minum eluted with *n*-hexane–ethyl acetate (1:1) to give a colorless oil of **27** (54 mg, 90%): IR ν_{max} (neat) 1635 cm^{-1}; NMR δ (CCl_4) 1.25 (d, 3 H, J = 6 Hz, CH_3), 1.40–2.20 (m, 2 H), 2.20–2.70 (m, 1 H), 3.00–3.40 (br t, 2 H, NCH_2), 4.45 (s, 2 H, $PhCH_2N$), 7.15 (s, 5 H, aromatic); mass spectrum, m/e 203 (M^+), 198 ($M^+ - CH_3$), 112 ($M^+ - CH_2Ph$), 91; high-resolution mass spectrum calcd for $C_{13}H_{17}NO$, m/e 203.1306; found, 203.1306.

2-Methyl-3-oxohexahydropyrrolizine (54c). A solution of **52c** and **53c** (49 mg) and PtO_2 (2.5 mg) in EtOH (12 mL) was stirred under an atmosphere of hydrogen at room temperature for 3 h. Solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel eluted with ethyl acetate to give a colorless oil of **54c** (50 mg, quantitative): IR ν_{max} (neat) 1660 cm^{-1}; NMR δ ($CDCl_3$) 1.18 (d, J = 7 Hz, 3 H, CH_3), 1.1–1.7 (m, 2 H), 1.7–2.3 (m, 4 H), 2.3–3.3 (m, 2 H), 3.3–4.0 (m, 2 H).

5-Oxo-6-methyloctahydroindolizine (54e). From **52e**: A solution of **52e** (12.0 mg, 0.080 mmol) and PtO_2 (2 mg) in EtOH (10 mL) was stirred under an atmosphere of hydrogen at room temperature overnight. After the catalyst was filtered off, the solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel eluted with ethyl acetate to give a colorless oil of **54e** (10.7 mg, 88%): IR ν_{max} (neat) 1620 cm^{-1}; NMR δ ($CDCl_3$) 1.35–2.63 (m, 10 H), 1.15 (d, J = 7 Hz, CH_3), 3.14–3.72 (m, 2 H); mass spectrum, m/e 153 (M^+). From **53e**: A solution of **53e** (12.3 mg, 0.815 mmol) and PtO_2 (2 mg) in EtOH (10 mL) was hydrogenated in the same manner as **52e** to give **54e** (11.2 mg, 86.0%).

Registry No. **6**, 6278-91-7; **6** hydrazone, 86953-35-7; **7a**, 86968-38-9; **7b**, 86953-36-8; **11a**, 86953-37-9; **11b**, 86953-38-0; **12**, 86953-39-1; **13**, 86953-40-4; **13** hydrazone, 86953-41-5; **14a**, 86953-42-6; **14b**, 86953-43-7; **15a**, 86953-44-8; **15b**, 86953-45-9; **16**, 86953-46-0; **17**, 27610-96-4; **18**, 86953-47-1; **19**, 35804-44-5; **20**, 86953-48-2; **22a**, 64180-78-5; **22b**, 86953-49-3; **22c**, 86953-50-6; **22d**, 86953-51-7; **22e**, 86953-52-8; **22e** imine derivative, 86953-53-9; **23**, 50775-03-6; **24**, 53626-84-9; **25a**, 42023-19-8; **25b**, 50586-10-2; **25c**, 86953-54-0; **25d**, 52961-97-4; **25e**, 86953-55-1; **26a**, 72649-02-6; **26b**, 86953-56-2; **26d**, 86953-57-3; **26e**, 86953-58-4; **27**, 37672-46-1; **29**, 86953-59-5; **30**, 64841-39-0; **30** hydrazone, 86953-60-8; **31a**, 86953-61-9; **31b**, 86953-62-0; **32a**, 86953-63-1; **32b**, 86953-64-2; **33**, 86953-65-3; **34**, 86953-66-4; **35**, 86953-67-5; **36**, 86953-68-6; **37**, 86953-69-7; **38a**, 86953-71-1; **38b**, 86953-72-2; **39a**, 86953-73-3; **39b**, 86953-74-4; **40**, 86953-75-5; **41**, 86953-76-6; **42**, 86953-77-7; **43**, 86953-78-8; **44a**, 4030-18-6; **44b**, 56475-80-0; **44c**, 86953-79-9; **44d**, 75844-69-8; **37** hydrazone, 86953-70-0; **45a**, 86968-39-0; **45b**, 86953-80-2; **45c**, 84766-91-6; **45d**, 86953-81-3; **46** (Y = OEt), 141-97-9; **46** (Y = CH_3), 123-54-6; **47a**, 86953-82-4; **47a'**, 86953-83-5; **47b**, 86953-84-6; **47b'**, 76460-90-7; **47c**, 86953-85-7; **47c'**, 86953-86-8; **47d**, 86953-87-9; **48**, 86953-88-0; **49c**, 86953-89-1; **49c** hydrazone, 86953-90-4; **49d**, 63459-12-1; **49d** hydrazone, 86953-91-5; **49e**, 86953-92-6; **49e** hydrazone, 86968-40-3; **50c**, 86953-93-7; **50d**, 86953-94-8; **50e**, 86953-95-9; **51c**, 86953-96-0; **51d**, 86953-97-1; **51e**, 86953-98-2; **52c**, 86953-99-3; **52d**, 86954-00-9; **52e**, 40163-21-1; **53c**, 86954-01-0; **53e**, 86954-02-1; **54c**, 86954-03-2; **54e**, 86954-04-3; **55**, 1148-11-4; **56**, 86954-05-4; **57**, 86954-06-5; **58**, 86954-07-6; benzylamine, 100-46-9; methyl vinyl ketone, 78-94-4; benzyloxycarbonyl chloride, 501-53-1; diethyl malonate, 105-53-3; 2,3-dibromopropene, 513-31-5; *N*-benzyl-4-bromo-4-pentenamide, 86754-08-7; acetylacetone, 123-54-6; 1-pyrrolidyl-1-cyclohexene, 1125-99-1; 3-bromopropyl 2-tetrahydropyranyl ether, 33821-94-2; 3-bromopropanol, 627-18-9; dihydropyran, 110-87-2; 3-aminopropanol, 156-87-6; 3-aminopropyl 2-tetrahydropyranyl ether, 75744-51-3; benzyl bromide, 100-39-0; 3-(benzylamino)propyl 2-tetrahydropyranyl ether, 86954-09-8.

Supplementary Material Available: Detailed experimental procedure of electrochemical oxidation of *N*-acyl cyclic amine **44** and condensation reaction of **45** with active methylene compound **46**, iodo-oxidation of hydrazone, and palladium-catalyzed carbonylation of vinyl halide (10 pages). Ordering information is given on any current masthead page.

