On the Mechanism of the Benzophenone-Sensitized Photolysis of 2,3-Diazabicyclo[2.2.1]hept-2-ene in the Laser Jet: Evidence for Intermolecular Triplet Diradical Reactions

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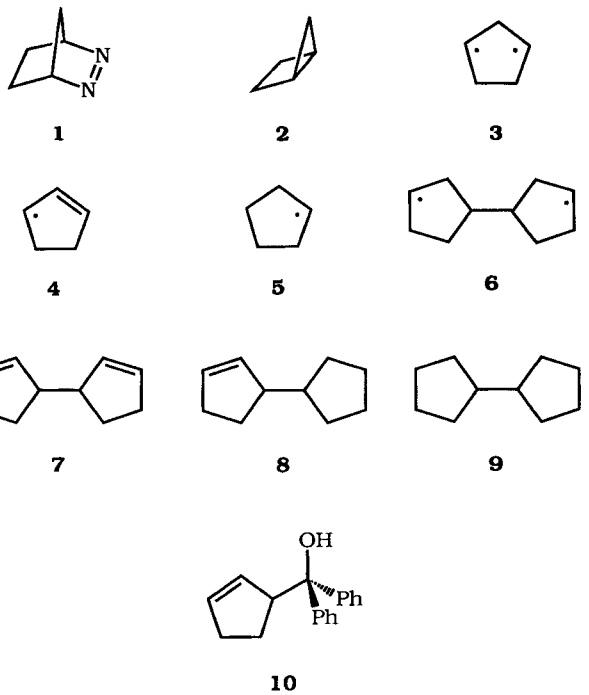
The benzophenone-sensitized laser jet photolysis of 2,3-diazabicyclo[2.2.1]hept-2-ene (**1**) affords, besides the previously reported cyclopentene and housane (**2**), also cyclopentane, cyclopentadiene, and the dimers bicyclopent-2-en-1-yl (**7**), 3-cyclopentylcyclopent-1-ene (**8**), and 1,1'-bicyclopentyl (**9**). As a model reaction, the pyrolysis of dimer **8** at 600°C/20 Torr leads to the other dimers **7** and **9** together with cyclopentadiene, cyclopentene, and traces of cyclopentane. Control experiments showed that H abstraction by the cyclopentane-1,3-diyl diradical (**3**) from cyclohexene (as model substrate for cyclopentene) and addition to housane (**2**) with formation of diradical **6** are unlikely pathways. Instead, the product data available can be best explained in terms of an intermolecular disproportionation of two diradicals **3** to give the cyclopent-2-en-1-yl (**4**) and cyclopentyl (**5**) radical pair, which is subsequently converted to the observed products by in-cage and out-of-cage coupling and H transfer reactions. Such intermolecular diradical chemistry becomes feasible due to the high steady-state concentrations (ca. micromolar) generated in the laser jet. Two-photon processes take place, but are of subordinate importance.

Azoalkanes are an important class of substrates for the generation of diradicals by thermal or photochemical extrusion of nitrogen[1]. Besides mechanistic interest[1c], such diradicals are convenient precursors of unusual organic structures[1b], which are difficult to generate by other synthetic methods.

The photochemistry of 2,3-diazabicyclo[2.2.1]hept-2-ene (**1**) has been the subject of intense investigations, which include the direct and triplet-sensitized[2], and the 185-nm[3] and laser jet[4] photochemical transformations. While the exclusive product in the direct and triplet-sensitized photolyses is housane (**2**), on 185-nm irradiation a signficant yield of cyclopentene has been observed. This fact has been explained[3] in terms of higher excited states of the cyclopentanediyl diradical **3**, which rearranges to cyclopentene by a 1,2-H shift.

