giospecific. Benzenesulfonamide is recovered quantitatively from the reduction step. Results of the application of this reaction sequence to several terpenes and other hydrocarbons are summarized in Table I.

Work is in progress to define the scope and limitations of this route to allylic thiols.

Experimental Section

General Methods. Infrared spectra were run on a Perkin-Elmer 457 spectrophotometer. ^1H NMR spectra were determined in the indicated solvent on a Perkin-Elmer R12 (60 MHz) or a Perkin-Elmer Hitachi R24A (60 MHz) instrument with tetramethylsilane as an internal standard. Mass spectra were obtained at an ionizing current of 200 μA and an ionizing voltage of 70 eV on a Micromass 16F instrument. Elemental microanalyses were performed by Service Central de Microanalyse du CNRS, F-69390 Vernaison, France. Optical activities were obtained in chloroform solutions by using a Perkin-Elmer 141 polarimeter.

The synthesized allylic thiols were not distilled because of their instability but were purified on a silica gel column with hexane or pentane as the eluent.

For reactions requiring dry solvents, tetrahydrofuran and diethyl ether were distilled from potassium and benzophenone. Hexane, pentane, and dichloromethane were distilled from calcium hydride.

N-Sulfinylbenzenesulfonamide was synthesized on a scale of several hundred grams by heating benzenesulfonamide with thionyl chloride; mp 72 °C (toluene).[16]

Typical Synthesis Procedure. 3,7,7-Trimethylbicyclo[4.1.0]hept-2-ene-4-thiol (4c). 3,7,7-Trimethylbicyclo[4.1.0]-hept-3-ene (3-carene; 5.71 g, 42 mmol) was added to a solution/suspension of **1** (8.12 g, 40 mmol) in dry ether (40 mL) at 0 °C under an argon atmosphere. After the mixture had been allowed to stand 1 h, the precipitate of **3c** (11.5 g, 85%) was separated by filtration. The solid **3c** (34 mmol) was added under argon to a suspension of $LiAlH_4$ (2.7 g, 71 mmol) in 150 mL of dry ether at 0 °C. The mixture was allowed to warm to room temperature, and acetone (3 mL)[17] and acidified water were added in succession. The mixture was extracted with ether, the ether was evaporated, and the residue was mixed with 50 mL of pentane. The insoluble benzenesulfonamide was separated by filtration (quantitative recovery), and the pentane was evaporated to give crude **4c**. The product was purified by chromatography on silica gel with hexane as the eluent; yield 5.0 g (88% from **3c**); spectroscopic data are in Table II.

Thiols **4a,b,d-g** (Table I) were prepared by the same procedure.

Acknowledgment. We thank Dr. P. Teisseire, Scientific Director, Roure Bertrand Dupont S.A, F 06332 Grasse, France, for generous gifts of terpenes.

Registry No. **1**, 6536-23-8; **2a**, 18172-67-3; **2b**, 7785-26-4; **2c**, 498-15-7; **2d**, 4497-92-1; **2e**, 563-34-8; **2f**, 17334-55-3; **2g**, 1195-32-0; **3a**, 88195-46-4; **3b**, 88195-47-5; **3c**, 88106-16-5; **3d** (isomer 1), 88106-17-6; **3d** (isomer 2), 88106-20-1; **3e**, 88106-18-7; **3f**, 74323-43-6; **3g**, 88106-19-8; **4a**, 88195-44-2; **4b**, 88195-45-3; **4c**, 88106-12-1; **4d**, 88106-13-2; **4e**, 88130-55-6; **4f**, 88106-14-3; **4g**, 88106-15-4.

Supplementary Material Available: Complete NMR spectra of compounds **3a-g** and IR and mass spectra of **4a-g** (5 pages). Ordering information is given on any current masthead page.

(15) Streith, J.; Pesnelle, P.; Ourisson, G. *Bull. Soc. Chim. Fr.* **1963**, 518.

(16) Kresze, G.; Wucherpfennig, W., In "Newer Methods of Preparative Organic Chemistry"; Foerst, W., Ed.; Academic Press: New York and London, 1968; Vol. V, 109; *Liebigs. Ann. Chem.* **1975**, 1725.

(17) When methyl acetate was added instead of acetone to destroy the excess $LiAlH_4$, terpenyl thioacetates were formed.

Synthesis of Some Azahomodiamantane Derivatives via Acidolysis and Photolysis of 1- and 4-Azidodiamantanes[1]

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Acidolytic and photolytic ring expansions of 1- (**1**) and 4-azidodiamantane (**2**) have been explored. Symmetrical bridgehead azide **2** afforded 9-substituted 10-aza-2(3)-homodiamantanes **6**, **7**, and **9** by photolysis and acidolysis. Unsymmetrical bridgehead azide **1** gave exclusively 11-hydroxy-12-aza-1(2)-homodiamantane (**12**) on acidolysis; however, photolysis of **1** in MeOH afforded a complex mixture due to anomalous side reactions. The simple MeOH adduct (**17**) to the major ring-expansion product 12-aza-1(2)-homodiamant-11-ene (**15**) was not stable under purification conditions, affording **12** (41%) and O-N Me migration product **19** (27%). An MeOH adduct, **18**, to 11-aza-2(3)-homodiamant-11-ene (**16**) as another possible ring expansion product was not obtained, but 12-methoxy-11-aza-2(3)-homodiamant-10-ene (**20**) was isolated as a minor product (9%). Hydrocyanation under photolytic conditions gave amino nitrile **22** (43%). Some other related conversions of above products such as acetylation and reduction have been reported also.