Photolytic Generation of Anti-Bredt Imines from 1-Azidobicyclo[2.2.2]octane, 1-Azidobicyclo[3.3.1]nonane, and 3-Azidonoradamantane[1]

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Received January 24, 1983

Photolysis of 1-azidobicyclo[2.2.2]octane (**18**), 1-azidobicyclo[3.3.1]nonane (**24**), and 3-azidonoradamantane (**37**) generated the corresponding bridgehead imines **12a**, **13**, **14**, **15**, and **16**, respectively. These bridgehead imines were trapped spontaneously with solvent methanol except for unreactive **14**, which was reduced with $NaBH_4$ to afford the corresponding azabicycle **28**. Hydrocyanation succeeded with imines **12a** and **13** to afford amino nitriles **21** and **30**, respectively, which were converted to novel iminohydantoins **22** and **32**. In the formation of methoxyamines **20**, **26**, **39**, and **40**, the intermediacy of bridgehead imines **12a**, **13**, **15**, and **16** was proved by photolysis of the azides at 77 K in a hydrocarbon matrix, followed by treatment with MeOH at 195 K to afford the methoxyamines. The reactivity of the bridgehead imines is discussed on the basis of Wiseman's stability criterion for bridgehead olefins. The selective ring expansion of unsymmetrical bridgehead azides **24** and **37** on photolysis is also discussed.

The synthesis and chemistry of anti-Bredt olefins have received considerable attention.[2] Adamantene, an extremely distorted bridgehead olefin, has been investigated extensively.[3] However, there are few studies on bridge-

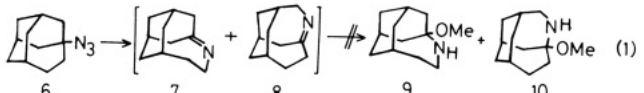
(1) Presented in part at the 4th International Conference on Organic Synthesis (IUPAC), Tokyo, Aug 22–27, 1982; Abstract C-I-7103. Synthesis of Adamantane Derivatives. 64. Part 63: Sasaki, T.; Eguchi, S.; Toi, N.; Okano, T.; Furukawa, Y. *J. Chem. Soc., Perkin Trans. 1*, in press.

(2) For recent reviews see: (a) Shea, K. J. *Tetrahedron* **1980**, *36*, 1683. (b) Becker, K. B. *Ibid.* **1980**, *36*, 1717. (c) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978.

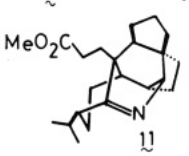
0022-3263/83/1948-4067$01.50/0

head imines, which are expected to be highly reactive also because of structural similarities to carbocyclic bridgehead olefins. Although a route to bridgehead imines via photolytic decomposition of bridgehead azides is known, systematic investigation of the generation and reactivity of bridgehead imines seems to be lacking. Bridgehead imines **1**–**5**, generated from the corresponding bridgehead

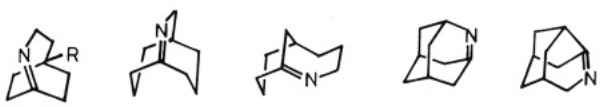
azides, are known to be reactive enough to be trapped with methanol.[4] On the other hand, bridgehead imines **7** and **8**, generated from 3-azidohomoadamantane (**6**), have been shown to be not reactive enough to be trapped with methanol (eq 1).[5] Furthermore, the imine **11** derived from



(1)



methyl homosecodaphniphyllate is known as an unusually stable bridgehead imine involving the 2-azabicyclo[3.3.1]non-1-ene system.[6] In this paper, we report generation of new bridgehead imines **12a**[7] and **13**–**16** via

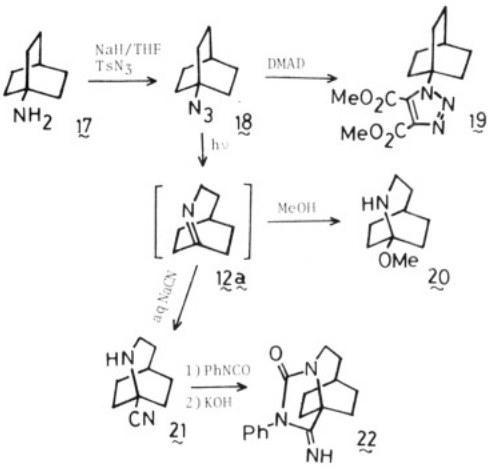


photolysis of bridgehead azides **18**, **24**, and **37**.[8]

Results

Synthesis of Bridgehead Azides. 1-Azidobicyclo[2.2.2]octane (**18**) was prepared in 83% yield from the known amine **17**[9] by treatment with *p*-tosyl azide and sodium hydride according to Quast and Eckert.[4b] The azide **24** was obtained from the corresponding alcohol **23**

Scheme I



with NaN_3–57% H_2SO_4 as previously reported.[10] The Beckmann rearrangement of 3-noradamantyl methyl ketoxime (**33**)[11] with *p*-tosyl chloride–pyridine gave selectively acetamide **34**, which was converted to amine **35** by acidic hydrolysis. The amine **35** was also obtained from carboxylic acid **36**[11] by the Curtius degradation. 3-Azidonoradamantane (**37**) was obtained in 92% yield from the amine **35** on treatment with *p*-tosyl azide–sodium hydride. Azides **18**, **24**, and **37** were all thermally stable, volatile oils with strong IR absorptions around 2100 cm^{-1}. They gave the corresponding 1,3-dipolar cycloadducts **19**, **25**, and **38**, respectively, in good yields on heating with dimethyl acetylenedicarboxylate at 100–120 °C (Schemes I–III).

Photolysis of Bicyclic Bridgehead Azides 18 and 24. Direct photolysis of the symmetrical azide **18** in methanol with a high-pressure mercury lamp through a Vycor filter yielded methoxyamine **20** in 90% yield. The structure was supported by analytical and spectral data. Similar results have been reported with the 4-methyl derivative by Quast and Seiferling.[7] Photolysis of **18** in an aqueous NaCN–*n*-hexane two-phase system with Adogen 464 as a phase-transfer catalyst afforded amino nitrile **21** (23%), which was converted to an iminohydantoin derivative **22** on treatment with phenyl isocyanate and alkali (Scheme I).[12] Photolysis of **18** in cyclohexane gave only uncharacterized polymeric products. These results suggest the formation of the highly reactive bridgehead imine **12a** on photodecomposition of **18** as postulated by Quast and co-workers on similar ring systems[4c,7] (see also the results of low-temperature photolysis).

Photolysis of the unsymmetrical bridgehead azide **24** in methanol yielded an oily product that exhibited IR absorptions at 3350 (NH), 1710 (C=O), and 1658 (C=N) cm^{-1} and characteristic ^1H NMR signals at δ 3.21 (s, OMe) and 2.91 (d, J = 4.0 Hz, NCH_2CH) in approximately 3:2 ratio. Purification by chromatography (neutral alumina) afforded only methoxy amine **26** in 18% yield, which had ^1H NMR signals also at δ 3.21 (s) and 2.91 (d) but no strong IR absorptions in the carbonyl region. These results suggest that the bridgehead imines **13** and **14** were produced by the photolysis of **24**, and only **13** was reactive enough to be trapped with methanol; **14** was not reactive enough to be trapped with methanol to give **27**, and survived. In order to confirm the generation of the imine **14**, the photolysis of **24** was carried out in the presence of

