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Rearrangement of 1-Noradamantyl and 1-Adamantylcarbene to Bridgehead Alkenes: Lifetimes of Two Bridgehead Carbenes in Solution

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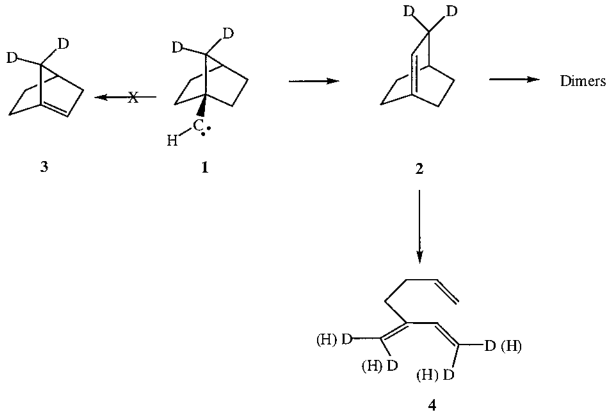
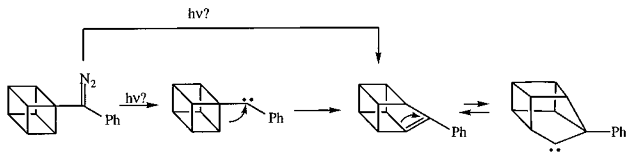
B3LYP density functional calculations with the 6-31G* basis set predict that 3-noradamantylcarbene **7** rearranges to adamantene **9** and protoadmant-3-ene **10** over barriers of 0.35 and 7.84 kcal/mol, respectively, after zero-point energy correction. The same level of theory predicts that 1-adamantylcarbene **8** rearranges to homoadamantene **11** over a barrier of 6.06 kcal/mol after zero-point energy correction. To test these predictions, the photochemistry of 3-noradamantyldiazirine **5** and 1-adamantyldiazirine **6** was studied. Photolysis of **5** and **6** in cyclohexane produces the known dimers of the strained alkenes. 1-Adamantylcarbene **8** can be trapped in solution with cyclohexane and piperidine. 1-Adamantylcarbene **8** can be trapped with pyridine to form an ylide upon laser flash photolysis (LFP) of **6**. 3-Noradamantylcarbene **7** cannot be intercepted with pyridine in LFP experiments. 3-Noradamantylcarbene **7** is not trapped with cyclohexane and is trapped with piperidine in only miniscule yield. The data indicates that 1-adamantylcarbene **8** is formed more efficiently from its diazirine precursor than is 3-noradamantylcarbene **7** and that the solution-phase lifetime of 1-adamantylcarbene **8** is at least 10 times longer than that of 3-noradamantylcarbene **7**.

I. Introduction

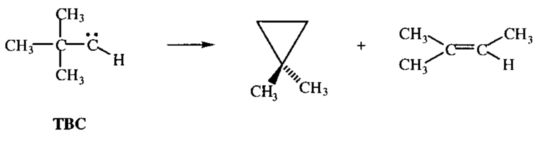
Chemists have been fascinated with bridgehead alkenes ever since Bredt promulgated his famous rule in 1924.[1] Carbene chemists have attempted to form bridgehead alkenes from bridgehead carbenes with considerable success, as illustrated below with 1-norbornylcarbene **1**.[2] In this case, the unstable bridgehead alkene rearranges to form a mixture of dideutero compounds where the labels ultimately reside in two possible positions. The analogous bridgehead nitrene-to-imine rearrangement has also been studied.[3]



Wilt attempted to generate the hydrocarbon variant of **1** from the tosylhydrazone salt precursor but was unable to identify carbene- or alkene-related products.[4] Kirmse et al. prepared the 7,7-dimethyl derivative of **1** in solution and isolated the dimers of the strained alkenes.[5] The Jones group prepared **1**-d_2 in the gas phase and isolated **4**-d_2, which arose by retro-Diels−Alder fragmentation of alkene **2**.[6] This result implies that the short bond of **1** migrates selectively, a result which has been successfully modeled by the calculations of Hadad and Sziemies[7] and their co-workers. Cubylphenylcarbene cannot be chemically trapped. Either it rearranges to homocubene too rapidly to permit efficient bimolecular chemistry or it is not formed efficiently from its diazo precursor.[8,9] Related rearrangements are known in the parent system and with homocubylcarbene.[9]



tert-Butylcarbene (TBC) has been studied in great detail. It isomerizes to trimethylethylene and 1,1-dimethylcyclopropane in the gas phase and in solution.[10] Ruck and Jones have shown that solvent modulates the ratio of products formed.[11]



TBC has no known bimolecular chemistry because the migration reactions traverse very small barriers and are extremely rapid. Armstrong et al. calculated that the reactions of TBC surmount barriers of 3.7 and 0.1 kcal/mol to form trimethylethylene and 1,1-dimethylcyclopropane, respectively.[12]

It can be posited that the strain developing in the bridgehead alkene products might raise the barrier to bridgehead carbene rearrangement relative to TBC, reduce the speed of the rearrangement, and increase the chances of detecting or trapping the bridgehead carbenes **7** and **8**. This led us to study the photochemistry of diazirines **5** and **6**. These diazirines were expected to provide entry to carbenes **7** and **8** which are known

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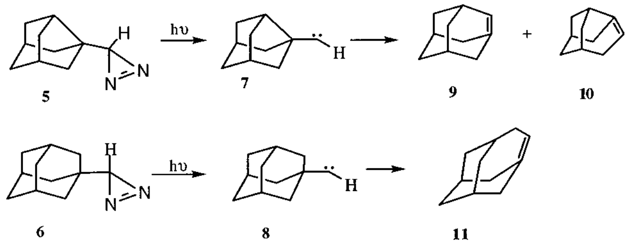


to rearrange to strained alkenes **9**−**11**.[2] Furthermore, diazirine precursors are convenient for laser flash photolysis (LFP), matrix isolation, and chemical trapping studies. Herein, we are pleased to report our results.

II. Experimental Section

General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-200 MHz or on a Bruker DRX-500 MHz spectrometer. Chemical shifts are reported in ppm with tetramethylsilane as an internal standard. Infrared spectra were recorded using a Perkin-Elmer 1710 Fourier transform spectrometer interfaced with a Perkin-Elmer 3700 data station. UV−vis spectra were recorded on a Milton-Roy Spectronic 3000 diode array spectrophotometer. GC−MS mass spectral analyses were performed on a Hewlett-Packard 6890 GC spectrometer with an HP-1 methylsiloxane capillary column (i.d. 100 μm, length 40 m, phase film thickness 0.25 μm) and a HP 5973 mass selective detector. Three kinds of lasers were used to perform LFP experiments: a Lambda Physik LPX-100 excimer laser (308 nm, 120 mJ, 17 ns), a Lumonics TE-861 excimer laser (351 nm, 60 mJ, 17 ns), and a Continuum PY62C-10 Nd:YAG laser (355 nm, 30 mJ, 2 ns).

