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($1.002 + R - R_0$) where $R$ is the ratio in the sample in question and $R_0$ is the ratio in unlabeled material. Good agreement was found between measurements of the two pairs of peaks. A fragment peak at $m/e$ 127 is also observed, attributed to the loss of benzoyl group. The ratio 129/127 in all samples was within experimental error identical with that in unlabeled material. This establishes that the $^{18}O$ label is in the carbonyl oxygen. First-order rate constants for exchange were evaluated as the slopes of plots of ln (excess $^{18}O$) vs. time.

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**Registry No. 2** (major isomer), 86239-10-3; **2** (minor isomer), 86287-25-4; **6**, 86239-11-4; **7**, 86239-12-5; $O_2$, 7782-44-7; *exo,exo*-2,3-norbornanediol, 16329-23-0; trimethyl orthobenzoate, 707-07-3; *exo,-exo*-2,3-norbornanediol monobenzoate, 77085-41-7.

**Supplementary Material Available:** Tables S1–S3 listing observed rate constants (1 page). Ordering information is given on any current masthead page.

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# Reluctant Azoalkanes: The Photochemical Behavior of Acyclic, Bridgehead-Centered Azoalkanes on 185- and 350-nm Irradiation

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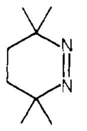
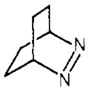
**Abstract:** Azo-1-adamantane (**1a**), azobicyclo[2.2.2]octanes (**1b** and **1c**), and azo-1-norbornane (**1d**) isomerize to the *cis*-azoalkanes but are reluctant to lose nitrogen directly upon long-wavelength irradiation. Use of 185-nm light is shown to enhance deazatization quantum yields considerably, though photoisomerization remains an important reaction. In the case of **1a** especially, thermolysis of the cis isomer is the dominant decomposition mechanism at long and probably at short wavelength; however, the cis isomer of **1d** is thermally stable. It follows that the second excited singlet state is responsible for deazatization of **1d**. The products of photolysis in pentane have been identified, and the amount of bridgehead radical hydrogen abstraction relative to recombination is found to increase under short-wavelength irradiation.

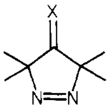
While azoalkanes have in general served an important role in the mechanistic elucidation of radical and diradical reactions[1] and as convenient precursors for unusual organic molecules,[2] a number of azoalkanes have recently received attention because of their low propensity toward conventional (λ >300 nm) photochemical deazatization. These "reluctant" azoalkanes include structure types A–D where the R groups in D are bridgehead-centered radicals. The long wavelength (λ >300 nm) photolysis of several reluctant azoalkanes could be significantly accelerated by employing elevated temperatures[3] and vapor-phase conditions[3a,b,g] or by introducing radical-stabilizing substituents[3d] and ring strain.[3d,g] Recently we reported that short wavelength (185 nm) radiation effectively promotes deazatization of structure types A[4], B,[4] and C.[5] In order to extend the generality of this wavelength dependence, it was of interest to determine whether azoalkanes of structure type D[6] were also photoreactive at 185 nm. Presently we confirm that photolysis of the bridgehead-centered, acyclic azoalkanes **1a–d** in solution is considerably more efficient at 185 nm than at long wavelengths.



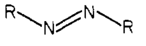
A



B



C



D

## Results

**Synthesis of *trans*-Azoalkanes 1.** The azoalkanes **1a–d** are all known[7] compounds, except **1c**, and were prepared by the usual sulfamide route.[8] The respective bridgehead amines were con-

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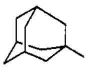
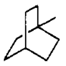
R—N=N—R

**1**

**1a**, R = 

**1c**, R = 

**1b**, R = 

**1d**, R = 

verted with sulfuryl chloride to the sulfamides, which were oxidized in good yield with sodium hypochlorite to the *trans*-azoalkanes **1**.[6b] The amine for the 4-methylbicyclo[2.2.2]octyl system, **1c**, was prepared from 4-methylbicyclo[2.2.2]octyl azide by catalytic hydrogenation.

**Irradiation Techniques.** The cis isomers of the azoalkanes **1c** and **1d** were generated in situ at 0 °C by irradiation with 351-nm laser light, in a Rayonet reactor at 350 nm or with a 500 W short-arc mercury lamp and a Corning 7-54 filter. The characteristic yellow color ($\lambda_{max}$ 423–455 nm)[6b] of the cis azoalkanes vs. their nearly colorless ($\lambda_{max}$ 365–369 nm) trans isomers served to monitor qualitatively as well as quantitatively the extent of trans → cis isomerization. *Cis*-**1d** was isolated by column chromatography on alumina for some of the experiments.

The 185-nm photolyses employed an immersion-type photoapparatus consisting of a Suprasil inner well bearing the 50-W hot cathode mercury resonance lamp, which was suspended in an outer Pyrex vessel.[9,10] The ca 0.004–0.01 M solutions of the azoalkane **1** in rigorously purified pentane were extensively purged with nitrogen gas to prevent formation of oxygenated products. For example, a control experiment revealed that azoalkane **1a** in undegassed solution gave significant amounts of 1-adamantanol, presumably arising from the reaction of 1-adamantyl radicals with molecular oxygen to produce 1-adamantyl hydroperoxide. Subsequent photolysis at 185 nm is expected to afford 1-adamantanol. Photolyses were usually not carried out to complete consumption of substrate because irradiation times over 10 min caused deposition of resinous material on the Suprasil surface.