(3) (a) Lenoir, D. *Tetrahedron Lett.* **1972**, 4049. (b) Lenoir, D.; Firl, J. *Justus Liebigs Ann. Chem.* **1974**, 1467. (c) Alberts, A. H.; Strating, J.; Wynberg, H. *Tetrahedron Lett.* **1973**, 3047. (d) Gano, J. E.; Eizenberg, L. *J. Am. Chem. Soc.* **1973**, *95*, 972. (e) Burns, W.; McKervey, M. A. *J. Chem. Soc., Chem. Commun.* **1974**, 858. (f) Adams, B. L.; Kovacic, P. *J. Am. Chem. Soc.* **1974**, *96*, 7014. (g) Burns, W.; Grant, D.; McKervey, M. A.; Step, G. *J. Chem. Soc., Perkin Trans. 1* 1976, 234. (h) Martella, D. J.; Jones, M., Jr.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1978**, *100*, 2896. (i) Schwartz, H.; Reetz, M. T.; Maier, W. F.; Wesdemiotis, C.; Chatziiosifidis, I.; Schilling, M. *Angew. Chem.* **1979**, *91*, 1019. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 952. (j) Cadogan, J. I. G.; Leardini, R. *J. Chem. Soc., Chem. Commun.* **1979**, 783. (k) Conlin, R. T.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.* **1979**, *101*, 7637.

(4) (a) Reed, J. O.; Lwowski, W. *J. Org. Chem.* **1971**, *36*, 2864. (b) Quast, H.; Eckert, P. *Justus Liebigs Ann. Chem.* **1974**, 1727. (c) Quast, H.; Eckert, P. *Angew. Chem.* **1976**, *88*, 150; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 168. (d) Becker, K. B.; Gabutti, C. A. *Tetrahedron Lett.* **1982**, *23*, 1883. (e) Lwowski, W. "Reactive Intermediates"; Jones, M., Jr., Moss, R. A., Eds.; Wiley-Interscience: New York, 1978; Vol. 1, p 200.

(5) Sasaki, T.; Eguchi, S.; Hattori, S.; Okano, T. *J. Chem. Soc., Chem. Commun.* **1981**, 1193.

(6) Toda, Y.; Hirata, Y.; Yamamura, S. *J. Chem. Soc., Chem. Commun.* **1970**, 1597. Toda, Y.; Hirata, Y.; Yamamura, S. *Tetrahedron* **1972**, *28*, 1477.

(7) Preparation, photolysis, and thermolysis of **12b** have been reported: Quast, H.; Seiferling, B. *Justus Liebigs Ann. Chem.* **1982**, 1553.

(8) Preliminary accounts of photolysis and acidolysis of **37** have been published: Sasaki, T.; Eguchi, S.; Okano, T. *Tetrahedron Lett.* **1982**, *23*, 4969.

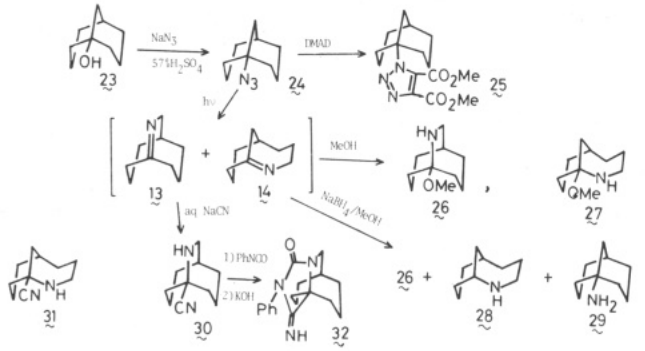
(9) Chae, W.-K.; Baughman, S. A.; Engel, P. S.; Bruch, M.; Özmeral, C.; Silagyi, S.; Timberlake, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 4824.

(10) Sasaki, T.; Eguchi, S.; Katada, T.; Hiroaki, O. *J. Org. Chem.* **1977**, *42*, 3741.

(11) Black, R. M.; Gill, G. B. *J. Chem. Soc., Chem. Commun.* **1970**, 972.

(12) Sasaki, T.; Eguchi, S.; Okano, T. *J. Org. Chem.* **1981**, *46*, 4474.

Scheme II

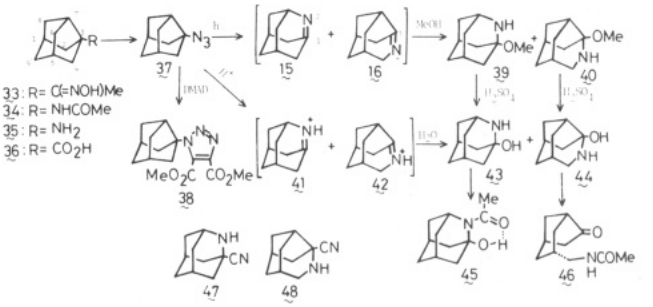


various amounts of $NaBH_4$ in methanol. The products in the presence of 5.0 molar equiv of $NaBH_4$ were the methoxy amine **26** (26%), 1-aminobicyclo[3.3.1]nonane (**29**) (5%), and 2-azabicyclo[4.3.1]decane (**28**) (40%) as the reduction product of the bridgehead imine **14**. Larger amounts of $NaBH_4$ resulted in increased formation of the bridgehead amine **29**.[10,13] Thus, in the presence of 14.5 molar equiv of $NaBH_4$, the products were **26** (19%), **29** (28%), and **28** (19%), and in the presence of 55.8 mol of $NaBH_4$, only the bridgehead amine **29** was isolated in 73% yield. The structure of **28** was supported by analysis and spectral data. The appearance of nine lines in the ^{13}C NMR spectrum was compatible with the unsymmetrical azabicyclic skeleton. The photolysis of **24** in an aqueous NaCN–*n*-hexane two-phase system gave an aminonitrile, **30**, but the isomeric amino nitrile **31** could not be detected. These results indicate that photolysis of **24** gave the bridgehead imines **13** and **14** in approximately a 1:2 ratio but either **14** did not react with cyanide anion or the corresponding amino nitrile **31** was too unstable to detect. The amino nitrile **30** was converted to iminohydantoin **32** with phenyl isocyanate and alkali (Scheme II).

Photolysis and Acidolysis of 3-Azidonoradamantane (37). Direct photolysis of 3-azidonoradamantane (**37**) in methanol at room temperature yielded a mixture of methoxyamines **39** and **40**, which was purified by chromatography on neutral alumina to afford **39** and **40** in 35% yields, respectively. Compound **39** exhibited two ^1H NMR singlets at δ 3.40 (1 H) and 2.25 (2 H)[14] due to the bridgehead protons, and seven carbon resonances in the ^{13}C NMR spectrum, supporting the symmetrical 2-azaadamantane structure. Compound **40** revealed an ABX-type multiplet at δ 2.6–3.1 (2 H) assignable to the methylene protons adjacent to NH in the ^1H NMR spectrum and 10 resonances in the ^{13}C NMR spectrum, which were compatible with the given 4-azaprotoadamantane structure **40**. The structures of **39** and **40** were also supported by acidic hydrolysis to the hydroxy derivatives **43** and **44**, respectively, which were the acidolysis products of **37**.