The azido group is one of the more versatile functional groups for synthesis of nitrogen-containing organic compounds.[2] For example, introduction of azido group into bi- and tricyclic systems followed by acidolytic[3] and/or photolytic[4] ring expansions provides a convenient route to aza-bridged polycyclic systems. Various aza-modified adamantanes and related derivatives have been prepared recently by this methodology.[3,4b,d-f,i,j] As an extension of these studies, we now report the synthesis of 1- and 4-

(1) Synthesis of Adamantane Derivatives. 67. Part 66: Sasaki, T.; Eguchi, S.; Okano, T. *J. Am. Chem. Soc.* **1983**, *105*, 5912.

(2) For a general review, see: Sheradsky, T. "The Chemistry of the Azido Group"; Patai, S., Ed.; Interscience: New York, 1971, Chapter 6.

(3) (a) Sasaki, T.; Eguchi, S.; Katada, T.; Hiroaki, O. *J. Org. Chem.* **1977**, *42*, 3741. (b) Sasaki, T.; Eguchi, S.; Toi, N. *Heterocycles* **1977**, *7*, 315. (c) Margosian, D.; Kovacic, P. *J. Org. Chem.* **1981**, *46*, 877. (d) Margosian, D.; Speier, J.; Kovacic, P. *Ibid.* **1981**, *46*, 1346.

(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., Int. Ed. Engl.* **1976**, *15*, 168. (d) Sasaki, T.; Eguchi, S.; Toi, N. *J. Org. Chem.* **1979**, *44*, 3711. (e) Sasaki, T.; Eguchi, S.; Okano, T. *Ibid.* **1981**, *46*, 4474. (f) Sasaki, T.; Eguchi, S.; Hattori, S.; Okano, T. *J. Chem. Soc., Chem. Commun.* **1981**, 1193. (g) Becker, K. B.; Gabutti, C. A. *Tetrahedron Lett.* **1982**, *23*, 1883. (h) Quast, H.; Seiferlings, B. *Justus Liebigs Ann. Chem.* **1982**, 1553. (i) Sasaki, T.; Eguchi, S.; Okano, T. *Tetrahedron Lett.* **1982**, *23*, 4669. (j) Sasaki, T.; Eguchi, S.; Okano, T.; Wakata, Y. *J. Org. Chem.* **1983**, *48*, 5250.

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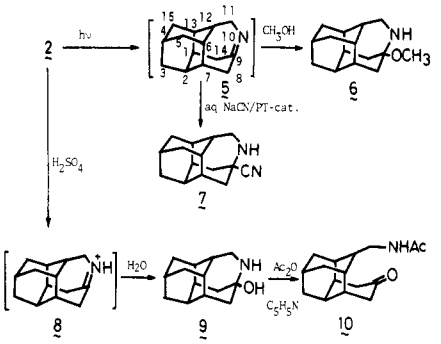
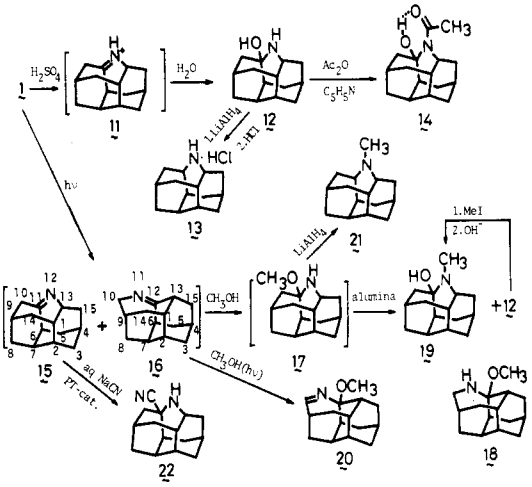
Scheme I



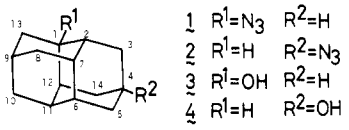
Scheme II



azidodiamantanes and their acidolytic and photolytic ring expansions to some novel azahomodiamantane derivatives.[5-8]

Results and Discussion

The starting bridgehead azides **1** and **2** were obtained in 79% and 76% yields, respectively, from the corresponding alcohols **3** and **4**[9] by treatment with NaN_3–57% H_2SO_4.[3a]



1 R^1=N_3 R^2=H
2 R^1=H R^2=N_3
3 R^1=OH R^2=H
4 R^1=H R^2=OH

Direct photolysis of the symmetrical azide **2** in methanol through a Vycor filter afforded a single product **6** in 83% yield, which was characterized as the expected methoxy amine. ^1H NMR spectrum exhibited a characteristic doublet for 2 H at δ 2.98 (J = 4 Hz) due to the NCH_2CH of the 9-azabicyclo[3.3.2]decane system.[3c,4b,e,j] The ^{13}C NMR spectrum had 11 resonances in agreement with the C_s symmetry of the molecule **6**. The formation of **6** is indicative of the formation of bridgehead imine **5** on the basis of our recent observations of low-temperature photolysis of some bridgehead azides[4j] as well as reported spectral evidence for some related bridgehead imines in low-temperature N_2 and Ar matrices by Michl's group[10a] and Dunkin's group.[10b] The bridgehead imine **5** could be trapped by cyanide under phase-transfer-catalyzed conditions (NaCN–Adogen 464–H_2O–*n*-hexane) to afford amino nitrile **7** (23%; Scheme I).