All reagents were purchased from commercial sources and used without purification unless noted otherwise. All reactions were carried out in flame-dried flasks under an argon atmosphere. 1-Adamantanecarboxylic acid was purchased from Aldrich. Freon-113 was purified by passage through a neutral alumina column just prior to use. Diethyl ether, tetrahydrofuran, and cyclohexane were distilled over sodium and benzophenone and stored under argon. Methanol was distilled from sodium methoxide. Pyridine was refluxed over potassium hydroxide and then distilled. It was stored protected from light in a brown bottle with potassium hydroxide under an atmosphere of dry argon. Pentane was distilled over P_2O_5. Dichloromethane was distilled from CaH_2 and stored protected from bright light in a brown bottle with Linde type 4 Å molecular sieves and under an argon atmosphere. Piperidine was dried by distillation prior to use. All distillations were performed under an inert argon atmosphere.

Synthesis. *3-Noradamantyldiazirine (5)*[13a−c] was synthesized by the method of Likhotvorik et al.[13d] and Tae et al.[14] Methyl ethers **15** and **17**[15] were synthesized and had spectral properties consistent with those described in the literature. An authentic sample of Diels−Alder adduct **23** was generously provided by Professor Jones of Princeton University.

1-Adamantyldiazirine (6).[13] The diazirine was synthesized by the procedure of Likhotvorik et al.[13d] 1-Adamantane carboxaldehyde (0.65 g, 4 mmol) was dissolved in 12 mL of anhydrous THF. The solution was cooled to 0 °C with an ice bath, placed under an argon atmosphere, and protected from direct light with foil paper. A lithium bis(trimethylsilyl)amide (1 M) solution in THF (8 mL, 8 mmol) was added dropwise via syringe. The reaction mixture was stirred for 30 min at 0 °C and then cooled to −30 °C. A solution of hydroxylamine-*o*-sulfonic acid (0.48 g, 4 mmol) in dry diglyme (5 mL) was then added dropwise. The mixture was allowed to warm to 0 °C and was then stirred for an additional 30 min. A solution of freshly prepared *tert*-butylhypochlorite (0.45 mL, 4 mmol) in *tert*-butanol (0.5 mL) was then added via syringe. For small-scale reactions, *tert*-butylhypochlorite was added in one portion, but for larger-scale (10 mmol or more) reactions, the addition was performed dropwise to prevent explosive decomposition of the diazirine. The solution was stirred at 0 °C for 1 h more, poured over crushed ice, and then extracted with pentane. The combined organic solutions were washed several times with water and brine and then dried over sodium sulfate. After removal of the solvent in vacuo, the crude diazirine (yellow liquid) was purified by column chromatography on silica gel with pentane as the eluant. The purification process was monitored by the UV absorption at 350 nm of the fractions collected. In this manner, 0.29 g (42%) of a colorless liquid, which was pure by GC−MS, was collected. The diazirine was stored in the freezer, in the dark, and under an argon atmosphere. ^{1}H NMR ($CDCl_3$): δ 0.41 (s, 1H), 1.29 (m, 6H), 1.51 (m, 3H), 1.60 (m, 3H), 1.86 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 28.32, 29.79, 31.80, 36.94, 39.64. IR: 1588 cm^{-1}. UV (pentane): max 340 and 352 nm. Anal. GC−MS: [M^+] calcd for $C_{11}H_{16}N_2$, 176.1317; found, 1 peak, 176.13040.

Isolation of the Dimers of Homoadamantene (11).[16] 1-Adamantyldiazirine **6** (250 mg) was dissolved in 15 mL of cyclohexane. The mixture was photolyzed overnight at 350 nm in a cold room at 4 °C. A GC−MS study revealed one major peak for the cyclohexane insertion adduct ($M^+ = 232$), four peaks (two intense and two smaller ones) for the dimers of homoadamantene ($M^+ = 296$), and other unidentified impurities. The solution was concentrated in vacuo. The crude mixture was purified by preparative TLC using UV−vis active silica plates and hexane as the eluant. The top layer of silica was extracted with hexane. GC−MS analysis showed the presence of only the cyclohexane adduct and the major dimers of homoadamantene. It was possible to obtain a mixture of the two major dimers by successive recrystallization from 2-propanol, but this mixture could not be separated further. The dimers did not contain resonances due to alkenyl carbons or protons.

N-(3-Noradamantyl)piperidine (14). 3-Noradamantyl carboxylic acid (104 mg, 0.626 mmol) in 5 mL of dicloromethane was stirred with 258 mg (2.0 equiv) of dicyclohexylcarbodiimide (DCC), 10 mg of *p*-(dimethylamino)pyridine (DMAP), and 213 mg (4 equiv) of piperidine. The mixture was stirred for 2 h, and the amide product was purified by column chromatography (elution with 30% ethyl acetate in hexanes). The amide was reduced by 24 mg (0.626 mmol) of lithium aluminum hydride (LAH) in refluxing ether for 2 h, quenched with a 5% aqueous sodium hydroxide solution, filtered, and concentrated. The mixture was column chromatographed (elution with 50% EtOAc in hexanes).The yield of the amine was 91%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.42 (br s, 6H), 2.16 (s, 2H), 1.97 (m, 1H), 1.71−1.10 (m, 16H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 67.2, 55.9, 49.1, 48.5, 43.83, 43.80, 37.4, 35.5, 26.0, 24.2. MS (EI) *m/z* (rel intensity): 219 (M^+, 18), 135 (5), 98 (100), 84 (20). HRMS (EI): [M^+] calcd for $C_{15}H_{25}N$, 219.1987; found, 219.1981.

1-Methoxyadamantane (15).[15] 1-Adamantanol (0.15 g, 1 mmol) was mixed with 60% of NaH (0.08 g, 2 mmol) and CH_3I (2 mL) in tetrahydrofuran (THF). It was stirred overnight. The mixture was chromatographed (10% ethyl acetate in hexane). The yield was 99%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.20 (s, 3H), 2.12 (s, 3H), 1.71 (s, 6H), 1.62 (d, 3H, $J = 12.2$ Hz), 1.57 (d, 3H, $J = 12.2$ Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 71.8, 47.7, 40.9, 36.4, 30.4. MS (EI) *m/z* (rel intensity): 166 (M^+, 42), 135 (9), 109 (100), 94 (9), 79 (10).