Not yet understood is the formation of a transient yellow color (lifetime ca. 24 h at 20 °C) in the 185-nm photolysis of all azoalkanes but **1a**. The color corresponds to a broad absorption extending out to 500 nm with a $\lambda_{max}$ of 400 nm; hence, it is not due to *cis*-azoalkane. Molecular oxygen is not responsible for the formation of this color because it still appeared in a control experiment under rigorously degassed conditions. Both the *cis*- and *trans*-azoalkanes **1d** produced the same spectrum. This transient is surely not the trialkylhydrazyl radical $R_2NNR$, because such radicals are expected to have their $\lambda_{max}$ at ca. 250 nm.[11] Furthermore, it is unlikely that the yellow product corresponds to one of the late GC peaks because it is too labile to survive GC conditions.

The long-wavelength photolyses were carried out in a Rayonet photoreactor equipped with 350-nm lamps. The transient yellow color that was associated with the 185-nm irradiations was not observed in these studies. Because loss of nitrogen from **1c** was inefficient using conventional mercury lamps, photolysis was carried out with the 351-nm line of a 18-W argon ion laser at 60 °C for 2.5 h.

**Product Analyses.** The products were identified by comparison of retention times and GC-mass spectra with those of the authentic materials. The complex chromatograms obtained in most cases revealed unreacted azoalkane RN=NR, the alkane RH (hydrogen abstraction by the alkyl radical R· from the solvent), the dimer RR (self-coupling of the alkyl radicals R·), and the cross-coupling product $RC_5$ between pentyl radicals derived from the pentane solvent and R·. Numerous other minor products were ignored. Control experiments showed that the pentane solvent and the photolysis products were stable toward 185-nm irradiation. Hydrocarbon product formation by 254-nm radiation, the major output of the 185-nm lamp,[9] was discounted by irradiating the azoalkanes **1** with pure 254-nm light (Rayonet photoreactor).

For the quantitative product analysis (Table I), the amount of azoalkane consumed and the amounts of alkane RH and dimer RR formed were determined by capillary gas chromatography (CGC) for **1d** and by conventional GC for **1a**–**1c**. The GC response factors of the authentic products were calibrated by using concentration ranges close to those produced in the photolyses. The cross-coupling product $RC_5$ was quantitated for all azoalkanes except **1d**. In the latter case, an authentic sample was not available but no GC peak was seen that could be assigned as 1-pentylnorbornane. Considerable amounts of nonvolatile residues were found after evaporation of the solvent and volatile products, accounting for the low mass balances in Table I.

The possibility of hydrazine (RNH–NHR) formation was disproved in the 185-nm photolysis of **1d** by first preparing the authentic hydrazine by catalytic hydrogenation of the azoalkane. Under rigorously deaerated conditions, the authentic hydrazine showed a CGC peak with a retention time about twice that of the azoalkane whereas irradiated **1d** gave no peak in this region. On exposure to air, the hydrazine was converted into *trans*-**1d**, as confirmed by CGC injection.

**Quantum Yields.** The quantum yields (cf. Table I) of azoalkane consumption and product (RH, RR, and $RC_5$) formation at 185 nm were based upon the cis–trans isomerization of cyclooctene ($\Phi = 0.32$) as actinometer.[12] The discrepancy between the quantum yield of azoalkane consumption ($\Phi_{-azo}$) and product formation ($\Phi_{prod}$) is again due to the fact that the $\Phi_{prod}$ term includes only volatile products quantitated by GC.

Although considerable effort was expended to determine the efficiency of *cis* ⇌ trans isomerization at 185 nm, only qualitative results were obtained. In none of the 185-nm irradiations of the trans isomers was it possible to detect appreciable amounts of cis isomer. Despite the broad yellow absorption that develops immediately on 185 nm exposure, UV analysis in the region of cis isomer absorption (423–455 nm) should have enabled us to detect the cis azoalkane if it had been formed in >5% yield. Control experiments using monochromatic 254-nm light showed that *cis*-**1d** was efficiently isomerized to trans. Since most of the output of the 185-nm lamps is at 254 nm,[9] failure to observe buildup of cis is understandable. Irradiation of *cis*-**1d** at 185 nm gave considerable isomerization (ca. 54%) to its trans isomer, but the presence of 254-nm light prevented the determination of quantum yields.