Treatment of **2** with concentrated H_2SO_4 in $CHCl_3$ afforded 10-aza-2(3)-homodiamantan-9-ol (**9**, 91%) via a bridgehead iminium ion **8**. Acetylation of **9** with acetic anhydride–pyridine gave a ring-opened keto amide, **10**, $\nu_{C=O}$ 1687 and 1630 cm^{-1}.[11] These results are quite similar to those obtained for 1-azidoadamantane,[3a,4b,e] because both bridgehead imines **5** from **2** and 4-azahomoadamant-3-ene from 1-azidoadamantane are strained imines with an (*E*)-1-azacycloheptene moiety.

A problem confronted in ring expansions of unsymmetrical azides is regioselectivity.[4a,f,g,i,j] However, unsymmetrical 1-azidodiamantane (**1**) afforded 11-hydroxy-12-aza-1(2)-homodiamantane (**12**) as the sole isolable product (93%) on acidolysis with concentrated H_2SO_4–$CHCl_3$ (Scheme II). Structure **12** was supported by reduction to the parent 12-aza-1(2)-homodiamantane (**13**) with $LiAlH_4$ (83%). Appearance of seven resonances in ^{13}C NMR spectrum of **13**·HCl was compatible with the C_2 symmetry of **13**. Acetylation of **12** with Ac_2O–pyridine gave a ring-retained *N*-acetyl derivative, **14**, $\nu_{C=O}$ 1608 cm^{-1}. Such ring-retained *N*-acetylation is also reported recently for 1-hydroxy-2-azaadamantane due to adamantane ring stability.[4i,j] The rigid molecular framework of **12** inhibits the ring-opening as suggested by molecular model studies. The regioselective acidolytic ring expansion of **1** to **12** is consistent with the larger migratory aptitude of a *sec*-alkyl group (C_{1-2} or C_{1-12} bond migration) than a primary alkyl group (C_{1-13} bond migration) because the migratory aptitude *i*-Pr ≃ cyclohexyl ≫ Et ≃ Me is well established in acidolytic rearrangement of *tert*-alkyl azides.[2] The statistical factor also favors the formation of **12**.

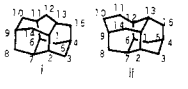
In contrast to the acidolysis, photolytic ring expansion of **1** in methanol was complicated by anomalous side reactions as well as nonregioselectivity. Direct photolysis of **1** in methanol afforded a mixture of several products which was purified by successive chromatography on neutral alumina and silica gel columns. The major product was the amino alcohol **12** (41%) which was identical with

(5) For some of carbocyclic diamantane chemistry, see: Cupas, C.; Schleyer, P. v. R.; Trecker, D. J. *J. Am. Chem. Soc.* **1965**, *87*, 917. Gund, T. M.; Osawa, E.; Williams, V. Z., Jr.; Schleyer, P. v. R. *J. Org. Chem.* **1974**, *39*, 2979. See also ref 9.

(6) For synthesis of 3-heterodiamantanes, see: Krishnamurthy, V. V.; Fort, R. C., Jr. *J. Org. Chem.* **1981**, *46*, 1388.

(7) (a) Although the formation of isomeric lactams, 11-aza-2(3)-homodiamantan-10-one and/or 10-aza-2(3)-homodiamantan-11-one in the Schmidt reaction of 3-diamantanone has been described, their complete characterization and conversions to the corresponding amines seem not to be studied: Blaney, F.; Faulkner, D.; McKervey, M. A. *Synth. Commun.* **1973**, *3*, 435. (b) The Beckmann rearrangement of 3-diamantanone with hydroxylamine-*O*-sulfonic acid has been reported also to give the ring-expanded lactam presumably as a mixture of regioisomers, but their further purification and characterization are not described: Novoselov, E. F.; Isaev, S. D.; Yurchenko, A. G.; Vodichka, L.; Trshiska, Y. *Zh. Org. Khim.* **1981**, *17*, 2558; *J. Org. Chem. USSR (Engl. Transl.)* **1981**, *17*, 2284.

(8) There are two isomeric homodiamantanes, pentacyclo[7.4.1.1^{4,13}.0^{2,7}.0^{6,11}]pentadecane (i) and pentacyclo[7.4.1.1^{4,13}.0^{2,7}.0^{6,12}]-pentadecane (ii). We use the new trivial names 1(2)-homodiamantane for i and 2(3)-homodiamantane for ii, respectively, for convenience.



(9) Gund, T. M.; Nomura, M.; Schleyer, P. v. R. *J. Org. Chem.* **1974**, *39*, 2987. Gund, T. M.; Schleyer, P. v. R.; Unruh, G. D.; Gleicher, G. J. *Ibid.* **1974**, *39*, 2995 and references cited therein.

(10) (a) Michl, J.; Radziszewski, G. J.; Downing, J. W.; Wiberg, K. B.; Walker, F. H.; Miller, R. D.; Kovacic, P.; Jawdosiuk, M.; Bonacic-Koutecky, V. *Pure Appl. Chem.* **1983**, *55*, 315. (b) Dunkin, I. R.; Shields, C. J.; Quast, H.; Seiferling, B. *Tetrahedron Lett.* **1983**, *24*, 3887. See also: (c) Sheridan, R. S.; Ganzer, G. A. *J. Am. Chem. Soc.* **1983**, *105*, 6158.

