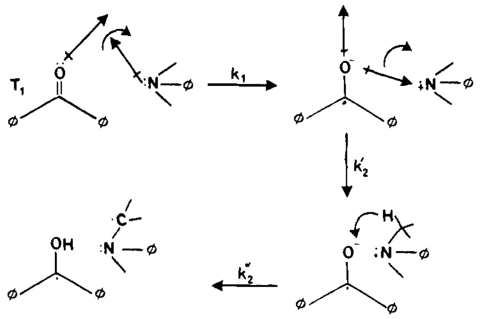
Scheme I



events, however, occur too rapidly to be resolved by our experiment. The singlet radical anion decays with a rate constant of 5.0×10^8 s^{-1}.

At 10 ns after photolysis, the equilibrium constant for the ketyl radical/radical anion equilibrium is similar for the photoreduction by both 1.0 and 5.0 M DMA (Table I). However for the photoreduction by DEA we observe a shift in the equilibrium in favor of the ketyl radical upon an increase in amine concentration. An increase in amine concentration results in a decrease in the dielectric of the medium. This in turn destabilizes the ion pair with respect to the ketyl radical. Examining the equilibrium constants in Table I, we observe that the equilibrium constants for photoreduction by 1.0 M DEA are more sensitive to a lowering in dielectric than the corresponding values for 1.0 M DMA. The increased sensitivity of the ketyl radical/radical anion equilibrium in the DEA system can be explained within the Born continuum approximation[18] by postulating an increased internuclear separation in the contact ion pair. This increased separation results from the increased steric hindrance in the contact ion pair with an increase in alkyl chain length.

In summary (Scheme I) the dynamics and solvent dependences of the primary processes of the photoreduction of benzophenone by DMA and DEA have been elucidated by using picosecond absorption spectroscopy. The first step, k_1, involves electron transfer from an amine not directly involved in solvating the carbonyl moiety of the ketone. The resulting solvent-separated ion pair diffuses together, k_2', forming the contact ion pair from which the proton is then transferred, k_2''.

Acknowledgment. The research is supported by a grant from NIH (No. EY02922-02) and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also thank Peter Wolynes and Dan Calef for extremely helpful discussions.

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Thermolysis and Photolysis of the Azoalkane 2,3-Diazatricyclo[4.3.0.$0^{4,9}$]non-2-ene: Generation and Transformation of the Bicyclo[2.2.1]heptane-2,7-diyl Diradical

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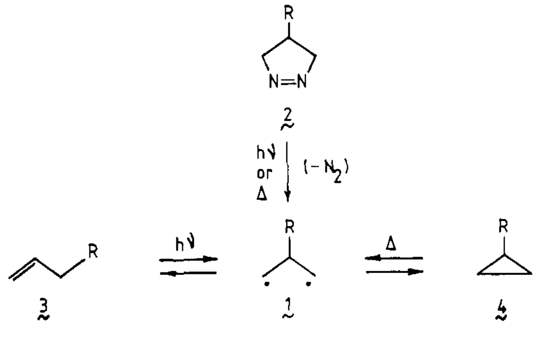
Abstract: The trimethylene diradical bicyclo[2.2.1]heptane-2,7-diyl (**5**) was generated via denitrogenation of the azoalkane 2,3-diazatricyclo[4.3.0.$0^{4,9}$]non-2-ene (**6**) by means of vacuum flash pyrolysis, tetramethyl-1,2-dioxetane chemienergization, direct photolysis at 350 nm by excitation of the n,π* azo chromophore, and benzophenone sensitization. It is concluded that the thermally equilibrated singlet-state and triplet-state diradicals **5** exclusively cyclize into tricyclo[3.2.0.$0^{4,6}$]heptane (**7**). For the vibrationally excited ("hot") diradical (**5**), rearrangement into bicyclo[3.2.0]hept-2-ene (**10**) competes, although inefficiently, with cyclization. Fragmentation of **5** into 3-vinylcyclopentene (**8**) and rearrangement into norbornene (**9**) are not observed.