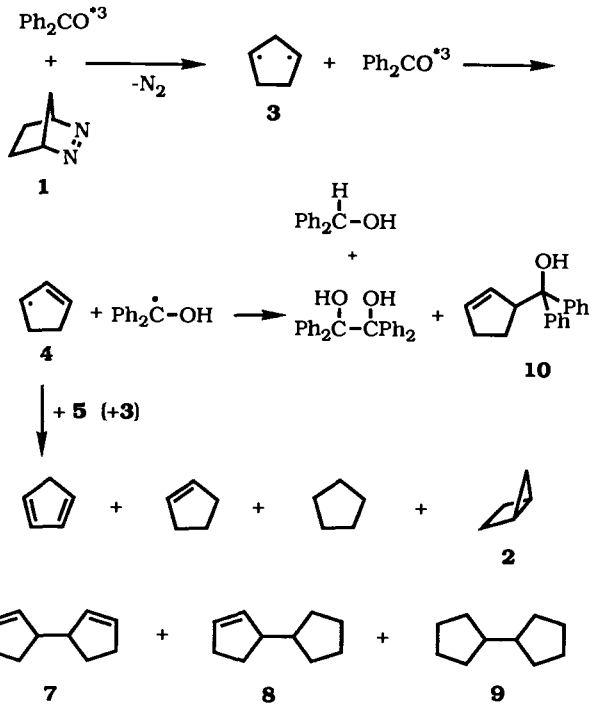


1 **2** **3** **4** **5** **6** **7** **8** **9** **10**

The advantage of the 185-nm photolysis is the possibility of working with light of high energy, and thereby the excitation to higher energy electronic states becomes feasible[5]. In contrast, the laser jet technique enables the generation of high light intensities[6], extraordinary conditions under which high steady-state concentrations of transient species can be produced in the liquid phase and multi-photon processes become accessible. Thus, the benzophenone-sensitized photolysis of azoalkane **1** in the laser jet[4] gives as main products housane (**2**) and cyclopentene; in addition, three dimeric products have been detected but not identified. Dimer formation derives from coupling of triplet diradicals, which constitutes an unusual intermolecular event for such short-lived transients as the triplet cyclopentane-1,3-diyls, but has been observed for the much longer lived non-Kekulé diradicals[7].

If triplet diradicals can dimerize under laser jet photolysis conditions, they may also disproportionate on *intermolecular* encounter and eventually lead to cyclopentadiene, cyclopentene, and cyclopentane as monomeric products, besides bicyclo[2.1.0]pentane by *intramolecular* cyclization (Scheme 1). A careful product analysis of the laser jet photochemistry of azoalkane **1** seemed justified to assess

Scheme 1. Possible products in the benzophenone-sensitized laser jet photolysis of azoalkane **1**



whether cyclopentene results from an *intramolecular* two-photon process of the short-lived triplet cyclopentane-1,3-diyl, as previously proposed[4], or from *intermolecular* disproportionation, or even from both processes.

Results and Discussion

The products, which result from the benzophenone-sensitized laser jet photolysis of 2,3-diazabicyclo[2.2.1]hept-2-ene (**1**) were identified by a comparison of their NMR data and capillary GC coinjections with authentic samples. By these means it was possible to assess the structure of the dimeric products mentioned previously[4]. Additionally, small amounts of cyclopentadiene and cyclopentane were detected. By means of capillary GC and HPLC analyses the quantitative product distributions were determined (Scheme 1, Table 1).

A possible reaction pathway constitutes H abstraction by triplet-excited benzophenone from the cyclopentane-1,3-diyl diradical to afford the diphenylhydroxymethyl and cyclopent-2-en-1-yl (**4**) radicals as intermediates, which can be identified by means of the products derived therefrom (Scheme 1). Thus, their coupling would generate the alcohol **10**, which was postulated to be formed in the photochemical reaction of benzophenone in cyclopentene[8]. Additionally, the diphenylhydroxymethyl radical itself can abstract a hydrogen atom from the diradical **3** to give benzhydrol or dimerize to benzpinacol[9]. However, the experimental results reveal that in the benzophenone-sensitized laser jet photolysis of 2,3-diazabicyclo[2.2.1]hept-2-ene only trace amounts (conversion: 1%) of the above mentioned benzophenone-derived products were observed.