(11) For acetylation of 4-azahomoadamantan-3-ol to the corresponding ketoamide, see: Padegimas, S. J.; Kovacic, P. *J. Org. Chem.* **1972**, *37*, 2672. Cf. also ref 4f.

the sample obtained from the acidolysis of **1**. The formation of **12** is evidently due to hydrolysis of methoxy amine **17** as an initial methanol adduct to the bridgehead imine **15** as discussed below. As a second product, *N*-methyl derivative **19**, was obtained in 27% yield. The ^1H NMR spectrum of **19** revealed a characteristic singlet for 3 H at δ 2.57 assignable to NCH_3. The other ^1H NMR signals and 15 resonances in the ^{13}C NMR spectrum led us to assign **19** as the N-methylated product of **12**. This structure was confirmed by the formation of **19** on methylation of **12** with MeI–alkali. Furthermore, a stable methoxy imine, **20**, was obtained (9%) as the third product. ^{13}C NMR spectrum of **20** exhibited 11 lines, indicating the inherent C_s symmetry of the molecule. This fact suggested that **20** should be derived from 11-aza-2(3)-homodiamant-11-ene (**16**) as the alternative initial ring-expansion product of **1**. The appearance of the characteristic ^1H NMR doublet for 1 H at δ 8.20 (J = 6 Hz) as well as the ^{13}C NMR doublet for 1 C at δ 169.3 indicated the 11-aza-10-ene structure of **20**.[12] Furthermore, appearance of a singlet ^1H NMR signal at δ 3.31 (3 H) due to a OCH_3 group and of a singlet ^{13}C NMR signal at δ 93.5 assignable to the quaternary C_{12} led us to determine the structure of **20** as shown. Although none of the expected methoxy amines **17** and **18** as the direct methanol adduct to bridgehead imines **15** and **16**, respectively, were isolated in the above photolysis of **1** in methanol, the ^1H NMR spectrum of the crude photolysate revealed a strong singlet at δ 3.26 assignable to the OCH_3 group of **17** but no signals around δ 2.57 due to the NCH_3 group.[13] $LiAlH_4$ reduction of the crude photolysate in refluxing tetrahydrofuran unexpectedly afforded *N*-methyl amine **21** instead of **13** in 45% yield along with uncharacterized side products. These facts indicate that methoxy amine **17** was the primary photoproduct but that isomerization to **19** and hydrolysis to **12** occur during alumina chromatography. Also, in the $LiAlH_4$ reduction, the isomerization takes precedence over reduction of **17** to **13**. Such a novel isomerization[14] of **17** to **19** and facile hydrolysis of **17** to **12** may be ascribed to steric repulsion and geometrical constraints, although the detailed mechanism remains to be clarified.

Photolysis of **1** under phase-transfer-catalyzed hydrocyanation conditions afforded amino nitrile **22** (43%) along with many uncharacterized side products.

The ratio of isolated products[15] suggests only a regioselective photo-ring expansion of **1** (in favor of intermediate **15**) in contrast to the regiospecificity observed in expansion of the symmetrical azide **2**. The importance of conformation on the regioselectivity of the photorearrangement of alkyl azides has been postulated by Abramovitch and Kyba.[16] However, there seems to be little energy difference between the conformers leading to **15** and **16** for the present instance, and other factors such as geometrical constraint and ring strain may influence the regiochemistry also.[17]

In summary, symmetrical bridgehead azide **2** affords 10-aza-2(3)-homodiamantane derivatives by both acidolysis and photolysis, while unsymmetrical azide **1** gives exclusively 12-aza-1(2)-homodiamantane derivative **12** by acidolysis and a rather complex mixture involving **12**, *N*-methyl derivative **19**, and 11-aza-2(3)-homodiamant-10-ene derivative **20** by photolysis.

Experimental Section[18]

1-Azidodiamantane (1). To a stirred and ice-cooled suspension of 1-diamantanol (**3**;[9] 204 mg, 1.00 mmol) in $CHCl_3$ (5 mL) and 57% H_2SO_4 (2 mL) was added portionwise solid NaN_3 (300 mg, 4.62 mmol). After the stirring was continued for 2 days at room temperature, the mixture was diluted with water (20 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined extracts were washed with saturated aqueous $NaHCO_3$ solution and dried (Na_2SO_4). Removal of the solvent under water aspirator pressure on a rotary evaporator and chromatography of the residue on a short silica gel column (*n*-hexane–CH_2Cl_2) gave the azide **1** as colorless crystals: 180 mg (79%); mp 113–116 °C; IR (KBr) 2910, 2085, 1440, 1255 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.3–1.3 (m): mass spectrum, m/e (relative intensity) 201 ($M^+ - N_2$, 18), 188 (38), 105 (35), 94 (38), 91 (50). Anal. Calcd for $C_{14}H_{19}N_3$: C, 73.32; H, 8.35; N, 18.32. Found: C, 73.39; H, 8.38; N, 18.13.

4-Azidodiamantane (2). Treatment of 4-diamantanol (**4**;[9] 100 mg, 0.49 mmol) with NaN_3 (250 mg, 3.85 mmol) in $CHCl_3$ (5 mL) and 57% H_2SO_4 (5 mL) for 2 days and a workup as above gave the azide **2** as colorless crystals: 85 mg (76%); mp 84–86 °C; IR (KBr) 2910, 2852, 2075, 1440, 1255 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.98 (br s, 3), 1.9–1.6 (m, 16); mass spectrum, m/e (relative intensity) 201 ($M^+ - N_2$, 36), 187 (100), 93 (36), 91 (44), 79 (40). Anal. Calcd for $C_{14}H_{19}N_3$: C, 73.32; H, 8.35; N, 18.32. Found: C, 73.36; H, 8.49; N, 18.17.