The behavior of 1,3-diradicals such as the trimethylenes **1** has been an active area of mechanistic research[1] during the last decades. These elusive reaction intermediates can be conveniently prepared via thermal or photochemical denitrogenation of the corresponding azoalkanes,[2,3] the pyrazolines **2** (eq 1). Although the rearrangement of the trimethylenes **1** into the alkenes **3** is according to thermochemical estimates[1f] by 8 kcal/mol more exothermic than cyclization into the cyclopropane **4**, the latter is kinetically the preferred process by 2 kcal/mol; in fact, matrix isolation work on the related 1,3-cyclopentanediyl diradical suggests that the activation energy for cyclization is <2 kcal/mol.[3] Alternatively the 1,3-diradical **1** can be generated photochemically[4]



(1)

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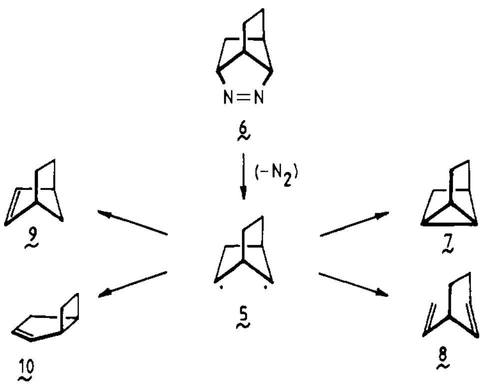
Table I. Product Composition of the Vacuum Flash Pyrolysis, Direct and Benzophenone-Sensitized Photolysis, and TMD-Chemienergized Thermolysis of Azoalkane **6**

activation mode	conditions	product yields, %[a] 7	10	11	unidentified	product balance, %
VFP	ca. 400 °C at 0.2 Torr	2.4 ± 0.1		97.6 ± 0.1		98
Δ	80-85 °C; 2 h, TMD (benzene)	50.7 ± 2.9[b]				100
hν	300–330 nm, $Ph_2C=O$ (pentane)[c,d]	99 ± 2				99
hν	350 nm (pentane)[c]	92.8 ± 0.1	5.0 ± 0.1		2.2 ± 0.1[e]	100

[a] Analyzed by GC (cf. Experimental Section for details). [b] Remainder is unreacted azoalkane **6**. [c] Rayonet photoreactor was employed. [d] A $K_2Cr_2O_7/K_2CO_3$ filter was used to avoid direct photolysis. [e] This material consisted of at least three C_7H_{10} isomers, none of which corresponded to norbornene and/or 3-vinylcyclopentene as confirmed by GC (capillary)-MS, with authentic samples.

from the alkene **3** or thermally[1b] from the cyclopropane.[4]

In this context it was of interest to explore the behavior of a geometrically rigid and strained trimethylene, by placing the 1,3-diradical sites into a bicyclic skeleton as in the hitherto unknown bicyclo[2.2.1]heptane-2,7-diyl (**5**). The 1,3-diradical **5** was to be generated via thermal and photochemical denitrogenation of the recently reported[5] azoalkane **6** (eq 2).

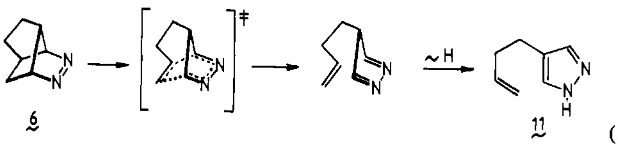


(2)

Possible transformations of the 1,3-diradical **5**, which are energetically feasible, include cyclization into tricyclo[3.2.0.0^{4,6}]heptane (**7**), fragmentation into 3-vinylcyclopentene (**8**), and the uncommon rearrangements, i.e., 1,2-alkyl shifts of the C_5-C_6 dimethylene bridge,[1a] into norbornene (**9**) and bicyclo[3.2.0]hept-2-ene (**10**). 1,2-Shift of the bridgehead hydrogen at C_1 is unlikely because anti-Bredt olefins would result. Herein we report on the results of the vacuum flash pyrolysis (VFP), direct and triplet-sensitized photolysis, and chemienergization by tetramethyl-1,2-dioxetane (TMD) of azoalkane **6** in the interest of generating the 1,3-diradical **5** and assessing its chemical comportment. The results of the product compositions are summarized in Table I and are discussed below.

