Treatment of 5 with tosyl azide and sodium hydride in THF (20-25 °C, 48 h) gave the azide 2 as a colorless liquid, IR(neat) 2105 cm<sup>-1</sup> (91%).

Direct photolysis of 2 in MeOH (27.0 mM solution, 100 w high pressure mercury lamp, Vycor filter, room temperature, 2.5 h) yielded two methoxyamines 8 and 9 (ca. 1:00:1:17 ratio on <sup>1</sup>H NMR analysis), which were isolated in 38 and 43% yields, respectively after chromatography on

alumina Compound 8 had characteristic two singlets at  $\delta$  3.40 (1H) and 3.25 (2H) due to bridgehead protons in  $^1\text{H}$  NMR spectrum, and seven carbon resonances [ $\delta$  82.6(s), 50.3(d), 47.6(q), 40.9(t), 36.4(t), 36.1(t), 29.9(d)] in  $^{13}\text{C}$  NMR spectrum,<sup>7</sup> supporting the shown structure 8. The second product 9 revealed an ABX type multiplet assignable to the methylene protons adjacent to NH at  $\delta$  2.6-3.1 in  $^1\text{H}$  NMR spectrum, and ten lines in  $^{13}\text{C}$  NMR spectrum,<sup>8</sup> which were compatible with the given azaprotadamantane structure 9. The formation of 8 and 9 suggests strongly that highly strained 1 and 7 were generated by photolysis of 2 and they were trapped spontaneously by MeOH<sup>9,10</sup>. The observed product ratio of 8 and 9 (1.00:1.13 based on isolated amounts) is quite noteworthy because virtually statistical ring-expansions on the azide N (i.e., in 1:2 ratio) have been reported in the photolysis of unsymmetrical bridgehead azides such as 1-azidonorbornane<sup>3a</sup> and 3-azidohomoadamantane.<sup>3d,11</sup> Recently, Kyba and Abramovitch<sup>12</sup> rationalized the nonstatistical photomigrations observed for s- and t-alkyl azides by the conformational factor of excited azido group rather than the intrinsic migratory aptitude of the alkyls. However, there seems little energy differences between the relevant conformers A (preferred for  $\text{C}_{3-2}$  bond migration based on the Abramovitch-Kyba model)<sup>13</sup> and B (preferred for  $\text{C}_{3-7}$  bond shift) from a molecular model study on 2. The preferential  $\text{C}_{3-7}$  bond photomigration of 2 may be ascribable to the total strain energy difference between 1 and 7.<sup>14,15</sup> It is apropos here to compare the migratory aptitude of the  $\text{C}_{3-7}$  and  $\text{C}_{3-2}$  bonds on a cationic nitrogen<sup>16</sup>. Thus, 2 was decomposed with conc  $\text{H}_2\text{SO}_4$  to yield acidolysis products 10 (58%) and 11 (20%). Compound 10 was identified as 1-hydroxy-2-azaadamantane by comparison with an authentic sample.<sup>17</sup> The structure of 11 was established as shown on the basis of spectral and the following chemical evidences. Acid hydrolysis of 8 and 9 gave also 10 and 11. Treatment of 10 with  $\text{Ac}_2\text{O}$ -pyridine afforded a ring-retained N-acetyl derivative 15 as an oil (79%), while the same acetylation of 11 gave a ring opened acetylaminoketone 14, mp 95-97 °C (52%).

The observed selectivity (1.00:0.34) between the  $\text{C}_{3-7}$  bond migration on the cationic N to give 12 and the  $\text{C}_{3-2}$  bond migration to give 13 is ca. 3 times higher than that (1.00:1.13) in the photomigration. On the other hand, 3-azidohomoadamantane is found to give only the statistical ring enlargement even in the acidolysis.<sup>18</sup> Hence, the present preferential formation of 12 to 13 is most reasonably attributable to the relative strain energies which are also the main factor in cationic rearrangements like adamantane rearrangements<sup>19,20</sup>. The same factor might control the migratory aptitudes of the  $\text{C}_{3-7}$  and  $\text{C}_{3-2}$  bonds in the photo-

Scheme I



rearrangement of 2 also in view of the initiation by an electron deficient orbital on N<sub>α</sub> of the azido group<sup>12,13</sup> but less effectively because of the excited state nature of the reaction.<sup>21</sup>

In summary, we have found that 2-azaadamant-1-ene (1) and 4-azaprotoadamant-3-ene (7) or their equivalents were readily generative in a unique ratio by photorearrangement of 2. Further studies are now in progress to detail the properties of 1 and related bridgehead imines.

#### References and Footnotes

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- 3) Reported photorearrangements of bridgehead azides to the bridgehead imines heretofore involve 1-azidonorbornane (a), 1-azidoadamantane (b), 9-azidotriptycene (c), 3-azidohomoadamantane (d), and 1-azidobicyclo[3 2 1]octane (e) (a) Reed, J O , Lwowski, W

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- 4) IUPAC nomenclature of 1 and 2 is 2-azatricyclo[3.3.1.1<sup>3,7</sup>]dec-1-ene and 4-azatricyclo[4.3.1.0<sup>3,8</sup>]dec-3-ene, respectively
  - 5) Black, R. M., Gill, G. B. J. Chem. Soc., Chem. Commun. 1970, 972
  - 6) Satisfactory analytical and spectral data were obtained for all new compounds reported
  - 7) All NMR data were measured in CDCl<sub>3</sub> using Me<sub>4</sub>Si as internal standard at 60 MHz for <sup>1</sup>H and 15.04 MHz for <sup>13</sup>C
  - 8) <sup>13</sup>C NMR δ 96.6(s), 49.3(d), 48.2(q), 42.4(d), 41.2(t), 39.2(t), 38.3(t), 34.7(d), 32.4(t), 27.8(d)
  - 9) Without appropriate nucleophiles like MeOH, 1 and 2 seem to polymerize affording only an intractable material as found by photolysis of 2 in cyclohexane.
  - 10) This is our tentative conclusion because defined products were obtained only in MeOH
  - 11) However, a regiospecific photo- and thermal ring expansion of 1-azidobicyclo[3.2.1]octane has been reported very recently (ref 3e). There seems a possibility that the isomeric bridgehead imines were produced as well but they were not trapped by MeOH
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  - 18) The acidolysis product was analyzed by GLC after reduction to the corresponding amines, 4-azatricyclo[5.3.1.1<sup>3,9</sup>]dodecane and 5-azatricyclo[4.4.1.1<sup>3,9</sup>]dodecane. Our unpublished results. Cf. also ref 3d
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  - 21) For mechanistic details, further investigations are clearly required

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