9-Methoxy-10-aza-2(3)-homodiamantane (6). A stirred solution of **2** (75 mg, 0.33 mmol) in methanol (90 mL) was irradiated with a 100-W high-pressure mercury lamp through a Vicor filter at room temperature under argon for 2 h (GLC monitors). After removal of the solvent under reduced pressure, the residue was chromatographed on a neutral alumina (Woelm, activity grade III) column, eluting with C_6H_6–CH_2Cl_2 to give the methoxy amine **6** as colorless crystals: 68 mg (82%); mp 111–113 °C; IR (KBr) 3420, 3310, 2905, 2870, 1075 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.22 (s, 3), 2.98 (d, J = 4 Hz, 2), 2.0–1.5 (m, 17), 1.58 (s, 1, disappeared on shaking with D_2O); ^{13}C NMR ($CDCl_3$) δ 86.7 (s, 1C), 49.6 (t, 1 C), 47.3 (q, 1 C), 46.3 (d, 1 C), 44.9 (t, 2 C), 40.0 (t, 2 C), 39.2 (d, 2 C), 38.3 (t, 1 C), 36.9 (d, 2 C), 36.7 (d, 1 C), 26.9 (d, 1 C); mass spectrum, m/e (relative intensity) 233 (M^+, 22), 218 (100), 204 (49), 203 (49), 202 (53), 106 (35), 91 (51), 77 (39), 57 (40), 55 (35), 43 (39). Anal. Calcd for $C_{15}H_{23}NO$: C, 77.21; H, 9.94; N, 6.05. Found: C, 77.21; H, 9.90; N, 6.05.

9-Cyano-10-aza-2(3)-homodiamantane (7). A vigorously stirred mixture of **2** (93 mg, 0.41 mmol), NaCN (5 g, 10 mmol),

(12) For spectral data of 4-azahomoadamant-4-ene, see ref 3b and 4d.

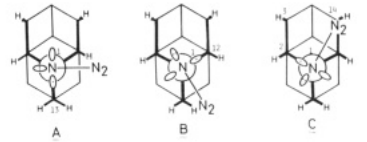
(13) Several unassignable weak signals also appeared at around the methoxy proton region.

(14) For a review on 1,3-alkyl migrations, see: Landis, P. S. "Mechanism of Molecular Migrations"; Thyagarajan, B. S., Ed.; Interscience: New York, 1969; Vol. 2, pp 43–63.

(15) We assume tentatively that the methoxyimine **20** is derived from the imine **16** presumably via photoisomerization to 11-aza 10-imine followed by oxidation and addition of MeOH and/or via photooxidation of **18**, although the reported photoisomerization of strained 4-azahomoadamant-3-ene to the stable 4-imine[10a] seems to be quite complicated. We thank one of the referees for this information. For oxidation of amines, see: Chow, Y. L. "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum: New York, 1980; Vol. 1, Chapter 3. For facile air oxidation of 5-benzyl-4-azahomoadamant-4-ene, see ref 4d.

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

(17) Among three possible conformers A–C leading to bridgehead imines based on the Abramovitch–Kyba model, C (C_{1-2} bond migration to **15**) must be the most unfavorable one because of steric repulsion between N_2 and H_{3syn} (H_{14syn}); however, there seems no decisive difference between A (C_{1-13} bond migration to **16**) and B (C_{1-12} bond migration to **15**).



(18) Melting points were taken in a sealed tube on a Yanagimoto micromelting 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 JEOL 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. Mass spectra were obtained with a JEOL JMS-D10 mass spectrometer at 75 eV. Microanalyses were carried out by using a Perkin-Elmer 240B elemental analyzer. GLC analyses were performed with a JEOL JGC-20K gas chromatograph on a 1- or 2-m silicone SE-30 column at 180–250 °C.

and Adogen 464 (0.3 mL) in *n*-hexane (250 mL) and water (30 mL) was irradiated with a 100-W high-pressure mercury lamp through a Quartz filter at room temperature under argon for 2.6 h (GLC monitored). The organic layer was separated, and the aqueous layer was extracted with ether (2 × 50 mL). The combined organic layer and extracts were washed successively with saturated NaCl solution and water and dried ($MgSO_4$). After removal of the solvent, the oily residue was chromatographed on a silica gel column (CH_2Cl_2–AcOEt) to give the amino nitrile **7** as colorless crystals: 21 mg (23%); mp 148–150 °C; IR (KBr) 3400, 2905, 2225, 1445 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.06 (d, J = 4 Hz, 2), 2.93 (s, 1, D_2O exchangeable), 2.3–1.5 (m, 17); mass spectrum, m/e (relative intensity) 228 (M^+, 100), 227 (38). Anal. Calcd for $C_{15}H_{20}N_2$: C, 78.90; H, 8.83; N, 12.27. Found: C, 78.72; H, 8.60; N, 12.09.

9-Hydroxy-10-aza-2(3)-homodiamantane (9). To an ice-cooled stirred solution of azide **2** (76 mg, 0.33 mmol) in $CHCl_3$ (2 mL) was added 97% H_2SO_4 (0.3 mL) dropwise, and the stirring was continued for 2 h at room temperature. The mixture was diluted with water (10 mL), and the separated aqueous layer was washed with ether (10 mL), basified with 20% aqueous NaOH under ice cooling, and extracted with CH_2Cl_2 (4 × 10 mL). The combined extracts were washed with saturated aqueous NaCl solution and dried (Na_2SO_4). Removal of the solvent gave a residue which was recrystallized from benzene to afford **9** as colorless crystals: 66 mg (91%); mp 174–176 °C; IR (KBr) 3440, 3265, 2905, 2870, 1465, 1445, 1107, 1088 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.95 (d, J = 4 Hz, 2), 2.36 (br s, 2, D_2O exchangeable), 2.1–1.6 (m, 17); mass spectrum, m/e (relative intensity) 219 (M^+, 100), 204 (39), 202 (50), 201 (40). Anal. Calcd for $C_{14}H_{21}NO$: C, 76.67; H, 9.65; N, 6.39. Found: C, 76.79; H, 9.67; N, 6.24.