Discussion

To our surprise, the azoalkane **6** was rather stable toward thermolysis in solution. For example, on VPC injection at 300 °C azoalkane **6** is stable, but the 2,3-diazabicyclo[2.2.1]heptene (DBH) is completely decomposed. Apparently, the rigidity of this tricyclic azoalkane prevents nitrogen extrusion under the usual thermolysis conditions. However, under vacuum flash pyrolysis (VFP) at ca. 400 °C and 0.2 Torr, decomposition of azoalkane **6** could be induced, but the major product (97.6 ± 0.1%) was from the retro-Diels-Alder process shown in eq 3. (Table I). Although quite unusual, such cycloreversions have been reported recently.[6] The pyrazole **11** was fully characterized on the basis of its correct elemental composition and spectral data (cf. Experimental Section). In addition it was catalytically hydrogenated (Pd/C) to 4-(*n*-butyl)pyrazole, leaving no doubt about the structure assignment of the VFP product **11**.



(3)

The minor product (2.4 ± 0.1%) in the pyrolysis was tricyclo[3.2.0.0^{4,6}]heptane (**7**). No other products in amounts greater than 0.1% were formed. Control experiments revealed that tricycloalkane **7** was stable toward the VFP conditions. Thus, the thermally generated bicyclo[2.2.1]heptane-2,7-diyl diradical (**5**) cyclized exclusively into the tricycloalkane **7**, without fragmentation into **8** or rearrangement into **9** and **10**. This is of mechanistic significance, as will be discussed below.

Although the tricycloalkane **7** has been reported previously,[7] no complete characterization was attempted. Consequently, the necessary spectral data (IR, ^{1}H and ^{13}C NMR, and MS) are given in the Experimental Section. On electron impact at 70 eV the parent ion *m/e* at 94 amu is barely visible, but on chemical ionization with isobutane the parent ion is readily observed.[8] For identification purposes we have reproduced the 90-MHz ^{1}H NMR (complex multiplet at δ 1-3 ppm) and the IR (C-H region at 3200-2800 cm^{-1}) spectra (Figure 1). Even at 400 MHz, it is not possible to assign the proton resonance spectrum unequivocally.[9]

The acetone-sensitized photolysis was complicated by the fact that no appropriate filter could be found to allow selective n,π^* excitation of the C=O chromophore of acetone without irradiating the n,π^* azo chromophore. For this purpose we used tetramethyl-1,2-dioxetane (TMD) as the thermal source of triplet

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(8) We are grateful to Dr. G. Lange (University of Würzburg) for having run the mass spectra for us.

(9) We thank Dr. D. Scheutzow (University of Würzburg) for having run the NMR spectra for us. A complete discussion of the high-field NMR assignment will be the subject of a separate paper.