A separate study of **1d** using 193-nm light from a pulsed argon fluoride excimer laser proved more fruitful. Three quartz cells were prepared, each attached to a 1-cm cuvette and a break-seal. Solutions of 0.023 M *cis*-**1d**, *trans*-**1d**, and 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH, actinometer[4]) in hexane were placed into their respective cells and then degassed and sealed. After checking the initial UV spectrum, the quartz cells were placed successively into a holder, and the stirred solutions were subjected to 1140 laser pulses at 2 Hz. The UV spectra showed clearly that the isomers were interconverted. A control solution revealed some thermal or stray light induced isomerization during the course of the experiment, making the observed $\Phi_{c\rightarrow t}$ of 0.16 unreliable. However, $\Phi_{t\rightarrow c}$ was found to be 0.3 by HPLC analysis of initial and irradiated solutions. Nitrogen evolution was measured with a Töpler pump, showing that $\Phi_{N_2} \sim 0.05$ for both isomers. No sign of the yellow absorption that plagued the 185-nm irradiations was seen. Since solvent absorption rises very steeply in this region, it is possible that the 8-nm wavelength increase diminished the photoreaction of some solvent impurity. The extinction coefficients at 193 nm of *trans*- and *cis*-**1d** were found to be 16000 and 19500, respectively; hence, the azoalkanes were by far the major light absorbers despite the $a = 1.17$ absorbance of hexane.

Two experiments were carried out at long wavelengths, the first of which was to determine the quantum yield for trans ⇌ cis interconversion of **1d**. A solution of *trans*-**1d** was subjected to

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(9) Srinivasan, R.; White, L. S. *J. Am. Chem. Soc.* **1979**, *101*, 6389. The spectral output of this lamp is 20% at 185 nm, 80% at 254 nm.

(10) Caution must be exercised to avoid exposure to this lamp because of the exceedingly harmful effects of short-wavelength radiation.

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**Table I.** Product Distributions and Quantum Yields of the 185-nm Photodenitrogenation of Azoalkanes **1a–d** in Pentane

| azoalkane | | | products | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | absolute yields, %[a] | | | mass balance,[a,b] | quantum yields[c] | | | | |
| type | concn, M | consumption, %[a] | RH | RR | $RC_5$ | % | $\Phi_{RH}$ | $\Phi_{RR}$ | $\Phi_{RC_5}$ | $\Phi_{prod}$ | $\Phi_{-azo}$ |
| *trans*-**1a** | 0.010 | 57 | 35 | 12 | 4 | 89 | 0.18 | 0.06 | 0.02 | 0.26 | 0.29 |
| *trans*-**1b** | 0.004 | 78 | 37 | 5 | 0.3 | 54 | 0.10 | 0.01 | 0.0008 | 0.11 | 0.21 |
| *trans*-**1c** | 0.004 | 63 | 44 | 3 | 0.2 | 75 | 0.12 | 0.01 | 0.0005 | 0.13 | 0.17 |
| *cis*-**1c** | 0.004 | 73 | 45 | 6 | 1.5 | 72 | 0.12 | 0.02 | 0.004 | 0.14 | 0.20 |
| *trans*-**1d** | 0.005[d] | 46 (50) | 3 (3) | 2 (5) | | 11 (16) | 0.008 | 0.006 | | 0.014 | 0.13 |
| *cis*-**1d** | 0.005[d] | >95[e] | 4 (12) | 3 (6) | | 13 (39) | 0.011 | 0.009 | | 0.020 | 0.15 |

[a] Error ca. 5% of the stated value; averaged results of two–four independent measurements. [b] Appreciable amounts (20–30%) of undefined, nonvolatile residue were formed; mass balance is based on consumed azoalkanes. [c] 10-min irradiation times. [d] 27 mL of solution were used, all others 50 mL; values in parentheses are derived from photolyses in the presence of solid $K_2CO_3$. [e] Photoisomerization gave 47 (53)% of *trans*-**1d**.

pulsed nitrogen laser irradiation (337 nm), and the isomerization was monitored by UV. In the same cell holder, a solution of DBH was also irradiated and monitored by UV. Comparison of the extent of reaction in both tubes gave $\Phi_{t\rightarrow c} = 0.50$. In another experiment, a solution of *cis*-**1d** was irradiated at 366 nm in a merry-go-round concomitantly with a benzophenone–DBH actinometer. The evolution of the UV spectrum with time was corrected for back reaction,[13] and the value $\Phi_{c\rightarrow t} = 0.49$ was calculated from $\epsilon$ 123 of *cis*-**1d**.[6]

The following experiment demonstrates that long-wavelength irradiation of *trans*-**1a** leads to the labile cis isomer, which loses nitrogen thermally. Thus the hydrocarbon products do not arise by photodissociation of *trans*-**1a**. A 0.014 M degassed solution of the *trans* isomer in toluene was irradiated (366 nm) at 0 °C where *cis*-**1a** has a half-life of 22 h. After 1 h, 70% of the trans had gone to cis. The cold solution was then irradiated through a $NaNO_2$ filter which blocks all UV light but passes the visible light which *cis*-**1a** absorbs. The original UV spectrum of the trans isomer reappeared in full; moreover, measurement of the $N_2$ evolved showed that only 1.7% of **1a** had decomposed. Since thermolysis of *cis*-**1a** could have produced this small amount of $N_2$, we conclude that long-wavelength irradiation of either isomer causes only isomerization.