The azide **37** on treatment with concentrated sulfuric acid afforded the hydroxy amines **43** and **44** in 57% and 20% yields, respectively. Compound **43** was identified as 1-hydroxy-2-azaadamantane by comparison with an authentic sample.[15] The structure of **44** was established on the basis of spectral data and the following chemical evidence. Treatment of **43** with acetic anhydride–pyridine gave a ring-retained *N*-acetyl-2-azaadamantan-1-ol (**45**)

Scheme III



(79%), while the same acetylation of **44** afforded a ring-opened *N*-acetylamino ketone, **46** (52%).[16] This different behavior of **43** and **44** in acetylation supports the structures of the photolysis and acidolysis products of **37** (Scheme III). The photolysis of **37** in an aqueous NaCN–*n*-hexane two-phase system afforded only an intractable polymeric mixture; the expected amino nitriles **47** and **48** could not be isolated. These results suggest that highly strained bridgehead imines **15** and **16** were generated from **37** on photolysis and could be trapped by solvent MeOH, but in aqueous NaCN–*n*-hexane they decomposed before the attack of CN^- even under phase-transfer conditions.

Low-Temperature Photolysis of 18, 24, and 37. The isolation of methoxy amines **20**, **26**, **39**, and **40** from the photolysis of azides **18**, **24**, and **37** in MeOH is not a rigorous proof of the formation of the intermediate bridgehead imines **12a**, **13**, **15**, and **16**; the formation of methoxyamines directly from photoactivated bridgehead azides has been suggested by Reed and Lwowski in their work on the photo ring expansion of 1-azidonorbornane.[4a,e] Accordingly, we investigated the photolysis of the azides in a solid hydrocarbon matrix at low temperature in an attempt to establish the initial formation of the bridgehead imines. Photolysis of azide **18** in a matrix of isopentane–3-methylpentane at 77 K for 50 min, followed by treatment with MeOH–Et_2O at 195 K and workup at room temperature afforded methoxy amine **20** (53% yield based on unrecovered azide). Similar treatment of **24** gave a mixture of methoxy amine **26** (18%), imine **14** (52%), and unreacted azide **24** (30%), determined by ^1H NMR and GLC analyses. Similar treatment of azide **37** gave a mixture containing **39**, **40**, **37**, and polymeric materials in approximately 14:19:30:37 ratio (^1H NMR, IR, GLC, and TLC analyses). These results establish the formation of bridgehead imines **12a** and **13–16** by photolysis of the corresponding azides **18**, **24**, and **37**, respectively,[17] and that these bridgehead imines survive at 195 K to react with MeOH to afford the corresponding methoxy amines, except for imine **14**, which is not reactive toward MeOH even at room temperature.

Discussion

Reactivity of Bridgehead Imines. Maier and Schleyer have correlated the stability and reactivity of bridgehead olefins with the OS (olefin strain energy) values evaluated by using Allinger's MM1 empirical force field program.[18] This approach supports Wiseman's rule that all observable bridgehead olefins have the *E* double-bond moiety in an 8-membered or larger ring[19] and has allowed classification

(13) For phase-transfer catalyzed reduction of alkylazides see: Rolla, F. *J. Org. Chem.* **1982**, *47*, 4327.

(14) The value 3.25 (2 H) reported in ref 8 should read 2.25 (2 H) as given.

(15) (a) Stetter, H.; Tacke, P.; Gärtner, J. *Chem. Ber.* **1964**, *97*, 3480. (b) Gagneux, A. R.; Meier, R. *Tetrahedron Lett.* **1969**, 365.

(16) This behavior is very similar to 3-hydroxy-4-azahomoadamantane. Cf. ref 4b and: Kovacic, P.; Liu, J.-H.; Levi, E. M.; Roskos, P. D. *J. Am. Chem. Soc.* **1971**, *93*, 5801.

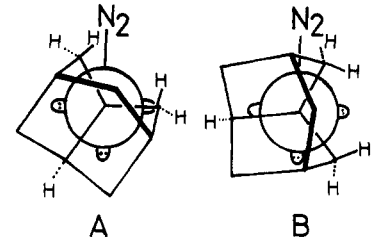
(17) The bridgehead imines are also photolabile to give some side products. For a review see: Padwa, A. *Chem. Rev.* **1977**, *77*, 37.

(18) Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891.

(19) Wiseman, J. R.; Pletcher, W. A. *J. Am. Chem. Soc.* **1970**, *92*, 956.

of bridgehead olefins into isolable (OS ≤ 17 kcal/mol), observable (17 kcal/mol ≤ OS ≤ 21 kcal/mol), and unstable ones (OS ≥ 21 kcal/mol). Although direct application of these quantitative predictions to bridgehead imines seems inappropriate without reasonable estimates of C=N double bond strain energy,[20] yet they suggest that bridgehead imines involving an (*E*)-1-azacyclooct-1-ene or larger ring may be isolable or observable at room temperature. In line with this prediction and reported results,[4-7,21] the bridgehead imines **12a**, **13**, **15**, and **16**, which contain (*E*)-1-azacycloheptene or (*E*)-1-azacyclohexene rings, are unstable and highly reactive, while the imine **14** containing an (*E*)-1-azacyclononene unit is stable and unreactive. Imines **12a**, **13**, **15**, and **16** react spontaneously with MeOH, whereas **14** does not. However, attempts to isolate **14** were not successful because of its sensitivity toward air and moisture, but the corresponding saturated amine **28** was obtained after reduction with $NaBH_4$ (Scheme II). Previously reported bridgehead imines **7**, **8**, and **11**, which contain bridged (*E*)-1-azacyclooctene rings, are also not reactive toward MeOH.[5,6,21,22] The more strained bridgehead imines **1–5**, which contain (*E*)-1-azacycloheptene or -azacyclohexene rings, are also known to react with MeOH spontaneously.[4] Therefore, it can be concluded that Wiseman's stability criterion for bridgehead olefins is also applicable to bridgehead imines.

Ring-Expansion Selectivity of Unsymmetrical Bridgehead Azides. The photolysis of unsymmetrical bridgehead azide **24** in MeOH at room temperature gave the methoxy amine **26** and the bridgehead imine **14** in 1.00:2.03 ratio (^1H NMR analysis), indicating nearly statistical ring expansion on N_α of the azido group. This is in accord with the reported results on 1-azidonorbornane[4a,e] and 3-azidohomoadamantane[5] but different from those on 1-azidobicyclo[3.2.1]octane.[4d] The authors of the last report isolated only the MeOH adduct (22%) of bridgehead imine **5** and postulated a regioselective ring expansion of the bridgehead azide to the more strained bridgehead imine **5**. However, two other bridgehead imines that could be formed from 1-azidobicyclo[3.2.1]octane, namely 2-azabicyclo[4.2.1]non-1-ene and 2-azabicyclo[3.3.1]non-1-ene, would contain (*E*)-1-azacyclooctene rings. Hence there is a possibility that these imines are also produced from the octyl azide but are not trapped with MeOH. The observed ratio of **39** to **40**, i.e., 1.00:1.17 (based on ^1H NMR analysis of the crude photolysate; 1.00:1.14 after isolation) from the azide **37** is noteworthy. Assuming sponteneous trapping of the highly strained imines **15** and **16** with MeOH, the results indicate a preferential migration of the C_{3-7} bond to the C_{3-2} bond of **37**. Recently, Kyba and Abramovitch[23] rationalized the nonstatistical photomigrations observed for acyclic *sec*- and *tert*-alkyl azides in terms of the conformational factor of the excited azido group rather than the intrinsic migratory aptitude of the alkyl groups. However, there seems to be little energy difference between the relevant conformers A (preferred for C_{3-2} bond migration in the Abramovitch–Kyba model)[24] and B (preferred for C_{3-7} bond shift) from examination of molecular models. The selective C^{3-7} bond migration is