*3-Noradamantyl Methyl Ether (**16**).* 3-Noradamantyl carboxylic acid (0.166 g, 1 mmol) was refluxed with LAH (0.15 g, 4 mmol) in THF overnight. It was worked up using a 5% aqueous sodium hydroxide solution. 3-Noradamantyl alcohol was isolated by column chromatography (33% ethyl acetate in hexane). The yield was 99%. The alcohol (0.15 g, 1 mmol) was mixed with 60% of NaH (0.08 g, 2 mmol) and CH_3I (2 mL) in THF. It was stirred overnight. The mixture was chromatographed (10% ethyl acetate in hexane). ^1H NMR (300 MHz, $CDCl_3$): δ 3.37 (s, 2H), 3.36 (s, 3H), 2.20 (s, 2H), 2.12 (t, 1H, $J = 6.7$ Hz), 1.72 (m, 2H), 1.60 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 79.9, 59.5, 49.8, 46.8, 44.1, 41.4, 37.7, 35.7. MS (EI) *m/z* (rel intensity): 166 (M^+, 17), 134 (52), 123 (37), 93 (100), 79 (74). HRMS (EI): calcd for $C_{11}H_{18}O$, 166.1358; found, 166.1356.

*2-Methoxyadamantane (**17**).*[15] 2-Adamantanone (0.75 g, 5 mmol) was stirred with LAH (0.19 g, 1 mmol) in ether overnight and quenched with a 5% aqueous sodium hydroxide solution. 2-Adamantyl alcohol was mixed with 60% of NaH (0.3 g, 1.2 equiv) and CH_3I (2 mL) in THF and stirred overnight. The mixture was chromatographed (10% EtOAc in hexane). The yield was 99%. ^1H NMR (500 MHz, $CDCl_3$): δ 3.33 (s, 3H), 3.32 (s, 1H) 2.01 (m, 4H), 1.9−1.6 (m, 8H), 1.45 (d, 2H, $J =$ 11.1 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 83.2, 55.2, 37.6, 36.5, 31.4, 31.3, 27.5, 27.4. MS (EI) *m/z* (rel intensity): 166 (M^+, 18), 134 (100), 119 (23), 92 (50), 79 (36).

*1-Adamantyl Acetate (**18**).* 1-Adamantanol (0.154 g, 1.01 mmol) was mixed with acetic anhydride (0.144 mL, 1.53 mmol), pyridine (0.165 mL, 2.04 mmol), and DMAP (20 mg) in 5 mL of dichloromethane. The mixture was stirred for 2 h and then was chromatographed (20% ethyl acetate in hexanes). ^1H NMR (200 MHz, $CDCl_3$): δ 2.07 (m, 9H), 1.96 (s, 3H), 1.59 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.5, 79.9, 41.1, 36.0, 30.6, 22.4. MS (EI) *m/z* (rel intensity): 194 (M^+, 1), 134 (100), 119 (17), 105 (15), 92 (90), 79 (35).

*3-Protoadamantyl Alcohol (**19**).*[17] Photolysis of 3-noradamantyldiazirine **5** in neat acetic acid produced almost equal amounts of adamantyl acetate **18** and protoadamantyl acetate **21**. The mixture was reduced by 2 equiv of LAH and purified by column chromatography (30% ethyl acetate in hexane). The mixture of adamantanol and protoadamantanol was separated using MPLC. ^1H NMR (300 MHz, $CDCl_3$): δ 2.50−2.30 (m, 2H), 2.10−1.5 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 79.9, 48.2, 44.6, 40.1, 39.4, 36.4, 33.4, 32.4, 27.8, 27.7. MS (EI) *m/z* (rel intensity): 191 (M^+, 1), 155 (2), 131 (3), 108 (100), 55 (29). ^1H NMR (300 MHz, $CDCl_3$): δ 2.24−2.15 (m, 2H), 2.07−1.27 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 79.6, 48.0, 44.4, 39.8, 39.2, 36.2, 33.2, 32.1, 27.6, 27.5.

*3-Protoadamantyl-p-nitrobenzoate (**20**).* 3-Protoadamantyl alcohol (30 mg) was mixed with 0.2 mL of pyridine, 50 mg of DMAP, and 100 mg of *p*-nitrobenzoyl chloride in 2 mL of dichloromethane. The mixture was refluxed for 7 h and then chromatographed (10% ethyl acetate in hexane). The yield was 72%. Mp: 182−184 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 8.25 (d, 2H, $J_{AB} = 8.7$ Hz), 8.16 (d, 2H, $J_{AB} = 8.7$ Hz), 2.55−1.35 (series of m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.2, 150.5, 137.5, 130.7, 123.6, 91.5, 46.2, 41.7, 39.8, 39.1, 35.8, 33.1, 27.6, 27.4, 26.7. HRMS (EI): calcd for $C_{17}H_{19}NO_4$, 301.1314; found, 301.1315.

*1-Adamantylcyclohexane (**24**).* 1-Adamantyldiazirine **6** (100 mg, 0.57 mmol) was dissolved in 2.1 mL of cyclohexane (freshly distilled over sodium) in a 3 mL glass vial. The solvent was not degassed. The vial was exposed to 350 nm radiation for 26 h. The progress of the reaction was monitored by observing the disappearance of the diazirine absorption at 340 nm. The cyclohexane was evaporated to give a crude orange mixture. The crude mixture was chromatographed on silica gel with pentane elution. The solvent was evaporated to yield 47−61 mg of white crystals. This mixture was sublimed for 1.5 h at 55 °C and 2.3 mmHg. This afforded 9 mg of pure cyclohexane insertion product **24**. GC−MS traces were used to estimate that an additional 5 mg of **24** did not sublime for a total of 14 mg (11% yield). ^{13}C NMR ($CDCl_3$): δ 2608, 27.1, 2902, 32.6, 33.5, 36.7, 43.4, 53.1. ^1H NMR ($CDCl_3$): δ 0.86−0.961 (m, 5H), 1.1 (t, 1H, $J = 12$ Hz), 1.25 (q, 2H, $J = 12$ Hz), 1.46 (td, 6H, $J = 2.2$, 19.9 Hz), 1.56−1.68 (m, 11H), 0.90 (t, 3H, $J = 20$ Hz). MS (EI) *m/z* (rel intensity): 232(5), 135(100), 107(8), 93(14), 79(14). The material which did not sublime also contained 43 mg of homoadamantene dimers (28%).

*1-Adamantylpiperidine (**25**).* 1-Adamantyldiazirine **6** (100 mg, 0.57 mmol) was dissolved in 2.1 mL of piperidine, freshly distilled over sodium. It was exposed (without degassing) to 350 nm radiation for 26 h to provide a clear solution. The solvent was evaporated to provide 130 mg of a yellowish oil. Preparative TLC was performed with MeOH/CH_2Cl_2 in a ratio of 1/18. The compounds were extracted from the silica gel and chromatographed again with CH_2Cl_2, and the portion of the plate not absorbing UV−vis light provided 25 mg of the piperidine insertion product. There was an additional 2 mg present in other fractions estimated from GC−MS for a 21% overall yield. The major byproducts were 11 mg of homoadamantene **11** dimers (7%) and a 20−30 mg fraction containing azine (11−16%). ^{13}C NMR of **25** ($CDCl_3$): δ 8.1, 20.9, 23.7, 31.7, 34.7, 41.8, 60.3, 78.2. ^1H NMR: δ 1.24 (m, 2H), 1.36 (d, 6H, $J = 2.5$ Hz), 1.49 (q, 4H, $J = 5.7$ Hz), 1.62 (m, 10H), 1.86 (s, 2H), 2.38 (t, 3H, $J = 5.0$ Hz). MS: [M + H] calcd, 234.2144; found, 234.2149.