**Thermolysis of *cis*-1c.** The activation parameters for thermal isomerization of *cis*- to *trans*-**1c** were determined by first irradiating the *trans*-isomer in pentane at 0 °C with the 351 laser line. The resulting yellow solution of *cis*-**1c** was then heated under isothermal conditions at a particular temperature, monitoring the rate of disappearance of absorption at 480 nm to avoid spectral overlap with *trans*-**1c**. A least-squares fit of the rate constants gave $\Delta H^{\ddagger} = 24.2 \pm 0.4$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = 5.2 \pm 1.2$ eu, close to the reported values for *cis*-**1b**.[6]

## Discussion

The following equations summarize the major results of this work and incorporate the existing knowledge of acyclic *cis*-azoalkanes.[6]

$$trans\text{-}\mathbf{1a} \xrightarrow[366\ \text{nm}]{h\nu} cis\text{-}\mathbf{1a} \xrightarrow{\Delta} \text{1-adamantyl}\cdot + N_2 \qquad (1)$$

$$cis\text{-}\mathbf{1a} \xrightarrow[>400\ \text{nm}]{h\nu} trans\text{-}\mathbf{1a} \text{ but no } N_2 \qquad (2)$$

$$trans\text{-}\mathbf{1a\text{-}d} \xrightarrow[185\ \text{nm}]{h\nu} N_2 + 2R\cdot \rightarrow RH + RR \qquad (3)$$

$$trans\text{-}\mathbf{1d} \xrightarrow[337\ \text{nm}]{h\nu} cis\text{-}\mathbf{1d}\ (\Phi = 0.5) \qquad (4)$$

$$cis\text{-}\mathbf{1d} \xrightarrow[366\ \text{nm}]{h\nu} trans\text{-}\mathbf{1d}\ (\Phi = 0.5) \qquad (5)$$

$$trans\text{-}\mathbf{1d} \xrightarrow[193\ \text{nm}]{h\nu} cis\text{-}\mathbf{1d}\ (\Phi = 0.3) + N_2\ (\Phi = 0.05) \qquad (6)$$

$$cis\text{-}\mathbf{1d} \xrightarrow[193\ \text{nm}]{h\nu} trans\text{-}\mathbf{1d}\ (\Phi \sim 0.16) + N_2\ (\Phi = 0.05) \qquad (7)$$

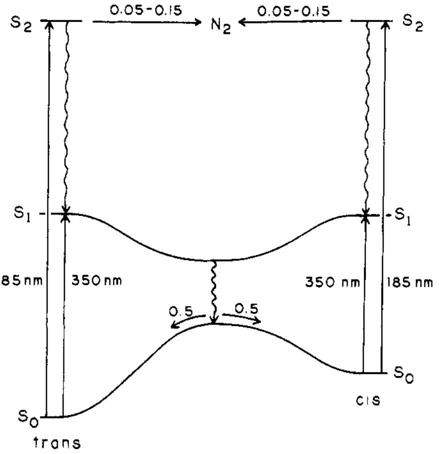

**Figure 1.** Energy diagram of azoalkane singlet states.

It is apparent from Table I that 185-nm irradiation promotes deazatization of bridgehead azoalkanes (eq 3). The question that immediately arises is whether this decomposition occurs via direct photolysis of the trans isomer or whether isomerization to cis is the only photochemical act. Since deazatization is a facile thermal reaction of many cis azoalkanes, these possibilities are not easily distinguished.

The results with **1d** are revealing because *cis*-**1d** is completely stable at ambient temperature. The observed deazatization must therefore have occurred by direct photolysis of *trans*-**1d**. This mechanism is a likely contributor to the photolysis of the other azoalkanes, but for **1a** particularly, photoisomerization followed by thermolysis of the cis isomer is also possible. Thus, for **1a** it is known[6b] that warming the cis isomer gives about equal amounts of nitrogen and the trans isomer (eq 1). Low-temperature irradiation of **1a–c** at 185 nm might have revealed the contribution of each mechanism, but no equipment was available to carry out such experiments.

Long-wavelength irradiation of trans bridgehead azoalkanes produces the cis isomer, which thermally decomposes or isomerizes back to trans, depending on its structure. The results obtained with **1d** (eq 4,5) suggest that the quantum yield in both directions is 0.5, in accord with earlier results for acyclic azoalkanes.[14] Irradiation of the *cis*-azoalkanes merely causes reisomerization to *trans* with negligible loss of nitrogen (eq 2).

These results can be rationalized in terms of Figure 1. Long-wavelength excitation of either isomer produces $S_1$, which partitions itself equally to trans and cis ground states without losing nitrogen. Any decomposition that happens to occur is due to thermolysis of the often labile cis isomer. Short-wavelength irradiation produces the second excited singlet ($S_2$) state, which has an efficient decay channel, presumably internal conversion to $S_1$. Once formed, $S_1$ decays to both isomers, as described above. A certain fraction (5–15%) of the highly energetic $S_2$ states un-

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Table II. Product Distribution of the 350-nm Photodenitrogenation of Azoalkanes 1a-c in Pentane

| azoalkane | | | | | products | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | absolute yields, %[a] | | | |
| type | concn, M | time, h | temp, °C | consumption, % | RH | RR | $RC_5$ | mass balance,[a,b] % |
| **1a** | 0.01 | 5 | 35 | 99.5 | 69.0 | 24.0 | 1.5 | 93.5 |
| **1b** | 0.02 | 6 | 65 | >99 | 81.7 | 17.4 | *c* | 99.1 |
| **1c** | 0.004 | 2.5 | 60 | 91.3 | 66.0 | 17.1 | 1.2 | 97.3 |

[a] Error ca. 5% of the stated value; averaged results of at least two independent measurements; quantitated by conventional GC using anthracene as external standard. [b] Mass balance is based on consumed azoalkane. [c] Not determined.

dergoes C–N homolysis, leading to bridgehead radicals.