also reported in 3-noradamantylcarbene ring expansion to adamantene.[3h] This trend of selective C_{3-7} bond migration in the noradamantyl system is manifested in the acidolysis of **37**.[25,26] The observed selectivity, 1.00:0.17 (after correction by the statistical factor), of C_{3-7} bond migration (to afford **43**) to C_{3-2} bond migration (to give **44**) in the acidolysis of **37** is approximately 3 times higher than that (1.00:0.57–0.59) observed in the photolysis. The regioselective ring expansion of the noradamantyl ring to an adamantane rather than a protoadamantane ring is reasonably attributable to the tendency of the C_{3-7} bond to migrate rather than the C_{3-2} bond and to the larger ring strain release.[27] The same factors may control the migratory aptitudes of the C_{3-7} and C_{3-2} bonds in the photorearrangement of **37** in view of the initiation by an electron-deficient orbital on N_α of the azido group.

Conclusion

In summary, we have shown that bridgehead imines **12a**, **13**, **14**, **15**, and **16** are indeed generated from the azides **18**, **24**, and **37** by photolysis. Wiseman's stability criterion of bridgehead olefins is also applicable to bridgehead imines, i.e., the bridgehead imines involving the (*E*)-1-azacyclooctene unit belong to the class of imines on the boundary line of "reactive" and "unreactive" nature. The ring expansion ratio of unsymmetrical bridgehead azides by photolysis is generally statistical except for 1-azidonoradamantane (**37**).

Experimental Section[28]

1-Azidobicyclo[2.2.2]octane (18). To a stirred and ice-cooled suspension of sodium hydride (600 mg of 60% dispersion in mineral oil, 12.5 mmol) in anhydrous THF (20 mL) under nitrogen was added a solution of 1-aminobicyclo[2.2.2]octane (**17**)[9] (125 mg, 1.00 mmol) in THF (2 mL) and then a solution of *p*-tosyl azide (300 mg, 1.52 mmol) in THF (2 mL), and stirring was continued at room temperature for 2 days. The mixture was treated with methanol (2 mL) under ice cooling, poured onto ice water, and extracted with ether (4 × 10 mL). The combined extracts were washed with water (20 mL), dried ($MgSO_4$), and evaporated under reduced pressure to give an oily residue that was chromatographed

(20) Appropriate paramaters of aza analogues for molecular mechanics calculation are not available at present. Cf.: Osawa, E. "Nitrogen-Organic Resources"; Ban, Y.; Ed.; Hokkaido University, 1981; p 210.

(21) We thank Professor K. B. Becker for his kind suggestion that the bridgehead imine **8** should be an (*E*)-azacyclooctene rather than an (*E*)-azacycloheptene (see footnote of ref 5 and 4d). The reactivity difference between the imines **7** and **8** may be ascribable to the bridging ring size.

(22) The uniquely stable bridgehead imine **11** is known to be reduced to the corresponding amine with $NaBH_4$–MeOH, and hence, **11** seems to afford no stable methoxyamine (ref 6).

(23) Kyba, E. P.; Abramovitch, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 735.

(24) For another model see ref 4e, p 199.

(25) For a review see: Abramovitch, R. A.; Kyba, E. P. "The Chemistry of the Azido Group"; Patai, S., Ed.; Interscience: New York, 1971; Chapter 5.

(26) For the selective ring expansion of the noradamantylcarbinyl cation system see: Schleyer, P. v. R.; Wiskott, E. *Tetrahedron Lett.* **1967**, 2845.

(27) (a) The calculated protoadamantane strain energy is reported to be ca. 11.5 kcal/mol higher than that of adamantane: Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005. (b) Cf. also adamantane rearrangement: Engler, E. M.; Farcasiu, M.; Selvin, A.; Schleyer, P. v. R. *Ibid.* **1973**, *95*, 5769.

(28) Melting points were taken in a sealed tube on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were obtained on a Jasco IRA-1 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Jeol JNM-C-60HL instrument at 60 MHz and a Joel JNM-FX-60 FT NMR spectrometer at 15.04 MHz, respectively. Chemical shifts are reported in parts per million (δ) relative to Me_4Si as an internal standard in $CDCl_3$. Mass spectra were obtained with a Jeol Model JMS-D10 mass spectrometer at 75 eV. Microanalyses were performed with a Perkin-Elmer 240B elemental analyzer. GLC analyses were carried out by using a Jeol JGC-20 K gas chromatograph on a 1- or 2-m Silicone SE-30 column at 150–250 °C.

on a silica gel column eluting with *n*-pentane to afford the azide **18** as a colorless oil (126 mg, 83%): ^{1}H NMR ($CDCl_3$) δ 1.66 (s); mass spectrum, m/z 151 (M^+).

1-(Bicyclo[2.2.2]oct-1-yl)-4,5-bis(methoxycarbonyl)-1,2,3-triazole (19). A mixture of the azide **18** (52 mg, 0.34 mmol) and dimethyl acetylenedicarboxylate (DMAD) (49 mg, 0.35 mmol) in benzene (2 mL) was heated in a sealed tube at 100 °C for 24 h. Removal of the solvent and recrystallization of the solid residue from CH_2Cl_2–*n*-hexane afforded the triazole **19** as colorless crystals (90 mg, 89%): mp 135–136 °C; ^{1}H NMR ($CDCl_3$) δ 4.02 (s, 3 H), 3.93 (s, 3 H), and 2.5–1.6 (m, 13 H).

1-Azidobicyclo[3.3.1]nonane (24). This azide was prepared in 78–84% yields from the corresponding alcohol by treatment with NaN_3–57% H_2SO_4–$CHCl_3$ according to the reported procedure.[10]

1-(Bicyclo[3.3.1]non-1-yl)-4,5-bis(methoxycarbonyl)-1,2,3-triazole (25). A mixture of the azide **24** (48 mg, 0.29 mmol) and DMAD (46 mg, 0.32 mmol) in toluene (2 mL) was heated in a sealed tube at 120 °C for 40 h. Removal of the solvent and chromatography (silica gel, CH_2Cl_2–CH_3CO_2Et) afforded the triazole **25** as colorless crystals (86 mg, 96%): mp 73–75 °C; ^{1}H NMR ($CDCl_3$) δ 4.00 (s, 3 H), 3.92 (s, 3 H), and 2.6–1.6 (m, 15 H).