Acetylation of Amino Alcohol 9. A mixture of **9** (65 mg, 0.30 mmol) and acetic anhydride (1 mL) in pyridine (1 mL) was stirred at room temperature for 12 h and at 80 °C for 2 h. The mixture was diluted with water (40 mL) and extracted with CH_2Cl_2 (5 × 10 mL). The combined extracts were washed successively with saturated NaCl solution and 5% $NaHCO_3$ solution and dried (Na_2SO_4). Removal of the solvent and chromatography of the residue on an alumina (neutral, activity grade II–III) column, eluting with CH_2Cl_2–AcOEt, afforded 10-*endo*-[(acetylamino)-methyl]tetracyclo[7.3.1.$0^{3,8}$.$0^{4,11}$]tridecan-6-one (**10**) as colorless crystals: 38 mg (49%); mp 234–236 °C; IR (KBr) 3240, 3075, 2890, 1687, 1630, 1563 cm^{-1}; ^1H NMR ($CDCl_3$–Me_2SO-d_6) δ 7.7 (br m, 1, D_2O exchangeable), 2.92 (unsymmetrical t, J = 7 Hz, 2), 2.6–1.7 (m, 17), 1.80 (s, 3); mass spectrum, m/e (relative intensity) 243 ($M^+ - H_2O$, 54), 190 (100), 107 (38). Anal. Calcd for $C_{16}H_{23}NO_2$: C, 73.53; H, 8.87; N, 5.36. Found: C, 73.57; H, 8.89; N, 5.30.

11-Hydroxy-12-aza-1(2)-homodiamantane (12). Azide **1** (300 mg, 1.31 mmol) in $CHCl_3$ (5 mL) was treated with 97% H_2SO_4 (3 mL) for 2 h as above. The usual workup and recrystallization from benzene afforded **12** as colorless crystals: 266 mg (93%); mp 238–240 °C; IR (KBr) 3390, 3310, 2905, 1438, 1027 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.9 (m, 1), 2.29 (s, 2, D_2O exchangeable), 2.3–1.4 (m, 18); mass spectrum, m/e (relative intensity) 219 (M^+, 100), 190 (38), 94 (39), 91 (46). Anal. Calcd for $C_{14}H_{21}NO$: C, 76.67; H, 9.65; N, 6.39. Found: C, 76.56; H, 9.68; N, 6.38.

12-Aza-1(2)-homodiamantane (13). To an ice-cooled stirred suspension of $LiAlH_4$ (250 mg, 6.77 mmol) in anhydrous THF (20 mL) was added **12** (200 mg, 0.91 mmol) in THF (10 mL) under nitrogen. The mixture was heated to reflux for 20 h, and the cooled mixture was diluted with ether (50 mL) and 10% NaOH aqueous solution (2 mL), dried (Na_2SO_4), and filtered. The solid was washed with $CHCl_3$ (3 × 5 mL). The combined filtrate and washings were evaporated to give a solid residue which was dissolved in $CHCl_3$ (10 mL). The $CHCl_3$ solution was saturated with dry HCl gas and diluted with ether to afford the hydrochloride of **13** as colorless crystals: 181 mg (83%); mp >300 °C; IR (KBr) 3400, 2910, 2800–2650, 1590, 1435 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.5 (br s, 2, D_2O exchangeable), 4.0 (br s, 2), 2.6–1.5 (m, 18); ^{13}C NMR ($CDCl_3$) δ 55.3 (d), 40.0 (t), 36.6 (t), 35.7 (d), 31.9 (t), 24.8 (d) for each 2 C; mass spectrum, m/e (relative intensity) 203 (M^+ – HCl, 100), 202 (41). Anal. Calcd for $C_{14}H_{22}NCl$: C, 70.13; H, 9.25; N, 5.84. Found: C, 70.21; H, 9.12; N, 5.89.

Acetylation of 12. A mixture of **12** (60 mg, 0.26 mmol) and acetic anhydride (0.5 mL) in pyridine (0.5 mL) was stirred at room temperature overnight. The mixture was diluted with water (5 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined extracts were washed with water and dried (Na_2SO_4). Removal of the solvent gave a solid residue which was recrystallized from *n*-hexane–benzene to afford 11-hydroxy-12-acetyl-12-aza-1(2)-homodiamantane (**14**) as colorless crystals: 55 mg (80%); mp 99–101 °C; IR (KBr) 3250, 2905, 1608, 1438 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.76 (d, J = 1.5 Hz, 1, D_2O exchangeable), 3.8 (m, 1), 2.7–1.5 (m, 18); mass spectrum, m/e (relative intensity) 261 (M^+, 22), 243 (100), 91 (37). Anal. Calcd for $C_{16}H_{23}NO_2$: C, 73.53; H, 8.87; N, 5.36. Found: C, 73.45; H, 8.86; N, 5.28.

Photolysis of Azide 1 in Methanol. A solution of **1** (200 mg, 0.87 mmol) in methanol (90 mL) was irradiated under argon for 2.5 h as above (GLC monitored). After removal of the solvent under reduced pressure, the residue was dissolved in CH_2Cl_2 and was adsorbed on a short alumina (neutral) column overnight.[19] Elution with methanol and removal of the solvent gave a solid residue which was purified by successive chromatography on a silica gel columns, eluting with a CH_2Cl_2–AcOEt–MeOH solvent system to afford the following major products.