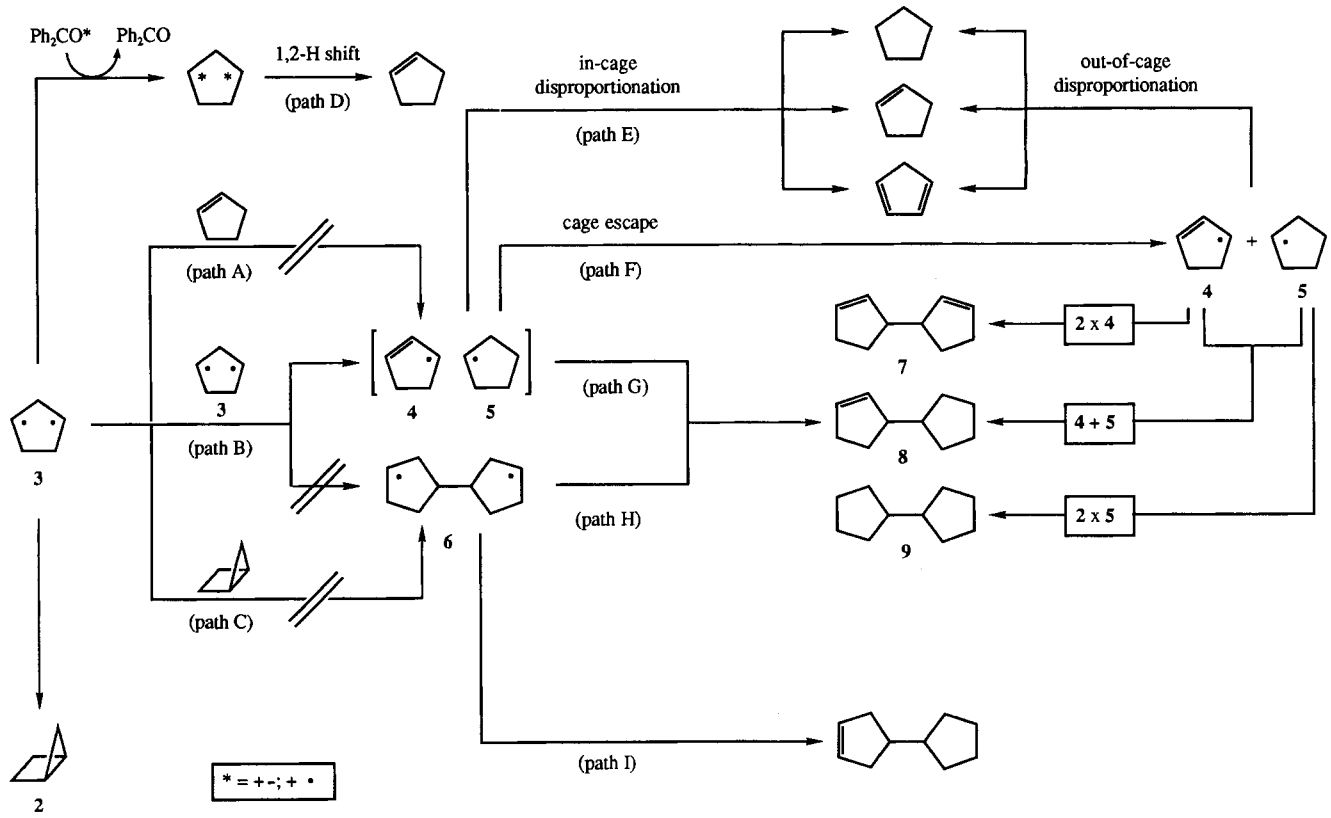
While bicyclo[2.1.0]pentane is formed by cyclization of the cyclopentane-1,3-diyl diradical (**3**), for the formation of cyclopentene there exist several possibilities besides 1,2-H shift[4] (Scheme 2, path D). For example, diradical **3** could abstract an allylic hydrogen from the cyclopentene product (Scheme 2, path A) to lead to the radical pair **4** and **5**, which on coupling would afford the dimer products (path G). To check whether such H abstraction is feasible, cyclohexene was used as H donor in the benzophenone-sensitized laser jet photolysis of azoalkane **1**. In analogy to the coupling product **7**, the formation of 3-cyclopentylcyclohex-1-ene

Table 1. Quantitative studies of the azoalkane-derived products in the benzophenone-sensitized laser jet photolysis of azoalkane **1** and the pyrolysis of **8**

Entry	Substrate	Conditions	Solvent	Conversion [%][a]	Product distribution[b] [%][c, d]					
							2[e]		**7**	**8**	**9**
1	**1**[f], Ph_2CO[g]	L.J.[h]	C_6H_6	33	2	11	48		8	26	5
2	**8**	600 °C	/	31	7	5	<1		3	69	15
3a	**1**[i], Ph_2CO[f], **2**[f]	L.J.[h]	$n\text{-}C_7H_{16}$	23	3	30	[j]		15	43	9
3b	**1**[i], Ph_2CO[f]	L.J.[h]	$n\text{-}C_7H_{16}$	23	2	20	[k]		16	51	11