The deazatization quantum yield enhancement caused by short-wavelength irradiation is in accord with an earlier gas-phase study on azoisopropane (AIP).[15] Whereas the quantum yield at 355 nm under 400 torr of $CO_2$ was 0.29,[14] the value at 200 nm and the same pressure was 0.97. Since the AIP work provided evidence for vibrationally excited isopropyl radicals, it is interesting to ask whether the product distributions in Tables I and II reveal any wavelength dependence. In fact, the ratio of RH to RR is higher for **1a–c** at 185 nm than at 350 nm. The change is very small for **1a** but in this case much of the 185-nm photolysis could be due to cis thermolysis. Despite the poor product balance in the 185-nm irradiation of **1b** and **1c**, the decrease in RR yield relative to the 350-nm results seems to be real. An increase of RH/RR could reflect a lower tendency of hot radicals to recombine or a greater probability of abstracting hydrogen from pentane. A "hot cage" reaction was postulated earlier in the photolysis of *tert*-butyl alcohol in cyclohexane.[16]

In summary, we conclude that 185-nm radiation decomposes azoalkanes of structure type D as well as A–C. It was not clear a priori that this would be the case because these compound types are reluctant for different reasons. Whereas the $^1n,\pi^*$ state of B and C fluoresces, that of D isomerizes and A decays radiationlessly. Excitation to a higher energy singlet state therefore overcomes all of these reluctance mechanisms.

## Experimental Section

Solvents and reagents were purified according to literature procedures to match reported physical constants. Melting points were determined on a Reichert Thermovar and are uncorrected. IR spectra were taken on a Beckman Acculab 4 and NMR spectra on a Hitachi Perkin-Elmer R-24B spectrometer at 60 MHz or a Varian EM390 at 90 MHz. UV spectra were measured on a Cary 17 or a Beckman DB-GT spectrophotometer. Preparative GC was carried out on a Varian 920, using a 3 m × 10 mm o.d. stainless-steel column packed with 20% Apiezon M on Chromosorb W. Product analyses were performed either on a Varian 1400 or a Carlo Erba Model 2900 FRACTOVAP (vide infra).

**Diazenes.** *N,N'*-Bis(4-methylbicyclo[2.2.2]oct-1-yl)sulfamide was prepared from 2.78 g (20.0 mmol) of 1-amino-4-methylbicyclo[2.2.2]octane and 0.42 mL (5.0 mmol) of sulfuryl chloride according to the literature procedure,[8] affording 1.18 g (69% yield) of colorless, crystalline solid: mp 207–209 °C (from benzene–hexane); IR (KBr) $\nu$ (cm$^{-1}$) 3285 (NH), 1322 (antisym. $SO_2$), 1135(sym., $SO_2$); $^1$H NMR (90 MHz, $CDCl_3$) $\delta$ 0.78 (s, 6 H, $CH_3$), 1.65 (center of AA'BB' pattern, 24 H), 4.11 (s, 2 H, NH); MS (70 eV), *m/e* (%) 341 ($M^+$, 20), 340 (84), 138 (76), 69 (100). Anal. Calcd for $C_{18}H_{32}N_2O_2S$: C, 63.49; H, 9.47; N, 8.23; S, 9.42. Found: C, 63.45; H, 9.47; N, 8.17; S, 9.46.

Bis(4-methylbicyclo[2.2.2]oct-1-yl)diazene was prepared from 1.17 g (3.43 mmol) of sulfamide, 10 mL (17.4 mmol) of aqueous NaOCl, and 77 mg (1.93 mol) of NaOH according to the literature procedure,[8] affording 745 mg (79% yield) of colorless crystals; mp 139–141 °C (from methanol); IR (KBr) $\nu$ (cm$^{-1}$) 2950, 2920, 2860, 1455, 1375, 1360, 1145, 1075, 990; $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 0.76 (s, 6 H, $CH_3$), 1.60 (center of AA'BB' pattern, 24 H); MS (70 eV), *m/e* (%) 274 ($M^+$, 1), 246 ($M^+ - N_2$, 1), 123 ($M^+ - N_2 - C_9H_{15}$, 100). Anal. Calcd for $C_{18}H_{30}N_2$: C, 78.78; H, 11.02; N 10.21. Found: C, 78.66; H, 11.10; N, 10.28.