12-Methoxy-11-aza-2(3)-homodiamant-10-ene (20) was obtained as a colorless solid after solvent removal: 19 mg (9%); mp 87–91 °C; IR (neat film) 2905, 1680, 1668, 1438, 1095, 1078 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.20 (d, J = 6 Hz, 1), 3.31 (s, 3), 2.6–1.3 (m, 17); ^{13}C NMR ($CDCl_3$) δ 169.3 (d, 1 C), 93.5 (s, 1 C), 46.4 (q, 1 C), 39.9 (d, 2 C), 39.4 (d 1 C), 37.2 (d, 1 C), 36.6 (d, 2 C), 34.9 (t, 2 C), 34.5 (d, 1 C), 31.8 (t, 2 C), 25.5 (d, 1 C); mass spectrum, m/e (relative intensity) 231 (M^+, 11), 201 (100). Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 78.10; H, 8.98; N, 5.87.

11-Hydroxy-12-methyl-12-aza-1(2)-homodiamantane (19) was obtained as colorless crystals: 55 mg (27%); mp 196–199 °C; IR (KBr) 3400, 2905, 1463, 1058, 1035 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.9–2.6 (m, 1), 2.57 (s, 3), 2.5–1.3 (m, 18), 1.40 (s, 1, D_2O exchangeable); ^{13}C NMR ($CDCl_3$) δ 88.5 (s), 59.9 (d), 47.0 (q), 40.6 (t), 39.1 (d), 38.7 (d), 38.5 (d), 38.1 (t), 37.3 (t), 36.7 (d), 36.1 (t), 32.9 (t), 29.5 (t), 27.2 (d), 25.7 (d) for each 1 C; mass spectrum, m/e (relative intensity) 233 (M^+, 100), 218 (39). Anal. Calcd for $C_{15}H_{23}NO$: C, 77.21; H, 9.94; N, 6.00. Found: C, 77.48; H, 9.78; N, 5.89.

The last fractions gave an amino alcohol as colorless crystals after recrystallization from benzene (78 mg, 41%), which was identical with **12** prepared from **1** by acidolysis on IR and ^1H NMR spectral and TLC comparisons.

Some other minor products could not be characterized.

12-Methyl-12-aza-1(2)-homodiamantane (21). The crude photolysate obtained from azide **1** (200 mg, 0.87 mmol) was added to a mixture of $LiAlH_4$ (300 mg, 7.90 mmol) in THF (15 mL) with ice cooling and stirring under nitrogen. The mixture was heated to reflux for 22 h. The cooled mixture was treated with 10% NaOH solution in order to decompose the excess reagent, and the resulting precipitates were filtered and washed with CH_2Cl_2 (2 × 10 mL). The aqueous layer of the filtrate was separated and extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layer, washings, and extracts were dried (Na_2SO_4). Removal of the solvent gave a solid residue which was chromatographed on a neutral alumina column (activity grade III, CH_2Cl_2–AcOEt) to afford the amine **21** as a colorless solid: 86 mg (45%); mp 208–211 °C; IR (KBr) 2890, 1457, 1435, 1388, 1237 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.0–2.7 (m, 2), 2.60 (s, 3), 2.3–1.2 (m, 18); ^{13}C NMR ($CDCl_3$) δ 61.6 (d, 2 C), 43.6 (q, 1 C), 38.6 (t, 2 C), 38.1 (d, 2 C), 37.1 (d, 2 C), 36.3 (t, 2 C), 33.8 (t, 2 C), 26.2 (d, 2 C); mass spectrum, m/e (relative intensity) 217 (M^+, 100), 216 (62). Anal. Calcd for $C_{15}H_{23}N$: C, 82.89; H, 10.67; N, 6.44. Found: C, 82.73; H, 10.59; N, 6.35.

Methylation of Amino Alcohol 12. A mixture of **12** (50 mg, 0.23 mmol) and methyl iodide (0.5 mL) in ether (10 mL) was allowed to stand overnight at room temperature. Removal of the solvent and excess methyl iodide gave a crystalline residue which was treated with 10% NaOH aqueous solution and ether (5 + 10 mL). The organic layer was separated, and the aqueous layer was extracted with ether (10 mL). The combined organic layer and extracts were dried (Na_2SO_4). Removal of the solvent gave a

(19) Elution without appropriate standing time gave a more complex mixture of products due to incomplete isomerization and hydrolysis.

residue which was chromatographed on a neutral alumina (activity I, CH_2Cl_2–AcOEt) column to afford the *N*-methyl derivative **19** (28 mg, 53%) which was identical with the sample obtained from **1** (IR and ^1H NMR spectral comparison).

11-Cyano-12-aza-1(2)-homodiamantane (22). A vigorously stirred mixture of azide **1** (225 mg, 0.98 mmol), NaCN (5 g, 102 mmol), and Adogen 464 (0.3 mL) in water (60 mL) and *n*-hexane (200 mL) was irradiated as above for 3.5 h. The workup and chromatography on a silica gel column (CH_2Cl_2–AcOEt) afforded the amino nitrile **22** as colorless crystals: 96 mg (43%); mp 186–188 °C; IR (KBr) 3355, 2920, 2230, 1437, 1138 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.3–3.0 (m, 1), 1.98 (s, 1, D_2O exchangeable), 2.5–1.3 (m, 18); mass spectrum, *m/e* (relative intensity) 228 (M^+, 100), 227 (38). Anal. Calcd for $C_{15}H_{20}N_2$: C, 78.90; H, 8.83; N, 12.27. Found: C, 78.71; H, 8.96; N, 12.07.