[a] Error ca. 3%, mass balance ca. 40–60% (relative to solvent peak as internal standard), a control experiment with isoprene under laser jet conditions showed that 40–50% vanish by evaporation. – [b] Identification of the products by coinjection with authentic material. – [c] Capillary GC analysis: Carlo Erba 6000 Vega series 2, column: R_{tx}-1, 30 m, 0.53 mm. – [d] The relative capillary GC peak areas were normalized to 100%, error of stated values ca. 5%. – [e] The retention times of these two products were the same, but the analysis on another column (Carlo Erba Fractovap 2900, column: Carbowax, 30 m, 0.25 mm) revealed a product distribution of cyclopentadiene/cyclopentene/cyclopentane = 1:5:1. – [f] 0.10 M. – [g] 0.20 M. – [h] 2 ml/min, 333–364 nm, 25°C, Ar gas, one cycle. – [i] 0.05 M. – [j] **2** is starting material. – [k] To allow a direct comparison with entry 3a, these products were left out in the normalization to 100%.

Scheme 2. Possible pathways for the product formation in the benzophenone-sensitized laser jet photolysis of azoalkane **1**



would be expected; but since it was not observed, this pathway (path A) can be excluded.

The strained bicyclo[2.1.0]pentane (**2**), the main product generated in the benzophenone-sensitized laser jet photolysis of azoalkane **1** by cyclization of the cyclopentane-1,3-diyl diradical (**3**), might serve as reaction partner for diradical **3** to form the coupling product **8** via the extended diradical **6** (Scheme 2, path C) by intramolecular disproportionation (path H). Thus, in the presence of bicyclo[2.1.0]pentane right from the start of the laser jet photolysis one should expect a higher yield of the coupling products. Since this was not the case (Table 1, entry 3), path C (Scheme 2) is also unlikely.

Furthermore, diradical **6**, a potential intermediate of the dimerization of the cyclopentane-1,3-diyl (**3**) according to path B (Scheme 2), would be expected to generate, in addition to the observed dimer **8** (Scheme 2, path H), the double-bond regioisomeric dimer along path I (Scheme 2). Since such a product was not detected, diradical **6** can hardly be a bona fide intermediate in the laser jet photolysis of azoalkane **1**. The latter fact also implies that bicyclo[2.1.0]pentane (**2**) did not serve as H donor for diradical **3**. If this were the case, the resulting bicyclo[2.1.0]-pent-2-yl radical[10] would have opened up to the cyclopent-3-en-1-yl radical, which through coupling would lead to products regioisomerically different from dimers **7** and **8**.

The formation of cyclopentane and cyclopentadiene (Table 1) suggests that diradical **3** has other reaction pathways available besides cyclization to bicyclo[2.1.0]pentane and 1,2-H shift of a higher excited state to form cyclopentene (Scheme 2, path D). For example, as previously postulated[11], diradical **3** may also disproportionate to the pair of radicals **4** and **5** (Scheme 2, path B). Such intermolecular disproportionation of short-lived intermediates as the cyclopentane-1,3-diyl diradical (**3**) has hitherto not been observed. Presumably, the high steady-state concentration (above micromolar) of the transient diradical **3**, which can be achieved under the extreme light intensities of the laser jet mode of operation (photon densities up to 10^{29} $h\nu/cm^2$ s)[6a], is responsible for this unprecedented bimolecular diradical chemistry. At these high diradical concentrations intermolecular disproportionation (Scheme 2, path B) can compete with intramolecular 1,2-H shift of higher excited states to cyclopentene or even with cyclization to housane (**2**).

To decide whether the formation of cyclopentene is an inter- or an intramolecular process, a mixture of deuterated and protonated 2,3-diazabicyclo[2.2.1]hept-2-ene (**1**) was photolysed in the laser jet. The mixture was analysed by GC-MS, but the isotopic pattern was too complex to assess whether only C_5H_8 and C_5D_8 (intramolecular) or also the crossover products C_5H_7D and C_5HD_7 (intermolecular) were formed. Consequently, this experimental approach to resolve this mechanistic query was abandoned.

If cyclopentane, cyclopentene, and cyclopentadiene were generated exclusively by intermolecular disproportionation (Scheme 2, path B), one should expect these products to be formed in a statistical ratio of 1:2:1. Since the observed distribution was about 1:5:1 (cf. footnote [e] in Table 1), we conclude that cyclopentene is formed both by intramolec-

ular disproportionation of the ground state diradical **3** and intermolecular 1,2-H shift of higher excited states (Scheme 2, paths B and D).