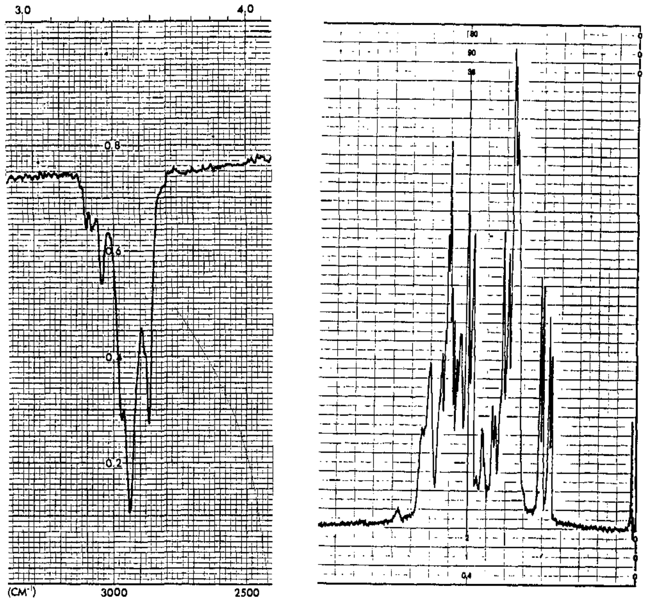


Figure 1. IR spectrum of 3200–2800-cm^{-1} aliphatic C–H region (left) and 90-MHz ^{1}H NMR spectrum of δ 1–3 ppm multiplet of tricyclo[3.2.0.0^{4,6}]heptane (**7**).

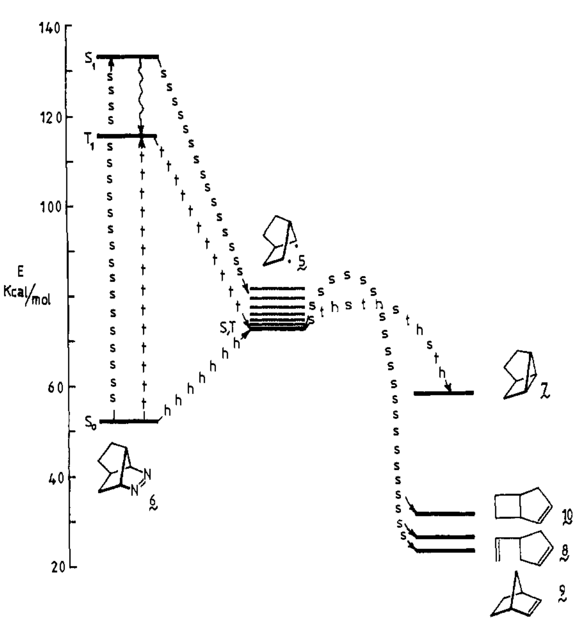
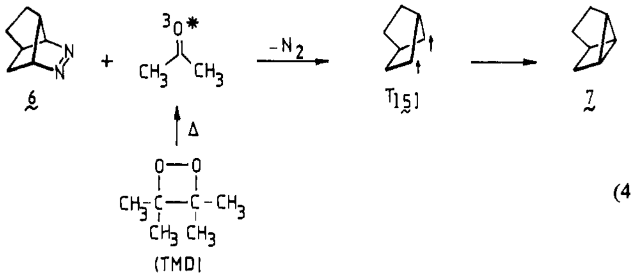


Figure 2. Qualitative energy level diagram of the thermal (–h–h–h–) and direct (–s–s–s–) and triplet-sensitized (–t–t–t–) photolytic denitrogenation of 2,3-diazatricyclo[4.3.0.0^{4,9}]non-2-ene (**6**).

acetone.[10] On heating a benzene solution of azoalkane **6** with TMD at 80–85 °C for 2 h (see Experimental Section for details), ca. 50% of **6** had been consumed, leading quantitatively (Table I) to the tricycloalkane **7**. Within the limits of GC detection (ca. 0.1%) no other products were observed. The TMD chemienergization is shown in eq 4. Similarly, the benzophenone-sensitized



(4)

photolysis in pentane at 300–330 nm, using a $K_2Cr_2O_7$–K_2CO_3 filter[11] (see Experimental Section for details) for selective excitation of the C=O chromophore, gave also the tricycloalkane **7** as the only product (Table I). Thus, the triplet 1,3-diradical **5**, formed by triplet sensitization, undergoes exclusively cyclization.

The direct photolysis of azoalkane **6** at 350 nm (n,π* excitation of the azo chromophore) in pentane (see Experimental Section for details) gave a more complex product picture (Table I). The major product (ca. 93% yield) was again tricycloalkane **7**, but ca. 5% of bicyclo[3.2.0]hept-2-ene (**10**) was also formed, together with ca. 2% unidentified products. The bicycloheptane **10** was identified by GC–MS on comparison with an authentic sample.