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Registry No. **1**, 87999-44-8; **2**, 87999-45-9; **3**, 30545-19-8; **4**, 30651-03-7; **6**, 87999-46-0; **7**, 87999-47-1; **9**, 87999-48-2; *endo*-**10**, 87999-49-3; **12**, 87999-50-6; **13**, 87999-51-7; **13**·HCl, 87999-52-8; **14**, 87999-53-9; **19**, 87999-55-1; **20**, 87999-54-0; **21**, 87999-56-2; **22**, 87999-57-3.

Conversions of *N*-Vinylpyridinium Cations into Tricyclic Cage Compounds

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1-Allyl-2,4,6-trimethyl- and 1-allyl-2,4,6-triphenylpyridinium cations are isomerized by mild alkali into the corresponding 1-propenylpyridinium cations. Strong base converts the latter and 1-vinyl-2,4,6-triphenylpyridinium cation salts into oxazatricyclononene isomers of the quaternary hydroxides. The elucidation of the structure and further transformations of the cage compounds are described.

Following our work on the preparation of *N*-vinylpyridiniums by dehydration of *N*-(2-hydroxyethyl)-pyridiniums,[1] we studied the base-catalyzed isomerization of *N*-allylpyridiniums. Not only did the isomerization succeed, but we also found that *N*-vinylpyridinium hydroxides undergo a remakable series of further transformations, which we have now elucidated.

Preparation of *N*-Allylpyridiniums (Table I). *N*-Allylpyridiniums **1**, **2a**, **2b**, **3**, **4**, and **5** were prepared from allylamine and the corresponding pyryliums by using the standard conditions.[2]

In view of the unusual transformations to be described, we obtained further[3] evidence to confirm the structures of the *N*-allylpyridinium salts. The ^1H NMR spectra[4a] for the *N*-allylpyridinium salts displayed as expected the pyridinium C-3 and C-5 proton signals as singlets in **1**, **2a**, **3**, and **4** (Chart I), as doublets in **2b**, and as multiplets in 1-allylpyridinium bromide. The remaining aromatic protons formed multiplets at δ 7.0–8.1.

The stepwise increase in the chemical shifts of the —CH= allyl proton signal in the sequence **4**, **2a**, **2b**, **1**, 1-allylpyridinium bromide, and **5** (found at δ 5.4, 5.45, 5.9, 6.0, 6.2, and 6.3 respectively) mirrors the shielding effect exerted by the phenyl groups in conformations where the —CH= hydrogens are above the phenyl rings. Such effects are smaller on the terminal allylic hydrogens (—C=CH_2). The cis terminal proton, in transoid relationship to the chemical bond linking the vinyl group to N^+–CH_2, resonates at lower field than the trans allylic.[3]

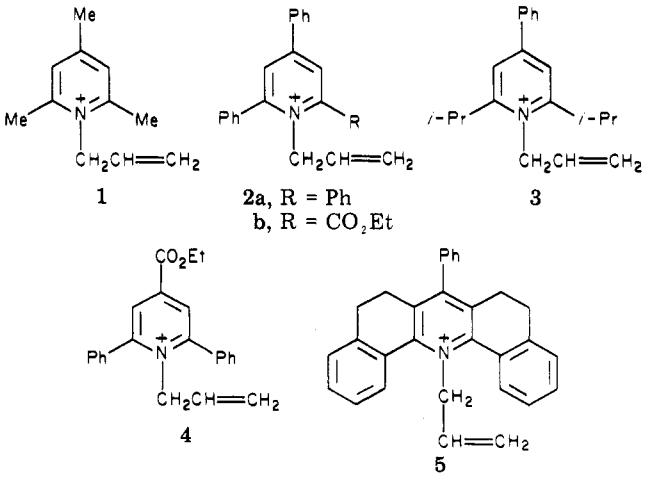
The infrared spectra of the *N*-allylpyridinium salts showed characteristic bands 1630–1600 cm^{-1} due to the pyridinium ring stretch and a strong and broad band due to the BF_4^- at 1050 cm^{-1}. The pyridinium salts **2b** and **4** b showed the ν C=O band at 1730 and 1735 cm^{-1}, respectively.

Table I. Physical Data of *N*-Allylpyridinium Salts

compd	yield, %	mp, °C	recrystallization solvent[a] (crystal form)	molecular formula[b]
1	72	81-83	C-E (P)	$C_{11}H_{16}BF_4N$
2a	68	164-166[c]	A-E (N)	$C_{26}H_{22}BF_4N$
2b	70	162-164	A-E (N)	$C_{23}H_{22}BF_4NO_2$
3	83	122	C-E (Pl)	$C_{20}H_{26}BF_4N$
4	64	166-168	A-E (N)	$C_{23}H_{22}BF_4NO_2$
5	72	202-204	EtOH (Pl)	$C_{30}H_{26}BF_4N$

[a] A = acetone; C = CH_2Cl_2; E = Et_2O; P = prisms; Pl = plates; N = needles. [b] Satisfactory analytical values (±0.2% for C, H, N) were reported for all salts. [c] Lit. mp 169-170 °C, Katritzky, A. R.; Cook, M. J.; Ikizler, A.; Millet, G. H. *J. Chem. Soc. Perkin Trans. 1* **1979**, 2501.

Chart I[a]



[a] 1-4 are tetrafluoroborates.

Isomerization of *N*-Allyl- to *N*-Vinylpyridiniums. 1-Propenylpiperidine is ca. 5 kcal more stable than 1-al-

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(4) Included in the supplementary material of this paper: (a) Table II of NMR data of *N*-allylpyridinium salts. (b) Scheme III of mass spectrum of **29**.

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