To provide additional evidence for the proposed disproportionation, the radicals **4** and **5** were generated independently by pyrolysis of 3-cyclopentylcyclopent-1-ene (**8**). As Table 1 reveals, except for housane (**2**) all the products observed in the laser jet photolysis of azoalkane **1** (entry 1) were also detected in the pyrolysis of dimer **8** (entry 2). This corroborates that the radicals **4** and **5** are indeed intermediates in the benzophenone-sensitized laser jet photolysis of azoalkane **1**.

In conclusion, at low steady-state concentrations, the diradical **3** exclusively cyclizes to bicyclo[2.1.0]pentane (**2**) (low-intensity photochemistry), while at higher concentrations (ca. micromolar)[12] in the laser jet photolysis (high-intensity photochemistry) of azoalkane **1** bimolecular reaction pathways such as con- and disproportionation (Scheme 2, path B) become feasible. Concurrently, at these high light intensities, the benzophenone-sensitized rearrangement of diradical **3** (Scheme 2, path D) to cyclopentene by way of a 1,2-H shift also takes place, but to a minor extent. Thus, in the laser jet unusual photochemistry of transient species such as the short-lived triplet cyclopentane-1,3-diyl diradicals can be observed.

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Experimental

HPLC analyses: Kontron analytical system (T-414 pumps, Uvikon 720LC spectrometer, Anacomp 220 integrator), RP-8 reversed phase column, ternary solvent mixtures of acetonitrile, methanol, and water as eluents. The products were detected at 215 nm. – GC analyses: Carlo Erba HRGC, Fractovap 2900 and 4100 and Vega Series 2 6000 with OV-1-, R_{tx}-1- and Carbowax-fused silica columns. – Preparative GC: Carlo Erba Fractovap 4200. – NMR: Bruker AC 200, AC 250, or WM 400.

Conventional Photolyses: Irradiations were carried out in Schlenk tubes. The solutions were degassed by at least three freeze-pump-thaw cycles and irradiated at the 333-, 351- and 364-nm lines of the INNOVA 100 argon ion laser (Coherent), supplied with UV optics. The beam was widened with a quartz lens ($f = 50$ mm) to a size of 1 cm in diameter.

Laser Jet Photolyses: The detailed experimental set-up as described previously was employed[6]. The beam of an argon ion laser was focussed onto the freely falling liquid stream of the photolysis solution by using a quartz lens ($f = 80$ mm). The stream was generated by means of a Bischoff 2200 HPLC pump and a 100-μm capillary. Before photolysis, the solutions were degassed by at least three freeze-pump-thaw cycles. While the samples were passed through the focal point, the irradiation chamber was kept under a positive argon gas pressure.

Synthesis of Authentic Compounds

2,3-Diazabicyclo[2.2.1]hept-2-ene (**1**) was prepared and purified according to a procedure in ref.[13]

Bicyclo[2.1.0]pentane (**2**)[14] was prepared by photolysis of 3.00 mg ($3.12 \cdot 10^{-5}$ mol) of **1** in 0.5 ml of *n*-heptane at 350 nm for 2.5 h.

3-Bromocyclopent-1-ene[15] and *3-bromocyclohex-1-ene*[16] were synthesized by following known procedures.

Bicyclopent-2-en-1-yl (**7**): A sample of 6.60 g (40.0 mmol) of 3-bromocyclopent-1-ene in 12.5 ml anhydrous THF was added dropwise to 0.98 g (40.0 mmol) of magnesium turnings in 12.5 ml of anhydrous THF by keeping the temp. at −10°C. After this addition, the cooling was stopped, and a vigorous reaction started. The mixture was stirred for 1 h at 20°C, then 42 ml of a saturated NH_4Cl solution was added to the ice-cold mixture. After extraction with ether and water, the product mixture was dried with Na_2SO_4, and distillation yielded 1.37 g (26%) of a colorless liquid; b.p. 73–75°C/28 Torr (ref.[17] 70°C/15 Torr). – ^{1}H NMR ($CDCl_3$): δ = 1.30–1.48 (m, 4H, $CHCH_2CH_2$), 1.78–1.96 (m, 4H, $=CHCH_2CH_2$), 2.08–2.32 (m, 2H, $CHCH=$), 5.48–5.74 (m, 4H, CH=CH). – ^{13}C NMR ($CDCl_3$): δ = 27.3/27.5 (t, $CHCH_2CH_2$), 32.0/32.2 (t, $=CHCH_2CH_2$), 50.5/50.9 (d, $CHCH=$), 130.70/130.73 (d, $CH=CH$), 133.5/133.7 (d, $CH=CH$).