**1-Bromo-4-methylbicyclo[2.2.2]octane.**[17] A mixture of 2.61 g of polyphosphoric acid (PPA), 25.9 g (95.8 mmol) of phosphorus tribromide, and 2.00 g (14.3 mmol) of 1-methyl-4-hydroxybicyclo[2.2.2]octane was stirred at room temperature for 3 days. An additional 2.00 g of PPA was added and the stirring was continued for 3 days. The solution was poured onto ice, and the residue in the flask was dissolved in water. The combined solutions were extracted with 4 × 100 mL of ether, and the ether layers were washed with 3 × 50 mL of water and dried over $Na_2SO_4$. Rotoevaporation of ether and sublimation of the residue (bath temperature ca 100 °C at 16 torr) gave 2.53 g (87%) of colorless crystals: mp 87–93 °C (unsealed; lit. 77%, mp 92–93 °C,[17b] 92–94 °C[17a]); IR ($CCl_4$) $\nu$ (cm$^{-1}$) 2950, 2920, 2860, 1460, 1380, 1320, 1140, 1005, 920, 830; $^1$H NMR (90 MHz, $CCl_4$) $\delta$ 0.77 (s, 3 H, $CH_3$), 1.56 (m, 6 H), 2.17 (m, 6 H).

**Authentic Compounds.** 1,1'-Biadamantane was synthesized according to the literature,[18] and a sample was kindly supplied by Professor J. W. Timberlake (University of New Orleans), and norborane was prepared by catalytic reduction of norbornene. 1,1'-Binorbornane was kindly provided by Professor T. G. Traylor (University of California, San Diego) while 1,1'-bi(bicyclo[2.2.2]octane) was a gift from Professor H. E. Zimmerman (University of Wisconsin). Bicyclo[2.2.2]octane (Chemical Samples Co.) was a gift from Professor W. E. Billups (Rice University) and adamantane was purchased from Aldrich Chemical Co.

**1-Methylbicyclo[2.2.2]octane.**[19] Under a nitrogen atmosphere, ca. 2 mL of 15% *tert*-butyllithium solution in hexane was added to a solution of 852 mg (4.19 mmol) of 1-bromo-4-methylbicyclo[2.2.2]octane in 10 mL of *n*-pentane and 5 mL of ether at −78 °C. After 80 min, 2 mL of water was added to the mixture at −12 °C. The reaction mixture was extracted with 50 mL of ether and the aqueous layer discarded. The organic layer was washed with 2 × 30 mL of water and dried over $Na_2SO_4$. The solvent was removed by distillation and the residue purified by preparative GC to give 54.8 mg of pure 1-methylbicyclo[2.2.2]octane as a colorless oil: $^1$H NMR (90 MHz, $CCl_4$) $\delta$ 0.73 (s, 3 H), 1.1–1.7 (m, 13 H).

**1-Methyl-4-pent-1-ylbicyclo[2.2.2]octane.** A solution of 4.61 g (30.5 mmol) of 1-bromopentane in 10 mL of dry ether was added dropwise to a magnetically stirred suspension of 735 mg (30.2 mmol) of Mg turnings in 20 mL of dry ether. After complete addition, the solution was stirred for 1 h at room temperature. This Grignard reagent was decanted into a 18.5 cm × 24 mm i.d. test tube containing 936 mg (4.61 mmol) of 1-bromo-4-methylbicyclo[2.2.2]octane. After it was flushed with nitrogen, the test tube was placed into an autoclave and heated at 92 °C for 18 h. After the mixture was cooled with an ice-bath and the tube opened, the reaction mixture was poured into a three-necked, round-bottom flask and the cylinder rinsed with 2 × 50 mL of ether. Under a nitrogen atmosphere, water was added to the mixture while cooling with an ice bath. The organic layer was separated and the aqueous layer extracted with 2 × 50 mL of ether. The combined ether layers were washed with 3 × 100 mL of water and dried over $Na_2SO_4$. The ether layer was removed by distillation and the residue purified by preparative GC to give 15.5 mg of 1-methyl-4-pent-ylbicyclo[2.2.2]octane as colorless oil: IR ($CCl_4$) $\nu$ (cm$^{-1}$) 2925, 2855; $^1$H NMR (90 MHz, $CCl_4$) $\delta$ 0.74 (s, 3 H), 0.8–1.3 (m, 11 H), 1.33 (s, 12 H); MS (70 eV), *m/e* (%) 194 ($M^+$, 38.7), 165 (100), 152 (5.8), 138 (7.2), 123 (52.8), 109 (32.8).