It was not possible to characterize the remaining 2% of the products of the photodenitrogenation of **6**. Capillary GC revealed that this fraction consisted of at least three components, whose mass spectra were all very similar, namely, C_7H_{10} isomers. By comparison with authentic materials, it could be conclusively shown by GC–MS that none of these components was either norbornene (**9**) or 3-vinylcyclopentene (**8**). The latter was prepared by coupling 3-bromocyclopentene with vinylmagnesium bromide.[12] 3-Vinylcyclopentene (**8**) and norbornene (**9**) were photostable under the conditions of the 350-nm photolysis of azoalkane **6**. Thus, it is mechanistically significant that the fragmentation product 3-vinylcyclopentene (**8**) and the rearrangement product norbornene (**9**) are not formed even in traces during the direct photolysis of azoalkane **6**.

The fact that the direct photolysis at 350 nm affords appreciable amounts of the rearrangement product bicyclo[3.2.0]hept-2-ene (**10**) besides the cyclization product tricycloalkane **7**, implies that a thermally equilibrated singlet-state 1,3-diradical **5** (as observed in the thermolysis) or triplet state (as observed in the TMD chemienergization or benzophenone sensitization) cannot be the precursor to the products of the 350-nm photolysis. We postulate that a vibrationally excited ("hot") 1,3-diradical **5** is involved. Presumably the latter contains sufficient internal energy so that the rather rare 1,2-alkyl shift[1a], as postulated in the rearrangement **5** → **10**, competes, although inefficiently, with cyclization into **7**. It is surprising that not even traces of fragmentation into **8** and rearrangement into **9** take place.

The following mechanistic conclusions emerge from our investigation concerning the chemical behavior of the bicyclo[2.2.1]heptane-2,7-diyl diradical (**5**): (a) its thermally equilibrated singlet state, generated in the thermal denitrogenation of azoalkane **6**, exclusively cyclizes into the tricycloalkane **7**; (b) its vibrationally excited ("hot") singlet state, obtained in the direct photolysis of **6** at 350 nm, besides cyclization rearranges into the bicycloalkene **10**, although inefficiently; (c) its triplet state, produced from **6** via benzophenone sensitization or TMD chemienergization, again only cyclizes; (d) the 1,3-diradical **5** does not fragment into 3-vinylcyclopropane (**8**) or rearrange into norbornene (**9**).

These mechanistic details are summarized in the qualitative energy scheme shown in Figure 2. In analogy to the 1,3-cyclopentanediyl diradical generated from the 2,3-diazabicyclo[2.2.1]heptene, it is assumed that a nitrogen-free bicyclo[2.2.1]hepten-2,7-diyl diradical (**5**) is formed. Thermochemical estimates by the Benson method[13] suggest that a nitrogen-free diradical **5** is energetically preferred. The ground-state energies (ΔH_f) of the azoalkane **6**, its 1,3-diradical **5**, and the possible products **7**–**10** have been estimated with the help of Benson's group additivity values.[1a,13] The triplet excited-state energy of the azoalkane **6** is not known, but should be ca. 63–65 kcal/mol by comparison with 2,3-diazabicyclo[2.2.1]heptene.[1a] The singlet excited-state energy was determined to be 81.4 kcal/mol from its absorption and fluorescence spectra. Furthermore, the ther-

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mally equilibrated singlet-state and triple-state diradicals **5** must be close in energy and readily interconvert since in the VFP-(singlet state) and TMD-energized (triplet state) denitrogenations only cyclizations are observed. Thus, irrespective of its mode of generation, the preferred reaction of the "cold" diradical **5** is cyclization.