3-Cyclopentylcyclopent-1-ene (**8**)[18]: To 1.40 g (60.0 mmol) of magnesium turnings in 10 ml of ether was added dropwise 8.57 g (57.5 mmol) of bromocyclopentane in 10 ml of ether to generate the Grignard reagent. The mixture was stirred for 15 min at room temp. (ca. 20°C), subsequently for 15 min under reflux. At 0°C a solution of 6.48 g (44.1 mmol) of 3-bromocyclopent-1-ene in 6 ml of ether was added. After stirring for 15 min at room temp. and for 2.5 h under reflux, the mixture was hydrolyzed by pouring onto 17 g of ice and worked up. Distillation yielded 1.12 g (19%) of a pale yellow liquid; b.p. 75–77°C/25 Torr (ref.[18a] 185–186°C/760 Torr). – ^{1}H NMR ($CDCl_3$): δ = 1.26–2.06 (m, 11H), 2.07–2.58 (m, 3H), 5.58 (m, 2H, CH=CH). – ^{13}C NMR ($CDCl_3$): δ = 25.3 (t), 25.5 (t), 28.8 (t), 30.7 (t), 31.1 (t), 32.1 (t), 45.8 [d, $=CHCH(CH)CH_2$ or $CH_2CH(CH)CH_2$], 51.2 [d, $=CHCH(CH)CH_2$ or $CH_2CH(CH)CH_2$], 130.2 (d, $CH=CH$), 134.4 (d, $CH=CH$).

3-Cyclopentylcyclohex-1-ene[19] was prepared according to the above method by using 1.40 g (60.0 mmol) of magnesium turnings. 8.57 g (57.5 mmol) of bromocyclopentane, and 7.10 g (44.1 mmol) of 3-bromocyclohex-1-ene to yield 1.55 g (23%) of a colorless liquid; b.p. 100–103°C/22 Torr (ref.[19] 105°C/25 Torr). – ^{1}H NMR ($CDCl_3$): δ = 1.04–2.04 (m, 16H, 7 CH_2, CH–CH), 5.64 (m, 2H, CH=CH). – ^{13}C NMR ($CDCl_3$): δ = 21.7 (t), 25.3 (t), 28.4 (t), 30.1 (t), 30.6 (t), 40.8 [d, $=CHCH(CH)CH_2$], 45.6 [d, $=CHCH(CH)CH_2$], 127.0 (d, $CH=CH$), 131.2 (d, $CH=CH$).

1,1'-Bicyclopentyl (**9**): A sample of 250 mg (1.84 mmol) of **8** in 2 ml of ethyl acetate was hydrogenated for 15 h at 20°C in the presence of ca. 1 mg platinum as catalyst. Removal of the solvent yielded 97.0 mg (38%) of a pale yellow liquid; b.p. 77–78°C/25 Torr (ref.[18a] 190–190.5°C/761.8 Torr). – ^{1}H NMR ($CDCl_3$): δ = 0.92–1.14 (m, 4H), 1.30–1.72 (m, 2H). – ^{13}C NMR ($CDCl_3$): δ = 25.3 (t, $CH_2CH_2CH_2$), 31.7 (t, $CHCH_2CH_2$), 46.3 (d, CH).

Cyclopent-2-en-1-yldiphenylmethanol (**10**)[20]: A mixture of 1.43 g (65.0 mmol) of magnesium turnings and 18 ml of anhydrous THF was cooled to −10°C. A cooled solution of 9.60 g (65.0 mmol) of 3-bromocyclopent-1-ene in 18 ml of THF was added during 30 min so that the temp. was kept below −10°C. The mixture was stirred at −10°C for 1 h, and 6.40 g (35.0 mmol) of benzophenone in 14.5 ml of THF was slowly added at −5°C. After stirring for 20 h at room temp., a saturated NH_4Cl solution (14.5 ml) was added to the ice-cold mixture. Extraction with ether (2 × 25 ml) and water (2 × 7 ml) and drying of the combined organic extracts with Na_2SO_4 yielded 6.20 g (71%) of an oily product. Purification of a 1.50-g sample by means of MPLC [column: 260 × 28 mm, Europrep 60–30 C18, 60 Å, 20–45 μ, 13 bar, 54 ml/min, eluent: CH_3CN/MeOH/H_2O (40:30:30), detection: λ = 220 nm] led to 290 mg