Chemical Trapping Studies. Constant volumes of a stock solution of diazirine (300 μL) were added to each cuvette. Varying amounts (0−100 μL) of a trapping agent were added, and the total volume of the solution was brought to 500 μL with the addition of solvent. All of the samples were placed in Pyrex cuvettes (0.5 mL thin glass cuvette), and the solutions were degassed for 2 min with a strong argon flow. The solutions were photolyzed at 350 nm using a Ray-o-net reactor equipped with 16 RPR-3500 bulbs. The experiment was performed overnight in a cold chamber at 4 °C. The temperature inside the reactor was approximately 15 °C. The yields of the products obtained upon decomposition of the precursors were measured by integration of the peaks obtained in the GC spectra. The compounds were identified by comparing their mass spectral fragmentation patterns and NMR spectra with data from the literature or from authentic samples. In a typical experiment, a stock solution of diazirine in cyclohexane was prepared with an optical density of 1.8 at 355 nm. The stock solution of diazirine (100 μL) was placed into several cuvettes. A different volume of the same trapping agent was added to each cuvette and the total volume adjusted to 200 μL with solvent (cyclohexane).

LFP Experiments. The LFP spectrometer has been described.[18] In all of the LFP experiments, the sample cells were fitted with a rubber septum, and the solutions were deoxygenated by passing a stream of argon through the sample for 2 min. The diazirine solutions utilized in LFP studies were contained in quartz cells for excitation at 308 or 351 nm. The cells were fabricated from square tubing purchased from VitroDynamics. Excitation with the Nd:YAG laser required Suprasil quartz fluorescence-free static cells purchased from Scientific products. An almost perfectly flat surface as in this type of quartz cell results in the minimum scattering of laser light. Low-temperature LFP experiments were performed using a fluorescence-free cell in a variable-temperature sample holder and a NESLAB RTE-110 proportional temperature controller to regulate the temperature.

Stock solutions of diazirines were prepared just prior to the LFP experiments. For experiments with the Nd:YAG laser, the different samples prepared had an absorbance close to 1.5 at 355 nm. For those experiments performed with the excimer lasers, the absorbance of the samples was close to 0.5−0.7 at 308 or 351 nm. The pyridine trapping agent was purified by distillation and stored over KOH pellets in a dark-brown bottle. Constant volumes (350 μL) of stock solutions of diazirine were placed into each cuvette. Varying amounts (0−150 μL) of pyridine were added. The total volume of the solution was maintained constant at 500 μL with the addition of solvent.

Matrix Isolation Spectroscopy. The colorless adamantyldiazirine **6** was placed in a U-shaped tube submerged in an acetone bath kept at −25 °C. The tube was connected to a closed cryogenic system cooled by helium (purchased from Air Products). Argon gas was flowed over the sample, and the resulting gaseous mixture of diazirine and argon was deposited onto the surface of a CsI window. The argon matrix was maintained at 14 K during the entire experiment. Ray-o-net lamps (254 and 350 nm) were used to photolyze the sample in the argon matrix. After exposure to light for a specified period of time, both the IR and UV−vis spectra were recorded. The UV−vis spectrum was measured with a Lambda 6 UV−vis spectrophotometer and the IR spectrum with an FTIR 2000 Perkin-Elmer spectrometer with 2 cm^{-1} resolution.

Calculations. All calculations were performed using the Gaussian94 suite of programs[19] available on four workstations in the Chemistry Department computer room. Other software, such as Spartan and Molecule, were also used during this study.

The geometries of the carbenes and olefinic products were fully optimized at the density functional level of theory B3LYP[20] using the 6-31G* basis set. C_1 symmetry was maintained during the optimizations. All of the stationary points were confirmed by harmonic-frequency calculations. The transition state involved in the rearrangement of the bridgehead carbene to the alkene product was found to have one imaginary frequency. For the modeling of the electronic spectra obtained during matrix experiments, the geometries optimized with the B3LYP/6-31G* level were employed. The IR analysis was based on the B3LYP/6-31G* level of theory. Modeling of the electronic spectra obtained in matrix isolation experiments was based on the INDO/S method of the ZINDO program.[21]

III. Results

III.1. Computational Chemistry. Calculations were performed at the density functional B3LYP/6-31G* levels of theory (DFT). We optimized the geometries of carbenes **7** and **8** in their closed-shell singlet states and the geometries of the transition states that correspond to the rearrangements of these carbenes to the requisite strained alkenes. The stationary points were verified by harmonic-frequency calculations. This demonstrated that all minima had positive frequencies and that the transition states had only one imaginary frequency. The results are summarized in Figures 1 and 2.

This level of theory (B3LYP/6-31G*) does a poor job of computing the singlet−triplet separations of carbenes[22] and thus was not used to study the triplet states of **7** and **8**. The higher-level calculations of Armstrong et al. [QCISD(T)/6-31+G(2d,p))//MP2/6-31G(d)+ZPC calculations][12] indicate that the singlet and triplet states of TBC are very close in energy, with the triplet state of TBC believed to be favored by 1−2 kcal/mol. We make no prediction of the ground-state multiplicities of **7** and **8** but expect that the singlet−triplet gap will be small in these carbenes and that rearrangements will proceed via the singlet states of carbenes **7** and **8**.

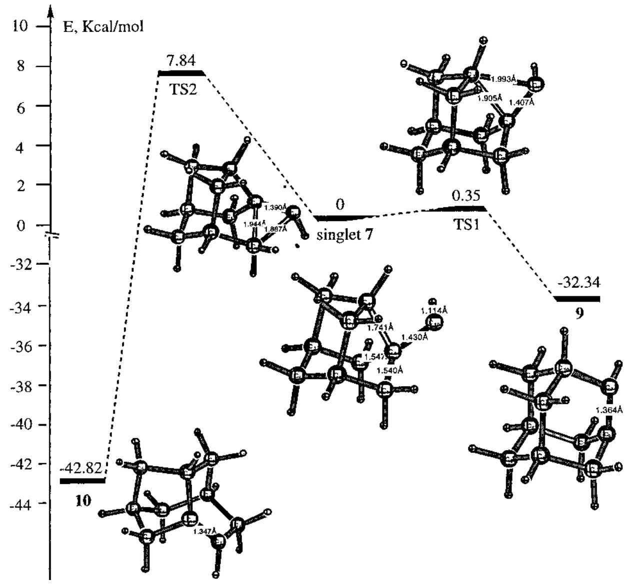


Figure 1. Relative energies of singlet 3-noradamantylcarbene **7**, adamantene **9**, and protoadamant-3-ene **10** and the barriers to carbene rearrangement calculated at the B3LYP/6-31G* level.