**4,4'-Dimethyl-1,1'-bi(bicyclo[2.2.2]octane).** A mixture of 758 mg (3.74 mmol) of 1-bromo-4-methylbicyclo[2.2.2]octane and 60 mg (2.47 mmol) of Mg turnings in 25 mL of dry ether was heated at reflux for 24 h while being stirred magnetically. To this Grignard reagent were added 310 mg (1.53 mmol) of the bromide and 100 mg silver chloride, and the mixture was refluxed for another 2 h. After cooling with an ice bath, a saturated aqueous ammonium chloride solution was added. The organic layer was separated and the aqueous layer extracted with 2 × 20 mL of ether. The combined organic layers were washed with 2 × 40 mL of water and dried over $Na_2SO_4$. Partial removal of the solvent by distillation and recrystallization from ether gave 169 mg (28%) of colorless prisms: mp 184–185 °C; IR ($CCl_4$) $\nu$ (cm$^{-1}$) 2940, 2910, 2860, 1460, 1380, 1360; $^1$H NMR (90 MHz, $CCl_4$) $\delta$ 0.71 (s, 6 H), 1.28 (s,

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24 H); MS (70 eV), *m/e* 246 ($M^+$, 100), 231 (2.2), 217 (71.5), 189 (10.6), 176 (22.5), 161 (13.4), 147 (25.5), 133 (9.7), 123 (56.1); Anal. Calcd for $C_{18}H_{30}$: C, 87.73; H, 12.27. Found: C, 87.53; H, 12.41.

**1-Pent-1-yladamantane.**[20] 1-Pentylmagnesium bromide was prepared from 3.28 g (21.7 mmol) of 1-bromopentane and 504 mg (20.7 mmol) of Mg turnings in 20 mL of dry ether and decanted into a glass cylinder that contained 656 mg (3.05 mmol) of 1-bromoadamantane. After the mixture was flushed with nitrogen, the cyclinder was placed into an autoclave and heated while being stirred at 110 ± 5 °C for 30 min. To the cooled mixture, 50 mL of ether was added, and the contents were transferred into a flask. The unreacted Grignard reagent was destroyed by addition of a saturated aqueous ammonium chloride solution. The aqueous layer was separated from the organic layer and extracted with 60 mL of ether. The combined ether layers were washed with 3 × 50 mL of water and dried over $Na_2SO_4$. The ether was removed and the residue was purified by preparative GC to give 177 mg of 1-pent-1-yladamantane as a colorless oil: $^1H$ NMR (90 MHz, $CCl_4$) $\delta$ 0.8–1.4 (m, 11 H), 1.44 (m, 6 H), 1.67 (m, 6 H), 1.93 (m, 3 H); MS (70 eV), *m/e* 206 ($M^+$, 2.9), 135 (100).

**1-Pent-2-yladamantane.** The same procedure as for 1-pent-1-yladamantane was used, affording 43 mg of 1-pent-2-yladamantane as a colorless oil after preparative GC collection, starting from 3.25 g (21.5 mmol) of 2-bromopentane, 511 mg (21.0 mol) of Mg turnings, and 802 mg (3.73 mmol) of 1-bromoadamantane. IR ($CCl_4$) $\nu$ ($cm^{-1}$) 2910, 2850, 1450; $^1H$ NMR (90 MHz, $CCl_4$) $\delta$ 0.6–1.5 (m, 11 H), 1.49 (m, 6 H), 1.64 (m, 6 H), and 1.93 (m, 3 H); MS (70 eV), *m/e* (%) 206 ($M^+$, 1.3), 135 (100). Exact Mass: Calcd for $C_{15}H_{26}$: 206.2035. Found: 206.2034.

**185-nm Photolysis of Diazenes.** The Srinivasan procedure[9] was followed for these photolyses. Pentane solvent was purified prior to use by successive treatment with fuming sulfuric acid and 0.5 N $KMnO_4$ in 3 M sulfuric acid, washing with water, drying over $Na_2SO_4$ and distillation from $LiAlH_4$. By this procedure it was possible to reduce the absorbance of the purified pentane to <0.3 (10 mm path length) at 200 nm. Before irradiation, the pentane solutions of the diazenes were deaerated by purging thoroughly with purified nitrogen for at least 30 min. The pentane solution was placed into the cylindrical photovessel, equipped with a 50-W hot cathode mercury resonance lamp, which was contained in a Suprasil immersion well. While maintaining the reaction temperature at ca. 25 °C by means of an external cooling jacket, the contents were irradiated for 10 min. Electronic spectra were recorded after photolysis. The identity of the photoproducts was assessed by comparison of GC retention times and spectral data with the authentic samples. In the case of 1,1′-binorbornane, GC–MS was also used for identification.

The qualitative product distribution (cf. Table I) of diazenes **1a–c** was determined relative to anthracene as an external standard on a Varian 1400 GC, using a 0.9 m × 2 mm glass column packed with 5% DC 200 on Chromosorb W (60–80 mesh). For the diazenes **1b** and **1c** the injector temperature was kept at 225 °C and the column temperature at 35 °C (low-boiling products) and 135 °C (high-boiling products). For the diazene **1a** the injector temperature was 241 °C and the column temperature 70 °C (low-boiling products) and 189 °C (high-boiling products). A Carlo Erba Model 2900 FRACTOVAP was employed for the quantitative product analyses of diazene **1d** using a 50-m OV-101 capillary column, which was operated at an injection temperature of 226 °C and a column temperature programmed from 60 to 180 °C. Anisole was added after photolysis for use as a standard.

Quantum yields at 185 nm (cf. Table I) were determined relative to photoisomerization of *cis*-cyclooctene, following the published procedure.[9] The quantitative product distribution and quantum yields are summarized in Table I.