(14%) of a pure colorless product. — IR (film): $\tilde{\nu} = 3540\,cm^{-1}$, 3050, 2930, 2840, 1650, 1590, 1485, 1435, 1310, 1270, 1160. — ^1H NMR ($CDCl_3$): $\delta = 1.50$ (s, 1H, OH), 1.60–1.88 (m, 2H, CH_2), 2.20–2.35 (m, 2H, CH_2), 3.96 (m, 1H, CH), 5.32 (m, 1H, C*H*=CH), 5.92 (m, 1H, CH=C*H*), 7.18 (m, 6H, aromatic H), 7.44 (m, 4H, aromatic H). — ^{13}C NMR ($CDCl_3$): $\delta = 24.6$ (t, CH_2CH_2CH), 32.6 (t, $=CHCH_2CH_2$), 55.0 (d, CH), 79.2 (s, COH), 125.7 (d), 126.3 (d), 127.2 (d), 128.0 (d), 128.5 (d), 129.7 (d), 136.5 (d), 146.1 (s, *ipso*-C), 147.6 (s, *ipso*-C).

Qualitative Laser Jet Product Studies: The products were identified by comparison of their ^1H- and ^{13}C-NMR spectra with those of an authentic sample and by capillary GC or HPLC by coinjection. For this purpose, a solution of 610 mg (6.35 mmol) of 2,3-diazabicyclo[2.2.1]hept-2-ene (**1**) and 2.36 g (13.0 mmol) of benzophenone in 20 ml of *n*-heptane was degassed by at least three freeze-pump-thaw cycles. After one cycle in the laser jet irradiation, the products were separated by preparative GC [monomers: 1.5-m column, 10% Apiezon L on Volaspher A2, 40°C (5 min), 35°C/min, 80°C (10 min), N_2, 1 kg/cm^2; dimers: 1.5-m column, 10% Apiezon L on Volaspher A2, 90°C, N_2, 1 kg/cm^2].

Quantitative Laser Jet Product Studies: The quantitative product studies were performed by capillary GC (OV-1, 60 m, 0.32 mm; R_{tx}-1, 30 m, 0.53 mm; Carbowax, 30 m, 0.25 mm) or HPLC (Merck Li Chro CART, Supersphere RP-8, 250 × 4 mm) with 1,2-dicyanobenzene as internal standard. The products were identified by coinjection with authentic material.

Control Experiments

Benzophenone-Sensitized Laser Jet Photolysis of 2,3-Diazabicyclo-[2.2.1]hept-2-ene (**1**) *with Cyclohexene as Additive:* A solution of 19.8 mg (0.200 mmol) of **1**, 73.0 mg (0.400 mmol) of benzophenone, and 16.0 mg (0.200 mmol) of cyclohexene in 2 ml of benzene was degassed, photolyzed in the laser jet for one cycle, and analyzed by GC (see Table 1).

Benzophenone-Sensitized Laser Jet Photolysis of **1** *with Bicyclo-[2.1.0]pentane* (**2**) *as Additive:* A sample of 39.6 mg (0.400 mmol) of **1**, dissolved in 4 ml of benzene, was photolyzed in the widened laser beam for 15 min to generate housane (**2**). Subsequently, 20.0 mg (0.200 mmol) of **1** and 73.0 mg (0.400 mmol) of benzophenone were added to the solution which was degassed, photolyzed for one cycle in the laser jet, and analyzed by GC (see Table 1).

Pyrolysis of 3-Cyclopentylcyclopent-1-ene (**8**): A sample of 100 mg (0.730 mmol) of **8** was pyrolyzed by volatilizing it at 100°C/20 Torr in a hot quartz tube (60 cm), which was kept at 600°C/20 Torr by external heating with a Nichrome wire. The effluent was collected in a receiving flask, cooled with liquid nitrogen. The resulting product mixture was analyzed by capillary GC (see Table 1).

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