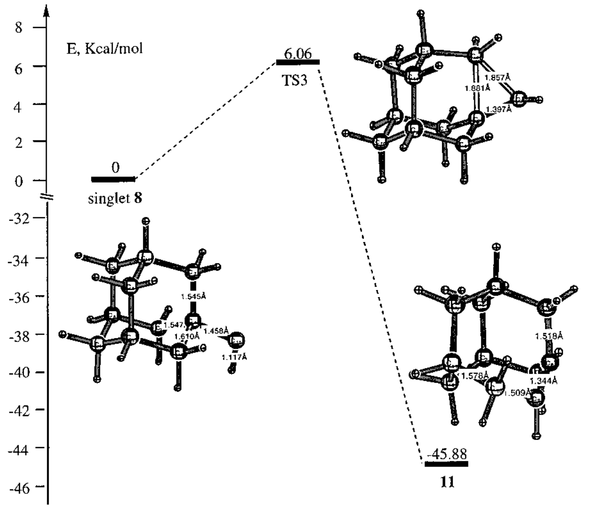
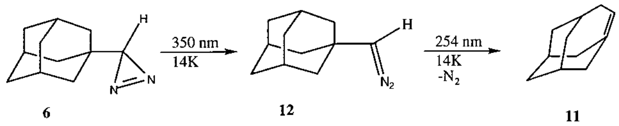


Figure 2. Relative energies of singlet 1-adamantylcarbene **8** and homoadamantene **11** and the barrier to their interconversion calculated at the B3LYP/6-31G* level.

DFT calculations indicate that the energy barrier to rearrangement of singlet 1-adamantylcarbene **8** is 6.06 kcal/mol. Thus, theory predicts that the singlet state of this carbene should be sufficently long-lived to be detectable by LFP experiments. The only bridgehead alkene formed upon ring expansion of 1-adamantylcarbene **8** (homoadamant-3-ene **11**) contains a *trans*-cycloheptene ring structure. 3-Noradamantylcarbene **7** contains two carbon−carbon bonds which can migrate to the carbenic center. Calculations predict that the kinetic product is adamantene **9** formed over a 0.35 kcal/mol barrier. Protoadamant-3-ene **10** is 11 kcal/mol more stable than adamantene **9**. The

SCHEME 1



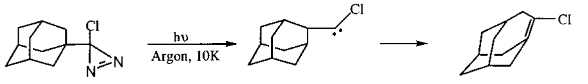
thermodynamic product of rearrangement of 3-noradamantylcarbene **7** (protoadamant-3-ene **10**) is formed over a barrier of 7.84 kcal/mol. Thus, theory predicts that the short bond will migrate, in good agreement with previously reported experimental and computational work on related bridgehead carbenes.[6,7] Calculations predict that 3-noradamantylcarbene **7**, like TBC,[12] will be too short-lived to be detected by LFP experiments. Carbocations behave in exactly the same way as the carbenes of this work, because it is the short bridge that migrates when there is a choice.[23]

The IR and UV−vis spectra of the strained alkenes were predicted by theory as described in the next section. The corresponding matrix spectroscopic data for adamantene **9** and protoadament-3-ene **10** have been reported previously.[14]

III.2. Matrix Isolation Spectroscopy. 1-Adamantyldiazirine **6** was evaporated directly onto a cold CsI window with a large excess of argon. The 14 K matrix spectra exhibited IR and UV−vis bands characteristic of 1-adamantyldiazirine **6**.

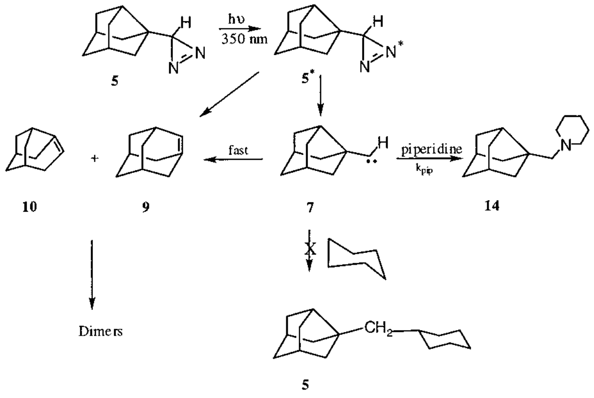
The IR spectrum of 1-adamantyldiazirine **6** contained an intense band at 1588 cm^{-1}, assigned to the N═N bond. 1-Adamantyldiazirine **6** also had two maxima in the UV spectrum at 342 and 350 nm. Photolysis of 1-adamantyldiazirine **6** at 350 nm led to a decrease in the intensity of these bands, which were replaced by a set of new absorption bands. We observed the appearance of a broad band at 250 nm in the UV spectrum and a band at 2100 cm^{-1} in the IR spectrum. These bands were assigned to diazo compound **12** (Scheme 1), formed by isomerization of the cyclic diazirine to its linear isomer. Subsequent photolysis of the diazirine at 350 nm led to an increased yield of the diazo compound and the complete disappearance of the bands characteristic of the diazirine moiety in both the IR and the UV spectra. Continuous irradiation of the diazo compound with 254 nm light generated a new band at 1630 cm^{-1} in the IR spectrum and a band at 260 nm in the UV spectrum. The spectra are given in the Supporting Information. Martella et al.[24] have reported that strained alkene **11** (also formed by the rearrangement of 1-adamantylcarbene **8**) has an IR transition at 1610 cm^{-1}. Density functional theory predicts that homoadamantene **11** will have a carbon−carbon double bond stretch at 1644 cm^{-1}. Thus, IR spectroscopy supports the formation of homoadamantene **11** upon photolysis of 1-adamantyldiazomethane **12** in argon, in accord with our expectations based on literature reports.[2] It was not possible to confidently assign other vibrational bands of homoadamantene **11** in the matrix because of low signal to noise.

There was no IR evidence for the presence of persistent 1-adamantylcarbene **8** in argon. Yao et al.[25] were able to detect adamantylchlorocarbene and its rearranged product chlorohomoadamant-3-ene upon photolysis of the appropriate diazirine precursor. The chloro substituent stabilizes the carbene which allows its direct detection in an argon matrix.



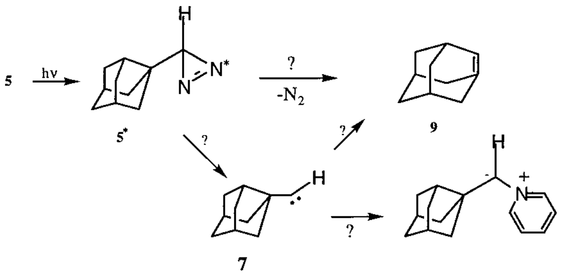
Excited-state calculations were performed with the B3LYP/6-31G* geometries in an effort to provide a picture of the excited-state electronic structure of the strained alkene. We also performed additional CIS and CISD calculations on the ground state of homoadamantene **11** using SCF MOs by the INDO/S method with the ZINDO program.[21] The strong absorption band observed at 277 nm is due to electron promotion from the π to the π* orbitals of the C═C bond of homoadamant-3-ene with an oscillator strength of 0.241. Thus, the changes in the UV spectrum induced by photolysis of 1-adamantyldiazomethane **12** in argon are also consistent with the formation of homoadamantene **11** in the matrix.