**Control Experiment of Product Stability toward 185-nm Light.** Under the same conditions as the photolysis of diazenes, 50 mL of 0.01 M norbornane in pentane was irradiated for 10 min. Anisole was added after irradiation as external standard, and the recovery of norbornane was determined by capillary GC to be 99.7%. A separate irradiation of the solvent alone gave no new peaks on capillary GC.

**350-nm Photolyses of Diazenes.** ***trans*-1a.** After nitrogen was bubbled for 30 min through the reaction mixture consisting of 45 mL of 0.01 M **1a** in pentane, the sample was irradiated in a Rayonet Photoreactor equipped with 350-nm lamps for 5 h in a Solidex vessel. The product data are shown in Table II.

***trans*-1c.** Into a Pyrex test tube were placed 3.5 mL of 0.004 M **1c** in deaerated pentane (see above) and ca. 20 mg of $K_2CO_3$ powder. The test tube was sealed and the solution irradiated for 2.5 h at 60 °C with the 351-nm line of the Coherent CR-18 Supergraphite argon ion laser. The product data are shown in Table II. After 7.5 min of irradiation at 0 °C with the 351-nm laser line, the electronic spectrum of the *cis*-**1c** product was taken, giving $\lambda_{max}$ 440 nm and $\epsilon$ 64. This extinction coefficient represents the lower limit (100% isomerization assumed), since the low value of the trans isomer does not permit assessing with certainty whether complete trans → cis isomerization had taken place.

**Trans → Cis Isomerization of 1c.** In a 10 × 10 mm UV cell were placed ca. 2 mL 0.01 M *trans*-**1c** ($\lambda_{max}$ 365 nm; $\epsilon$ 21) in deaerated pentane and ca. 20 mg $K_2CO_3$ powder.

After 7.5 min of irradiation at 0 °C with the 351-nm laser line, the electronic spectrum of the *cis*-**1c** product was taken, giving $\lambda_{max}$ 440 nm and $\epsilon$ 64. This extinction coefficient represents the lower limit (100% isomerization assumed), since the low value of the trans isomer does not permit assessing with certainty whether complete trans → cis isomerization had taken place.

**Irradiation of 1a–c at 366 nm.** Three milliliters of 0.02 M **1b** and **1c** in pentane were degassed in a square Pyrex cuvette, and the solutions were irradiated at 65 °C with 366-nm light from a filtered 500-W mercury short arc lamp. After the azoalkane was gone, as judged by UV analysis, the tubes were opened, and a 10-$\mu$L portion of *n*-tetradecane was added as an external GC standard. The solutions were then analyzed by GC on a 5 ft × $^1/_8$ in. 10% SE-30 column programmed from 125 to 200 °C at 4 °/min. Response factors were determined for the FID detector by using solutions of known concentration of tetradecane and authentic products.

**Kinetics of *cis*-1c to *trans*-1c Isomerization.** Degassed, sealed solutions of 0.004 M *trans*-**1c** in pentane were placed into a 10 × 10 mm UV cell and irradiated at 0 °C with the 351-nm laser line for 450 s. The cuvettes containing the yellow cis isomer were transferred into the cell compartment of a Cary 17 spectrometer, which was preheated at the specific temperature. Temperature was controlled to ±0.1 °C by an Ultrathermostat K5 of Colora Messtechnik GmbH. The decrease of the absorbance of the cis isomer was monitored at 480 nm, resulting in first-order rate plots. To obtain reproducible results, it was necessary to add ca. 20 mg of powdered $K_2CO_3$ to the solution. The rate constants ($10^{-4}$ $s^{-1}$) at various temperatures (°C) were 0.950 (22.1), 1.01 (22.9), 2.89 (30.8), 3.98 (32.0), 5.77 (35.1) 10.1 (40.2), 13.9 (42.0), 17.0 (43.1), 20.3 (44.9), 34.3 (49.8), 35.8 (50.3).

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**Registry No.** (*E*)-**1a**, 24325-56-2; (*Z*)-**1a**, 59388-63-5; (*E*)-**1b**, 78497-37-7; (*E*)-**1c**, 86689-22-7; (*Z*)-**1c**, 86689-23-8; (*E*)-**1d**, 59388-65-7; (*Z*)-**1d**, 59388-64-6; *N,N′*-bis(4-methylbicyclo[2.2.2]oct-1-yl)sulfamide, 86689-24-9; 1-methyl-4-hydroxybicyclo[2.2.2]octane, 824-13-5; 1-bromo-4-methylbicyclo[2.2.2]octane, 697-40-5; 1-methylbicyclo[2.2.2]octane, 19074-26-1; 1-bromopentane, 110-53-2; 1-methyl-4-pent-1-ylbicyclo[2.2.2]octane, 86689-25-0; 4,4′-dimethyl-1,1′-bi(bicyclo[2.2.2]octane), 80060-65-7; 1-bromoadamantane, 768-90-1; 1-pent-1-yladamantane, 50782-11-1; 1-pent-2-yladamantane, 28128-94-1; 2-bromopentane, 107-81-3; nitrogen, 7727-37-9.

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