***N*-Noradamant-3-ylacetamide (34).** To a stirred and cooled (5–10 °C) mixture of *p*-tosyl chloride (8.98 g, 47.1 mmol) in pyridine (40 mL) was added noradamant-3-yl methyl ketoxime[11] (**33**) (4.20 g, 23.5 mmol) portionwise during 20 min. After stirring for 15 h at room temperature, the mixture was diluted slowly with concentrated HCl (60 mL) and stirred for 3 h. The mixture was poured onto ice water and extracted with CH_2Cl_2 (5 × 30 mL). The combined extracts were washed successively with 5% aqueous $NaHCO_3$ and saturated aqueous NaCl and dried (Na_2SO_4). Removal of the solvent and recrystallization of the residue from CCl_4 gave the acetamide **34** as crystals (2.94 g, 70%): mp 130–133 °C; ^{1}H NMR ($CDCl_3$) δ 5.80 (br s, 1 H disappeared on shaking with D_2O), 2.6–1.4 (m, 13 H), and 1.94 (s, 3 H); mass spectrum, m/z 180 ($M^+ + 1$), 179 (M^+).

3-Aminonoradamantane (35). A. From the Acetamide 34. A mixture of **34** (1.80 g, 10.0 mmol) and concentrated hydrochloric acid (50 mL) in methanol (50 mL) was heated in a sealed tube at 110 °C for 24 h. The cooled mixture was poured onto ice water and extracted with CH_2Cl_2 (10 mL). The aqueous layer was basified with 50% aqueous NaOH under ice cooling and extracted with CH_2Cl_2 (4 × 10 mL). The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure at below 15 °C to afford a solid that was sublimed (100 °C (20 mm)) to give the amine **35** (1.07 g, 78%): mp 173–175 °C; ^{1}H NMR ($CDCl_3$) δ 2.20 (br s, 2 H), 2.1–1.3 (m, 11 H), and 1.61 (s, 2 H, disappeared on shaking with D_2O); ^{13}C NMR ($CDCl_3$) δ 63.8 (s), 52.0 (t), 46.2 (d), 43.9 (t), 37.9 (t), and 34.4 (t); mass spectrum, m/z 137 (M^+).

B. From the Carboxylic Acid 36. To a stirred and ice-cooled solution of NaN_3 (0.25 g, 3.9 mmol) in water (2 mL) was added dropwise a solution of 3-noradamantanecarboxylic acid chloride (prepared from the acid **36**, 0.16 g, 0.96 mmol, by heating in $SOCl_2$ for 3 h, IR 1785 cm^{-1} in neat film). After stirring for 0.5 h at room temperature, the mixture was diluted with water (10 mL) and workup in the usual way gave the acyl azide, IR (neat film) 2120 and 1695 cm^{-1}, which was heated in benzene (10 mL) under reflux for 6 h to afford the isocyanate (115 mg, 73% from **36**), IR (neat film) 2240 cm^{-1}. The isocyanate was stirred in acetone (1 mL) and concentrated HCl (2 mL) for 0.5 h. The mixture was washed with either (5 mL), the aqueous layer was basified (10% aqueous NaOH), and workup as above afforded the amine **35** (80 mg, 61% from **36**).

3-Azidonoradamantane (37). A mixture of the amine **35** (411 mg, 3.00 mmol), sodium hydride (1.50 g of 60% dispersion in mineral oil, 31.0 mmol), and *p*-tosyl azide (1.20 g, 6.00 mmol) in anhydrous THF (10 mL) was stirred in nitrogen for 2 days at room temperature. Workup as above the chromatography of the crude product gave the azide **37** as a colorless oil (436 mg, 92%): ^{1}H NMR ($CDCl_3$) δ 2.36 (br and unsymmetrical s, 3 H) and 2.2–1.4 (m, 10 H); mass spectrum, m/z 135 ($M^+ - N_2$).

1-(Noradamant-3-yl)-4,5-bis(methoxycarbonyl)-1,2,3-triazole (38). A mixture of the azide **37** (30 mg, 0.18 mmol) and DMAD (30 mg, 0.21 mmol) in toluene (5 mL) was heated in a sealed tube at 100 °C for 40 h. Removal of the solvent and chromatography (silica gel, C_6H_6–CH_2Cl_2–CH_3CO_2Et) of the residue gave the triazole **38** as crystals (56 mg, 100%): mp 70–72 °C; ^{1}H NMR ($CDCl_3$) δ 4.02 (s, 3 H), 3.94 (s, 3 H), 3.08 (t, J = 6 Hz, 1 H), and 2.6–1.5 (m, 12 H).

General Procedure for Photolysis of the Bridgehead Azides in Methanol. A solution of the azide (3.00 mmol) in methanol (100 mL) was irradiated with a 100-W high-pressure mercury lamp through a Vycor filter at ambient temperature for 2.5–3 h (GLC monitored). After the removal of the solvent under reduced pressure, the residue was chromatographed on a neutral alumina (Woelm, activity grade II–III) column eluting with C_6H_6–CH_2Cl_2 or CH_3CO_2Et.

1-Methoxy-2-azabicyclo[3.2.2]nonane (20). The photolysis of the azide **18** (453 mg, 3.00 mmol) as above and workup afforded the methoxy amine **20** as a colorless oil (419 mg, 90%): ^{1}H NMR ($CDCl_3$) δ 3.17 (s, 3 H), 2.92 (t, J = 7.0 Hz, 2 H), 2.0–1.4 (m, 11 H), and 1.51 (s, 1 H, disappeared on shaking with D_2O); mass spectrum, m/z 156 ($M^+ + 1$), 155 (M^+).

1-Methoxy-9-azabicyclo[3.3.2]decane (26). The photolysis of the azide **24** (160 mg, 0.97 mmol) as above and removal of the methanol under reduced pressure gave an oily residue (145 mg): ^{1}H NMR ($CDCl_3$) δ 3.21 (s overlapped on br s, ca. 1.00 + 1.34 H), 2.91 (d, J = 4.0 Hz, ca. 0.66 H), and 2.8–1.2 (m, ca, 13.3 H) (this corresponds to ca. 1.00:2.03 mixture of **26** and **14**).[29] Chromatography afforded the methoxy amine **26** as crystals (30 mg, 18%): mp 43–44 °C; ^{1}H NMR ($CDCl_3$) δ 3.21 (s, 3 H), 2.91 (d, J = 4.0 Hz, 2 H), and 2.1–1.5 (m, 14 H, decreased to ca. 13 H on shaking with D_2O); mass spectrum, m/z 169 (M^+).

The imine **14** or its hydrolysis product could not be obtained after chromatography.

1-Methoxy-2-azaadamantane (39) and 3-Methoxy-4-azaprotoadamantane (40). The photolysis of azide **37** (440 mg, 2.63 mmol) as above gave an oily product after removal of methanol which could be analyzed as ca. a 1.00:1.17 mixture of the methoxy amines **39** and **40** (based on the methoxy signal in ^{1}H NMR spectrum) contaminated with uncharacterized polymeric side products. The first fractions of chromatography on neutral alumina as above afforded 3-methoxy-4-azaprotoadamantane (**40**) as a colorless oil (182 mg, 40%): ^{1}H NMR ($CDCl_3$) δ 3.32 (s, 3 H), 3.2–2.6 (m, 2 H), 2.2–1.2 (m, 11 H), and 1.68 (s, 1 H, disappeared on shaking with D_2O); ^{13}C NMR ($CDCl_3$) δ 96.6 (s), 49.8 (d), 48.2 (t), 42.2 (d), 41.4 (t), 39.2 (t), 38.3 (t), 34.7 (d), 32.4 (t), 27.8 (d); mass spectrum, m/z 168 ($M^+ + 1$), 167 (M^+).