Analogous to the strain-free trimethylene diradical **1**, cyclization possesses the lower activation energy. Neither fragmentation, which would afford the considerably more stable (by ca. 25 kcal/mol) 3-vinylcyclopentene (**8**), nor rearrangement into norbornene (**9**) or bicyclo[3.2.0]hept-2-ene (**10**) can compete with cyclization. Thus, for the "cold" diradical **5** the fragmentation and the rearrangement channels leading respectively to 3-vinylcyclopentene (**8**) and norbornene (**9**) and bicyclo-alkene (**10**) have too high activation energies, although thermodynamically speaking they are considerably more stable than the tricycloalkane **7** product. Consequently, **7** is the kinetically preferred product. Only for the "hot" 1,3-diradical, formed in the 350-nm photolysis, can rearrangement into **10** compete with cyclization into **7**, but fragmentation products **8** and rearrangement product **9** are energetically still inaccessible. Of course, in the gas phase at low pressures for the "hot" diradical such higher energy channels would be more likely because vibrational deactivation would be minimized. In conclusion, our data suggest that the conformationally rigid bicyclo[2.2.1]hepta-2,7-diyl diradical (**5**) is predisposed to cyclization compared to the conformationally flexible 1,3-trimethylene **1**. Inspection of molecular models reveals that the 2p orbitals at the C_2 and C_7 radical sites overlap favorably in view of their locked-in conformation and this promotes cyclization.

Experimental Section

Boiling points and melting points are uncorrected. Infrared spectra were taken either on a Perkin-Elmer Model 283 or Beckman Acculab 4 spectrophotometers. The 60 MHz ^{1}H NMR spectra were measured on a Hitachi-Perkin-Elmer Model R-24B spectrometer. The high-field ^{1}H NMR and ^{13}C NMR spectra were taken for us by Dr. D. Scheutzow on a Bruker 4.22T instrument at 45.28 MHz. The UV spectra were determined on a Beckman DB-GT spectrophotometer. Elemental analyses were performed in house and were within the accepted ±0.3% limits for carbon, nitrogen, and hydrogen. Commercial reagents and solvents were purified to match reported physical and spectral properties. Known compounds used in this research were either purchased from standard sources or prepared according to literature procedures and purified to match the reported physical and spectral data.

Preparation of Azoalkane 6. The azoalkane **6** was prepared in 32% yield from the corresponding urazole as described,[5] mp 145–146 °C (lit.[5] mp 147–149 °C): ^{13}C NMR (15.08 MHz) in $CDCl_3$ δ (ppm) 18.28, 27.31, 31.81, 32.05, 55.19, 80.45, 85.35; UV (pentane) λ_{max} 345 nm (ϵ 239).

Vacuum Flash Pyrolysis of Azoalkane 6. Into a 10-mL, round-bottom flask was placed 30 mg of azoalkane **6** and the flask connected to the pyrolysis apparatus, consisting of a 40-cm long × 12 mm o.d. pyrex tube (heavy-walled), which was preheated at ca. 400 °C by means of an external Nichrome wire. The azoalkane was volatilized at 0.2 Torr by heating at ca. 100 °C into the hot tube and the effluent was collected in a dry ice cooled trap. The pyrolysis mixture consisted of 97.6 ± 0.1% 4-(3-butenyl)-1,2-pyrazole (**11**) and 2.4 ± 0.1% tricycloalkane **7**, as determined by GC using a 50-m capillary column packed with OV-101 and operated at injector and column temperatures at 150 and 71 °C, respectively, and a nitrogen flow of 1 mL/min.

The pyrazole structure **11** is based on the following data: ^{1}H NMR (60 MHz, CCl_4, Me_4Si) δ (ppm) 2.40 (m, 4 H, CH_2), 4.95 (m, 2 H, $=CH_2$, AB part of ABX system), 5.8 (m, 1 H, $=CH$, X part of ABX system), 7.32 (br s, 2 H, pyrrole); IR (CCl_4) ν (cm^{-1}) 3480, 3160, 3080, 2990, 2930, 1640, 1470; colorless liquid, correct elemental composition for the $C_7H_{10}N_2$ empirical formula. On catalytic reduction over 10% Pd/C in CH_2Cl_2, 4-(*n*-butyl)pyrazole was obtained as colorless liquid, bp 135–140 °C at 1 Torr, in 95% yield: ^{1}H NMR (60 MHz, CCl_4, Me_4Si) δ (ppm) 0.7–1.0 (t, 3 H, CH_3, $J = 7.0$ Hz), 1.1–1.8 (m, 4 H, CH_2) 2.3–2.6 (t, 2 H, $-CH_2Ar$, $J = 7.0$ Hz), 7.3 (s, 2 H, pyrrole), 9.8 (s, 1 H, NH); IR (CCl_4) ν (cm^{-1}) 3480, 3200, 2945, 2860, 1350, 1250, 1090; correct elemental composition for the $C_7H_{12}N_2$ empirical formula.