SCHEME 2



We have previously reported that the photolysis of 3-noradamantyldiazirine **5** in argon at 14 K produces adamantene **9**, as identified by IR and UV−vis spectroscopy and upon comparison of our spectra with the literature.[14] The strained alkenes adamantene **9** and protoadamant-3-ene **10** can be photochemically interconverted in argon at 14 K.[14] Much earlier studies had previously demonstrated that adamantene **9** is formed by rearrangement of 3-noradamantylcarbene **7**.[2,26]

III.3. LFP Studies. LFP of 3-noradamantyldiazirine **5** in pentane or benzene produces adamantene **9** ($\lambda_{\max}$ = 325 nm).[14] LFP of 3-noradamantyldiazirine **5** in the presence of pyridine fails to produce the transient spectrum of a carbene−pyridine ylide. Either the carbene is not formed efficiently upon photolysis of 3-noradamantyldiazirine **5** or it rearranges too rapidly (τ < 10 ps) for capture by pyridine (Scheme 2).



Rearrangement of **5*** (or a related diazirine ring-opened biradical) to adamantene **9** in concert with nitrogen extrusion would not be surprising. We have come to similar conclusions with cyclopropyl[27] and homocubyldiazirines.[9]

LFP of 1-adamantyldiazirine **6** in pentane fails to produce a UV−vis active transient. In the presence of pyridine, however, LFP of 1-adamantyldiazirine **6** produces the transient spectrum shown in Figure 3.

The transient is formed faster than the resolution of the spectrometer (Figure 4). The yield of the ylide is not influenced by the presence of oxygen. The yield (A_y) of ylide **13** is dependent on the concentration of pyridine (Figure 4). A plot of 1/A_y versus 1/[pyr] is roughly linear (Supporting Information). Division of the intercept by the slope of this plot gives $k_{PYR}\tau$,

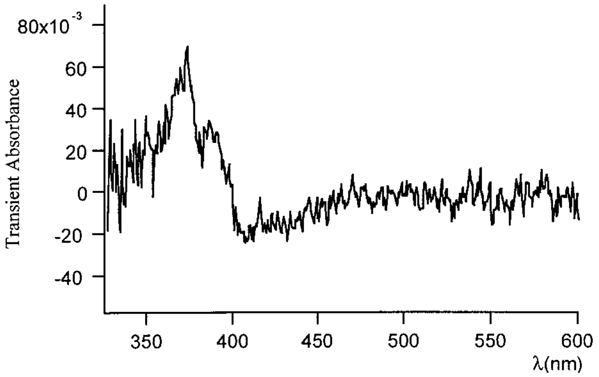


Figure 3. Transient spectrum of the pyridine ylide produced by LFP of 1-adamantyldiazirine **6** in pentane at ambient temperature.

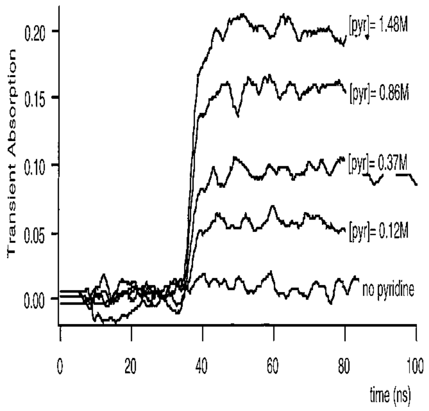


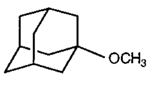
Figure 4. Optical yield of the pyridine ylide formed upon LFP of 1-adamantyldiazirine **6** as a function of pyridine concentration.

where τ is the lifetime of 1-adamantylcarbene **8** in the absence of pyridine and k_{PYR} is the absolute rate constant of the reaction of 1-adamantylcarbene **8** with pyridine. If $k_{PYR} = 1.0 \times 10^9$ M^{-1} s^{-1}, as is commonly observed,[28] one can deduce lifetimes of 1-adamantylcarbene of 1.5 ns in cyclohexane and 2.5 ns in cyclohexane-d_{12}. These results demonstrate that the lifetime of 1-adamantylcarbene **8** in the alkane solvent is limited, at least in part, by reaction with the solvent. This conclusion will be confirmed by product analysis (vide infra).

The ylide yield can be reduced in the presence of typical carbene quenchers such as methanol. A Stern–Volmer analysis of the quenching of the ylide can be used to obtain the rate constant for the reaction of adamantylcarbene with methanol. A plot of A_y^s/A_y versus [CH_3OH] is predicted and found to be linear with a slope of k_Q/k_{PYR}[pyr] (Supporting Information). Assuming again[28] that k_{PYR} is 1×10^9 M^{-1} s^{-1} and with constant [pyr] = 2.47 M, 1-adamantylcarbene **8** was found to have a rate constant of reaction with methanol $k_Q = 6 \times 10^9$ M^{-1} s^{-1}.

III.4. Chemical Trapping Experiments. *1-Noradamantylcarbene.* Photolysis of 3-noradamantyldiazirine **5** in either cyclohexane or benzene leads to products which have properties consistent with the previously described dimers of strained alkenes **9** and **10** (Scheme 2).[2,5,24] The dimers lack vinylic proton resonances in their NMR spectra and have the expected *m*/*z* ratios and fragmentation patterns of strained alkene dimers. Carbene–benzene and carbene–cyclohexane adducts, if formed, were produced in no more than trace quantities.

Photolysis of 3-noradamantyldiazirine **5** in neat methanol produced two methyl ethers, one of which was positively identified as 1-methoxyadamantane **15**, a product expected from trapping adamantene, by comparison with an authentic sample. The other product was neither **16** nor **17**, established by comparison with authentic samples.



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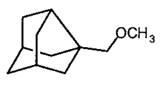

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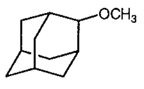

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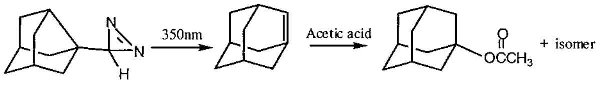
Carbenes react rapidly with alcohols to form ethers. Thus, the absence of **16** in the product mixture is consistent with an extremely rapid carbene rearrangement or direct formation of adamantene **9** from the excited 3-noradamantyldiazirine precursor (**5***; Scheme 2).

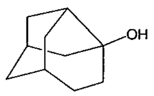
We have not identified the second methyl ether but speculate that it is the product of the trapping of protoadamant-3-ene **10** based on our work with acetic acid (vide infra).