The second fractions gave 1-methoxy-2-azaadamantane (**39**) as a colorless oil (158 mg, 35%): ^{1}H NMR ($CDCl_3$) δ 3.40 (br s, 1 H), 3.31 (s, 3 H), 2.25 (br s, 2 H), 2.1–1.6 (m, 10 H), 1.66 (s, 1 H, disappeared on shaking with D_2O); ^{13}C NMR ($CDCl_3$) δ 82.6 (s), 50.3 (d), 47.6 (q), 40.9 (t), 36.4 (t), 36.1 (t), 29.9 (d); mass spectrum, m/z 168 ($M^+ + 1$), 167 (M^+).

Photolysis of 24 in $NaBH_4$–MeOH. 2-Azabicyclo[4.3.1]decane (28). The azide **24** (396 mg, 2.40 mmol) was irradiated in the presence of $NaBH_4$ (456 mg, 12.0 mmol) in methanol (80 mL) as above for 3 h. The remaining $NaBH_4$ was decomposed by addition of concentrated hydrochloric acid (5 mL) to the mixture under ice cooling and the mixture was concentrated to ca. 20 mL under reduced pressure, diluted with water (100 mL), and washed with ether (20 mL). The aqueous layer was basified (10% aqueous NaOH) and extracted with ether (5 × 10 mL). The combined extracts were dried ($MgSO_4$) and evaporated to give an oil that was chromatographed on a neutral alumina column (CH_2Cl_2–CH_3CO_2Et–MeOH) to afford the methoxy amine **26** (105 mg, 26%), 1-aminobicyclo[3.3.1]nonane (**29**)[10] (21 mg as HCl salt, 5.0%), and 2-azabicyclo[4.3.1]decane (**28**)[30] as an oil (134 mg, 40%) that gave a crystalline hydrochloride: mp 210–213 °C dec; ^{1}H NMR ($CDCl_3$) (free amine) δ 3.31 (unsymm. s, 1 H), 2.97 (unsymm. t, J = 4.5 Hz, 2 H), and 2.4–1.2 (m, 14 H, decreased to ca. 13 H on shaking with D_2O); ^{13}C NMR ($CDCl_3$) (free amine) δ 50.8 (d), 45.0 (t), 32.6 (t), 30.5 (t), 29.6 (t), 28.5 (d), 28.2 (t), 25.1 (t), and

(29) This is based on the integrated signal ratio using the signals at δ 3.21 (OMe of **26** and C=NCH_2 of **14**) and 2.91 (CH_2NH of **26**) and should be considered as an approximate value because of contamination with some decomposition products such as amino ketone via hydrolysis and intractable polymeric products.

(30) The amine **28** could not be obtained by $NaBH_4$ reduction of crude photolysate in MeOH at room temperature due to rapid decomposition of the imine **14**; only the methoxy amine **26** was obtained in low yield.

18.1 (t); mass spectrum, m/z (free amine) 139 (M^+).

The photolysis of azide **24** (340 mg, 2.06 mmol) in $NaBH_4$ (1.15 g, 30.3 mmol)–MeOH (80 mL) for 3 h and workup as above gave **26** (65 mg, 19%), **28** (54 mg, 19%), and **29** (79 mg, 28%). Similarly, the photolysis of **24** (430 mg, 2.60 mmol) in $NaBH_4$ (5.50 g, 145 mmol)–MeOH (80 mL) afforded the bridgehead amine **29** (333 mg as HCl salt, 73%).

General Procedure for Hydrocyanation of Photochemically Generated Bridgehead Imines. A mixture of appropriate bridgehead azides (2–3 mmol), Adogen 464 (0.4 g), *n*-hexane (50 mL), and NaCN (5.0 g, 102 mmol) in water (10 mL) was vigorously stirred under argon and irradiated as above. After the disappearance of the azide (GLC) (ca. 5 h), the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (4 × 10 mL). The combined organic layer and extracts were washed with water (5 × 10 mL) and dried (Na_2SO_4). Removal of the solvent under reduced pressure gave a yellowish oil that was chromatographed on neutral alumina (activity grade II–III) column eluting with CH_2Cl_2–CH_3CO_2Et–MeOH.

1-Cyano-2-azabicyclo[3.2.2]nonane (21) from 18. The photodecomposition of **18** (453 mg, 3.00 mmol) as above and chromatography afforded the amino nitrile **21** as crystals (104 mg, 23%): mp 104–106 °C; ^1H NMR ($CDCl_3$) δ 3.96 (t, J = 6.0 Hz, 2 H), and 2.3–1.5 (m, 12 H, decreased to ca. 11 H on shaking with D_2O); mass spectrum, m/z 150 (M^+).

1-Cyano-9-azabicyclo[3.3.2]decane (30) from 24. The photolysis of **24** (330 mg, 2.00 mmol) as above and chromatography afforded the amino nitrile **30** as colorless crystals (47 mg, 14%): mp 65–68 °C; ^1H NMR ($CDCl_3$) δ 3.04 (d, J = 4.0 Hz, 2 H), and 2.1–1.5 (m, 14 H, decreased to 13 H on shaking with D_2O); ^{13}C NMR ($CDCl_3$) δ 125.1 (s), 57.1 (s), 51.1 (t), 38.2 (t), 35.5 (d), 31.0 (t), and 22.7 (t), mass spectrum, m/z 164 (M^+).

Iminohydantoin 22 from 21. A mixture of **21** (50 mg, 0.33 mmol) and phenyl isocyanate (41 mg, 0.34 mmol) in anhydrous CH_2Cl_2 was stirred for 1 day. After removal of the solvent, the residue was dissolved in EtOH (3 mL) containing KOH (10 mg) and the mixture was stirred for 2 days at ambient temperature. After removal of the solvent, the residue was treated with water to give crystals which were filtered and recrystallized from benzene to afford the iminohydantoin **22** as colorless crystals (62 mg, 68%): mp 176–178 °C; ^1H NMR ($CDCl_3$) δ 7.4–7.1 (m, 5 H), 3.63 (t, J = 6.0 Hz, 2 H), and 2.3–1.6 (m, 12 H); mass spectrum, m/z 269 (M^+).

Iminohydantoin 32 from 30. The similar reaction of **30** (47 mg, 0.29 mmol) with phenyl isocyanate (41 mg, 0.34 mmol) followed by alkaline treatment as above and workup afforded the iminohydantoin **32** as colorless crystals (29 mg, 36%): mp 137–139 °C; ^1H NMR ($CDCl_3$) δ 7.5–7.2 (m, 5 H), 3.61 (d, J = 4.0 Hz, 2 H), and 2.5–1.5 (m, 14 H); mass spectrum, m/z 283 (M^+).