The tricycloalkene **7** was collected by GC (Varian Aerograph Model 920) on a 1.5 m × 6 mm o.d. stainless steel column packed with 5% OV-101 on Chromosorb P and operated at injector and column temperatures of 150 and 50 °C and a H_2 flow of 20 mL/min. The structure is based on the following spectral data: 90-MHz ^{1}H NMR and the IR spectra as given in Figure 2; 400-MHz ^{1}H NMR ($CDCl_3$, Me_4Si) δ (ppm) 1.0–1.1 (pair of q, 1 H), 1.3–1.5 (m, 3 H), 1.5–1.6 (m, 1 H), 1.9–2.0 (m, 2 H), 2.1–2.3 (m, 2 H), 2.4–2.5 (m, 1 H); 22.5--MHz ^{13}C NMR ($CDCl_3$, Me_4Si) δ (ppm) 14.92, 22.72, 22.83, 25.64, 25.97, 35.18, 38.27; MS (70 eV) *m/e* (%) 94 (1), 91 (12), 79 (34), 77 (32), 66 (100), 39 (14); MS (chemical ionization by isobutane) *m/e* (%) 93 (100), 94 (11), 95 (41).

Direct Photolysis of Azoalkane 6. Into a Pyrex vessel was deposited ca. 15 mL of a 0.04 M solution of the azoalkane **6** in *n*-pentane (Spectroquality). The solution was irradiated in a Rayonet photoreactor, equipped with 350-nm lamps (black phosphor) for excitation of the n,π^* azo chromophore, until complete denitrogenation, as monitored by ^{1}H NMR. The photolysate was analyzed on a Carlo Erba Fractovap 2900 gas chromatograph, using a 50-m capillary column packed with OV-101 and operated at injector and column temperatures of 175 and 100 °C and a nitrogen flow of 1 mL/min. The quantitative results are given in Table I.

The products were identified by comparison with authentic materials using MS–GC. Control experiments (MS–GC) with authentic materials established that the unidentified products (ca. 2%), consisting of a mixture of at least three C_7H_{10} isomers, were not 3-vinylcyclopentene (**8**) and norbornene (**9**). The bicycloalkane **8** and norbornene (**9**) were stable toward the photolysis conditions of azoalkane **6**.

Benzophenone-Sensitized Photolysis of Azoalkane 6. Into a Pyrex vessel was deposited ca. 15 mL of a 0.01 M azoalkane and 0.1 M benzophenone solution in *n*-pentane (Spectroquality); the solution was irradiated at 300–330 nm in a Rayonet photoreactor, equipped with 300-nm lamps, using a $K_2Cr_2O_7$–K_2CO_3 filter,[11] until complete consumption of **6** as monitored by ^{1}H NMR. The photolysate was analyzed by GC as described above, and the results are summarized in Table I.

Tetramethyl-1,2-dioxetane (TMD) Chemienergization of Azoalkane 6. Into a Pyrex ampule was placed 120 μL a 0.02 M benzene solution of **6** containing 1.6 mg of TMD; the ampule was sealed under vacuum and heated in a temperature-controlled bath at 80–85 °C for 2 h until complete consumption of TMD, as monitored by ^{1}H NMR. Quantitative GC analysis on a Perkin-Elmer Model 900 gas chromatograph (using a 6 ft × $^1/_8$ in. stainless steel column packed with 10% SE-30 on Chromosorb P and operated at an injector temperature of 200 °C and a column temperature program rate of 16 °C/min, starting at 80 °C and terminating at 220 °C, and a nitrogen gas flow of 25 mL/min) gave the product composition listed in Table I.

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