Alkene dimers are observed upon photolysis of 3-noradamantyldiazirine **5** in methanol. Methanol is obviously only a moderately effective trap of adamantene ($k_{CH_3OH} = 8.4 \times 10^4$ M^{-1} s^{-1}).[14] Acetic acid traps adamantene **9** over 150-fold faster than does methanol ($k_{CH_3COOH} = 1.4 \times 10^7$ M^{-1} s^{-1}).[14] Photolysis of 3-noradamantyldiazirine **5** in neat acetic acid yields two isomeric adducts. No alkene dimers were formed in the more reactive solvent. One product was quickly identified as acetate **18**, the product expected from trapping adamantene **9**.



5 **9** **18**

The mixture of acetates formed on photolysis of 3-noradamantyldiazirine **5** was reduced with LAH, and the resulting mixture of alcohols was separated by chromatography.



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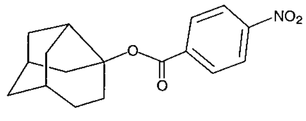
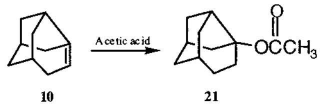


20

The NMR spectrum of one of the alcohols was identical with that reported for 3-protoadamantanol **19**.[16] A crystal structure of the *p*-nitrobenzoyl derivative **20** confirmed the structure (Supporting Information).

From these results, one can posit that protoadamant-3-ene **10** is formed along with adamantene **9** upon photolysis of 3-noradamantyldiazirine **5** in acetic acid and is trapped to give **21**.

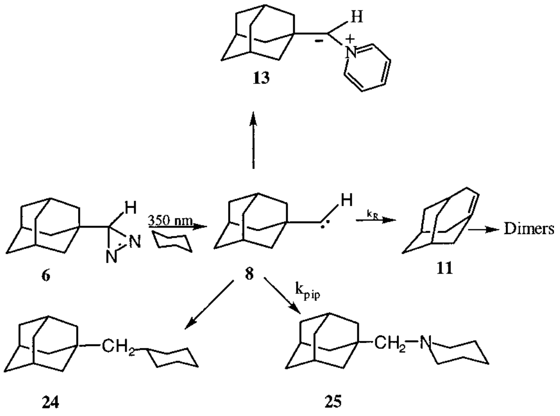


10 **21**

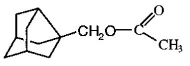
If the calculations are even approximately correct that relaxed 3-noradamantylcarbene **7** has a strong kinetic preference for the formation of adamantene **9** ($\Delta\Delta E_a \approx 7.5$ kcal/mol), then the result in acetic acid indicates either that protoadamant-3-ene **10** is formed from a rearrangement in the excited state of 3-noradamantyldiazirine **5** or that adamantene **9** and protoadamant-3-ene **10** interconvert in the presence of an acid catalyst.

Acetate **22**, which would arise from trapping 3-noradamantylcarbene **7**, was not observed. This is further evidence for either a very short lifetime of 3-noradamantylcarbene **7** or that it is simply not formed upon photolysis of 3-noradamantyldiazirine **5**. These conclusions are tempered by the possibility of

SCHEME 3

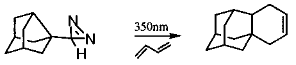


protonation of 3-noradamantylcarbene **7** (or of the diazo isomer of **5**) followed by fast cationic rearrangement.



22

To avoid cationic rearrangements, 3-noradamantyldiazirine **5** was photolyzed in the presence of butadiene. Photolysis of 3-noradamantyldiazirine **5** in benzene containing 1,3-butadiene (273 K) produced five adducts. The major adduct **23**, formed by a Diels−Alder reaction of adamantene **9**, was identified by comparison with an authentic sample kindly provided by Professor Jones of Princeton University.[17]



23

Photolysis of 3-noradamantyldiazirine **5** in piperidine, where cation formation is unlikely, leads to the formation of adduct **14** (Scheme 2) in only trace quantities ($<1\%$).

1-Adamantylcarbene. Photolysis of 1-adamantyldiazirine **6** in cyclohexane leads to the formation of carbene−solvent adduct **24** in 11% yield and dimers of homoadamantene **11** (Scheme 3) in 28% yield. This confirms that 1-adamantylcarbene **8** is produced upon photolysis of 1-adamantyldiazirine **6**, that it is sufficiently long-lived to undergo bimolecular chemistry (in contrast to TBC), and that its lifetime of 1.5 ns in cyclohexane is, in part, limited by reaction with solvent.

The mass spectra of all isomers of the dimers have base peaks at m/z 296 (M^+) and strong peaks at $m/z = 239$ and 135 with different intensity ratios for different isomers. The mixture of dimers, isolated as a white solid by successive recrystallization with 2-propanol, yielded two major products. The dimers did not have vinylic resonances in their proton or carbon NMR spectra. Our results with the dimers of homoadamantene mimic those of earlier workers.[2,5,17]

1-Adamantyldiazirine **6** was photolyzed in a 1/1 mixture of cyclohexane/cyclohexane-d_{12}. The ratio of cyclohexane to cyclohexane-d_2 adduct is equal to 1.3 by GC−MS. The C−H/C−D insertion ratio is very similar to the isotope effect on carbene lifetimes measured during the LFP experiments using pyridine as a kinetic probe.

Photolysis of 1-adamantyldiazirine **6** in neat piperidine produced the insertion adduct **25** (Scheme 3) in 21% isolated yield. As expected from Scheme 3, the yield of adduct **25** increases with increasing concentration of piperidine in cyclohexane (Supporting Information). Increasing the concentration of piperidine reduces the yield of both homoadamantene **11** dimers and carbene−cyclohexane adduct **24** (Supporting Information), as predicted by Scheme 3.

The absolute yield of the piperidine adduct derived from trapping 1-adamantylcarbene **8** is at least 10-fold larger than the yield of piperidine adduct derived from trapping 3-noradamantylcarbene **7**.

IV. Discussion

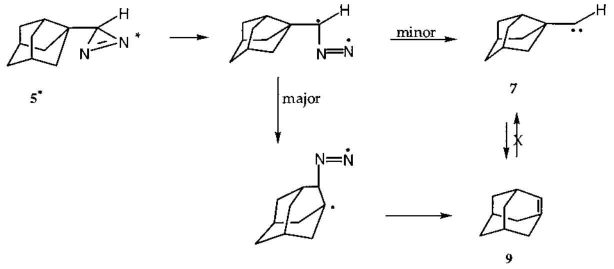
On the basis of numerous previous reports, we were confident that photolysis of diazirines **5** and **6** would produce strained bridgehead alkenes.[2−7,26] Again, given so much experimental and theoretical precedent, we expected that the 3-noradamantylcarbene **7** would prefer to migrate the short C−C bridge bond to form adamantene rather than to migrate a long bridge to form protoadamant-3-ene **10**.[2−7,26] B3LYP density functional theory calculations indicated that the preference is substantial. The calculated barriers to rearrangement of 1-noradamantylcarbene **7** to adamantene **9** and protoadamant-3-ene **10** are 0.35 and 7.84 kcal/mol, respectively. The low barrier of 3-noradamantylcarbene **7** rearrangement to form adamantene **9** is reminiscent of the low barrier (0.1 kcal/mol) to rearrangement of TBC.[12] The thermodynamic product of carbene rearrangement (protoadamant-3-ene **10**) is not the kinetic product of rearrangement (adamantene **9**). 1-Adamantylcarbene **8**, on the other hand, is predicted to surmount a barrier of 6.06 kcal/mol to form homoadamantene **11**. The key question of this work is whether 3-noradamantylcarbene **7** or 1-adamantylcarbene **8**, unlike TBC, is sufficiently long-lived to be detected by chemical trapping or by LFP methods.