General Procedure for Low-Temperature Photolysis of Azides 18, 24, and 37. The appropriate azide (10–25 mg) was dissolved in 1:1 (v/v) isopentane–3-methylpentane (0.50 mL) containing 1 mg of adamantane as an internal reference for GLC analysis. This solution in a quartz reaction tube (0.4-cm diameter and 20-cm length) was solidified under argon, immersed in liquid nitrogen in a Dewar flask with a quartz window (1-cm diameter and 6-cm length), evacuated, and irradiated with a 100-W high-pressure mercury lamp through a Vycor filter for 50 min. The reaction tube was filled with argon, moved carefully into a dry ice–acetone bath, and diluted with MeOH (0.2 mL) and Et_2O (0.2 mL) with a syringe. After standing for 0.5 h, the mixture was allowed to warm to room temperature. GLC analysis indicated 46.5–70% conversion of the azides into photoproducts. After removal of the solvent, the crude products were analyzed by TLC, IR, and ^1H NMR analyses.

A. Photolysis of 18. The azide **18** (11 mg, 0.073 mmol) in the pentane matrix was irradiated as above to give 46.5% conversion. Two runs were combined and crude products were purified on a neutral alumina plate (Merck type E, 60 F254) eluting with MeOH–$CHCl_3$ (0.5:100) to afford unreacted azide (9 mg, 41% recovery) and the methoxy amine **20** (5 mg, 53% based on unrecovered azide), identified by IR and ^1H NMR spectra.

B. Photolysis of 24. The photolysis of **24** (25 mg, 0.15 mmol) under the above conditions and treatment with MeOH–Et_2O gave a 69.6% conversion (GLC). Removal of the solvent gave an oil (22 mg) which was analyzed as a mixture of unreacted azide **24** (30%), the methoxy amine **26** (18%), and the imine **14** (52%) contaminated with some uncharacterized byproducts based on TLC, IR, and ^1H NMR spectral, and GLC analyses.

C. Photolysis of 37. The photolysis of the azide **37** (10 mg, 0.061 mmol) in the pentane matrix as above followed by treatment with MeOH–Et_2O gave a 70% conversion (GLC). Two runs were combined, and the solvent was removed at reduced pressure to give an oily product (18 mg), which was analyzed as a mixture of the unreacted azide **37**, the methoxy amines **39** and **40**, and uncharacterized polymeric materials in approximately 30:14:19:37 ratio based on ^1H NMR, IR, GLC, and TLC analyses.

Acidolysis of 37. 1-Hydroxy-2-azaadamantane (43) and 3-Hydroxy-4-azaprotoadamantane (44). To an ice-cooled and stirred mixture of $CHCl_3$ (5 mL) and concentrated H_2SO_4 (97%, 5 mL) was added the azide **37** (326 mg, 2.00 mmol) in $CHCl_3$ (0.5 mL). After the mixture was stirred for 0.5 h under ice cooling and 2 h at room temperature, it was poured onto ice water and the layers were separated. The aqueous layer was basified with 50% NaOH and extracted with $CHCl_3$ (5 × 10 mL). The combined extracts were dried (Na_2SO_4) and evaporated to dryness. The residue was chromatographed on a neutral alumina column (activity grade III–IV), eluting with a CH_3CO_2Et–MeOH system to afford the azaprotoadamantane **44** as colorless crystals in the first fractions (61 mg, 20%): mp 98–99 °C; ^1H NMR ($CDCl_3$) δ 3.88 (m, 2 H, disappeared on shaking with D_2O), 3.1–2.6 (m, 2 H), and 2.5–1.2 (m, 11 H); mass spectrum, m/z 153 (M^+).

The second fractions afforded the azadamantane **43** as colorless crystals (174 mg, 57%), mp 277–278 °C (lit.[15] 277–278 °C), which was identical with an authentic sample by spectral comparisons.

Hydrolysis of Methoxy Amines 39, 40 to 43, and 44. A. The methoxy amine **40** (200 mg, 1.20 mmol) in 20 N H_2SO_4 (10 mL) was heated at 100 °C for 30 h. The cooled mixture was poured onto ice water, basified with 20% NaOH, and extracted with CH_2Cl_2 (6 × 10 mL). The combined extracts were washed with saturated aqueous NaCl and dried (Na_2SO_4). Removal of the solvent and recrystallization of the solid residue from methanol afforded the hydroxy amine **44** as colorless crystals (159 mg, 87%), which was identical with the sample from the acidolysis of **37**.

B. The methoxyamine **39** (180 mg, 1.10 mmol) was hydrolyzed under the same conditions as above, and workup afforded the hydroxyamine **43** (160 mg, 97%), which was identical with the sample from the acidolysis of **37**.

***N*-Acetyl-1-hydroxy-2-azaadamantane (45).** A mixture of **43** (100 mg, 0.65 mmol), acetic anhydride (220 mg, 2.15 mmol), and pyridine (0.5 mL) was stirred under ice cooling for 24 h. The mixture was diluted with water (10 mL), stirred for 0.5 h, and extracted with CH_2Cl_2 (4 × 5 mL). The combined extracts were washed successively with 1 N hydrochloric acid, water, 5 % aqueous $NaHCO_3$, and saturated NaCl solution and dried (Na_2SO_4). Removal of the solvent and chromatography of the residue on a neutral alumina column (CH_2Cl_2–MeOH system) afforded the *N*-acetyl derivative **45** as a colorless oil (101 mg, 79%): ^1H NMR ($CDCl_3$) δ 8.72 (s, 1 H, exchangeable with D_2O), 4.10 (br, s, 1 H), 2.12 (br s, 2 H), 2.10 (s, 3 H), and 2.1–1.6 (m, 10 H); mass spectrum, m/z 195 (M^+).

***3-endo*-((Acetylamino)methyl)bicyclo[3.2.1]octan-6-one (46).** Compound **44** was acetylated under the same conditions as above, affording the *N*-acetyl amino ketone **46** as colorless crystals (53 mg, 52%): mp 95–97 °C; ^1H NMR ($CDCl_3$) δ 5.90 (br s, 1 H, exchangeable with D_2O), 3.24 (m, 1 H), 2.96 (m, 1 H), 2.68 (m, 1 H), 2.4–1.6 (m, 10 H), and 1.97 (s, 3 H); mass spectrum, m/z 195 (M^+).

Registry No. (*E*)-**14**, 87174-23-0; **17**, 1193-42-6; **18**, 87174-24-1; **19**, 87174-25-2; **20**, 87174-28-5; **21**, 87174-31-0; **22**, 87174-33-2; **24**, 63534-34-9; **25**, 87174-26-3; **26**, 87174-29-6; **28**, 282-54-2; **28**·HCl, 87174-30-9; **29**, 17530-64-2; **29**·HCl, 19388-60-4; **30**, 87174-32-1; **32**, 87174-34-3; **33**, 29844-81-3; **34**, 85616-63-3; **35**, 28224-43-3; **36**, 16200-53-6; **37**, 85616-64-4; **38**, 87174-27-4; **39**, 85616-67-7; **40**, 85616-68-8; **43**, 3015-19-8; **44**, 85616-69-9; **45**, 85616-70-2; *endo*-**46**, 87174-35-4; DMAD, 762-42-5; *p*-tosyl azide, 941-55-9.

Supplementary Material Available: IR and additional mass spectral peaks of **18**, **20–22**, **26**, **28**, **30**, **32**, **34**, **35**, **37**, **39**, **40**, **44**, **45**, and **46**; IR peaks of **19**, **25**, and **38**, and analytical data of all of these compounds (2 pages). Ordering information is given on any current masthead page.