LFP of 1-adamantyldiazirine **6** in the presence of pyridine produces a carbene−pyridine ylide; LFP of 3-noradamantyldiazirine **5** under the same conditions does not. LFP of 3-noradamantyldiazirine **5** produces adamantene as the only species detectable in LFP experiments.[14] Straightforward analysis of the pyridine ylide data yields a lifetime for 1-adamantylcarbene **8** of 1.5 ns (cyclohexane, ambient temperature), assuming that the absolute rate constant of the reaction of carbene with pyridine is 1×10^9 M^{-1} s^{-1}. This is a longer lifetime than that of perdeuteriomethylcarbene (0.5 ns) but a shorter lifetime than that of 2-*tert*-butylcyclopropylcarbene (15 ns) under similar conditions.[25]

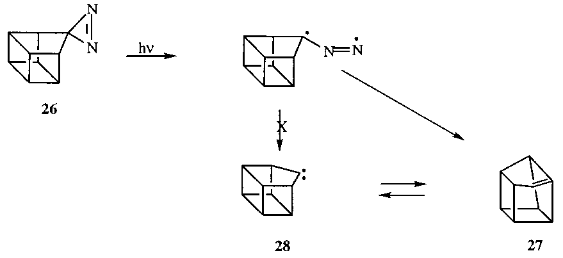
Continuous photolysis of diazirines **5** and **6** in cyclohexane produces the dimers of adamantene **9** and homoadamantene **11**, respectively. An adduct of 1-adamantylcarbene **8** and cyclohexane is formed in addition to the alkene dimers. This indicates that the lifetime of 1-adamantylcarbene **8** in cyclohexane is controlled, at least in part, by reaction with the solvent.

The yield of cyclohexane adduct and the yield of homoadamantene dimers decrease in the presence of piperidine, which traps the 1-adamantylcarbene **8** generated upon photolysis of 1-adamantyldiazirine **6**. A plot of the yield of the 1-adamantylcarbene−piperidine adduct/homoadamantene **11** dimers is linear. This indicates that some homoadamantene is formed by rearrangement of the trappable carbene and not exclusively from the excited state of diazirine precursor **6**.

Continuous photolysis of 3-noradamantyldiazirine **5** in cyclohexane, methanol, or acetic acid fails to produce an adduct of 3-noradamantylcarbene **7**, although in every solvent, evidence for the presence of adamantene can be obtained. Photolysis of 3-noradamantyldiazirine **5** in piperidine forms an adduct in very low yield ($<1\%$). Either 3-noradamantylcarbene **7** is not formed upon the photolysis of 3-noradamantyldiazirine **5** or it rearranges very rapidly ($\tau < 50$ ps). The deduced lifetimes of 3-noradamantylcarbene **7** and 1-adamantylcarbene **8** are consistent with the rearrangement barriers predicted by DFT calculations. We propose that substantial amounts of adamantene **9** are formed by a rearrangement in the excited state of the 3-noradamantyldiazirine precursor (**5***).



Several diazirine excited-state rearrangements have been recently postulated.[9,24] The most relevant and convincing precedent can be found with homocubyldiazirine.[9] Chen et al. demonstrated that photolysis of **26** leads to homocubene **27** and not homocubylidene **28** as the first trappable intermediate. In Chen's work, the strained alkene can subsequently isomerize to a carbene, a process which does not occur with adamantene **9**.[9] This is sensible because adamantene **9** is calculated to be 33.96 kcal/mol lower in energy than 3-noradamantylcarbene **7**, whereas **27** and **28** are essentially degenerate in energy.[29]



Why is the excited state of 3-noradamantyldiazirine **5** more prone to rearrangement than that of 1-adamantyldiazirine **6**? We speculate that the same structural factor (overlap of the migrating bond) that favors rapid rearrangement of 3-noradamantylcarbene **7** (0.35 kcal/mol) relative to 1-adamantylcarbene **8** (6.06 kcal/mol) operates in the analogous diazirine excited state. Thus, carbenes with small barriers to rearrangement will be very difficult to detect not only because of their short lifetimes but also because of facile rearrangements in structurally related precursors that lead to inefficient carbene formation.

Conclusions

Photolysis of 1-adamantyldiazirine **6** in argon at 14 K produces 1-adamantyldiazomethane and homoadamantene **11**, which were characterized by IR spectroscopy. 1-Adamantylcarbene **8** was not detected as a persistent species in the argon matrix. LFP of 1-adamantyldiazirine **6** produces a carbene-derived ylide in the presence of pyridine. 1-Adamantylcarbene **8** can also be trapped in solution with cyclohexane and with piperidine. Dimers of homoadamantene **11** are detected upon photolysis of 1-adamantyldiazirine **6**. An adduct of homoadamantene **11** and acetic acid was formed upon the photolysis of 1-adamantyldiazirine **6** in acetic acid. The lifetime of 1-adamantylcarbene **8** in cyclohexane is deduced to be ≈1.5 ns. This is consistent with B3LYP calculations with the 6-31G* basis set, which predict a barrier to the rearrangement of 1-adamantylcarbene **8** to homoadamantene **11** of 6.06 kcal/mol after zero-point energy correction. It is clear that 1-adamantylcarbene **8** is much longer lived than either TBC or 3-noradamantylcarbene **7**, neither of which can be trapped with pyridine in LFP experiments. 3-Noradamantylcarbene **7** can be trapped with piperidine but in only trace quantities. The data indicates that 3-noradamantylcarbene **7** has a lifetime in cyclohexane that is less than 50 ps. The data also indicates that 3-noradamantylcarbene **7** is formed very inefficiently from 3-noradamantyldiazirine **5**. The data is consistent with the rearrangement in the excited state of 3-noradamantyldiazirine **5** concurrent with the loss of nitrogen to efficiently form adamantene **9**, without the intermediacy of 3-noradamantylcarbene **7**.

Supporting Information Available: Computational chemistry data, UV−vis, IR, and mass spectra for the carbenes. This material is available free of charge via the Internet at http://pubs.acs.org.

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