

# Two-Photon Chemistry in the Laser Jet: Photoionization of the Diphenylmethyl Radical Generated by Norrish Type I Photocleavage of Benzhydryl Phenyl Ketone

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**Abstract:** It is shown that in the laser jet (LJ) mode (argon ion laser) the benzhydryl phenyl ketone (**1**) undergoes a two-photon reaction in  $\text{CCl}_4$  to yield benzhydryl chloride. The one-photon products are 1,1,2,2-tetraphenylethane (**3**), benzophenone, and 1,1,1-trichloro-2,2-diphenylethane (**4**). In methanol, on the other hand, our results suggest even a three-photon reaction in which benzhydryl methyl ether (**5**) is produced besides the one-photon products **3** and benzophenone. The ratios of the three-photon to one-photon products, i.e. **5** to **3**, depended on the wavelength (333 or 351 nm). The three-photon mechanism was established by a competition experiment, in which ketone **1** was irradiated in mixtures of  $\text{CCl}_4$  and methanol. The ratio of the two high-intensity products ether **5** and benzhydryl chloride showed a strong intensity dependence. We propose that the electronically excited diphenylmethyl radical **2\*** is photochemically ionized to the diphenylmethyl cation **2<sup>+</sup>** under the high-intensity LJ photolysis conditions and the latter trapped with methanol and deuteriomethanol to give the identical benzhydryl methyl ether (**5**). The fact that no deuterium-incorporated ether **5** was observed eliminates the carbene mechanism proposed in the literature, at least under our LJ photolysis conditions.

## Introduction

The diphenylmethyl radical (**2**) has been subject to several photophysical and photochemical<sup>1-10</sup> studies. Its first excited state **2\*** can be generated upon pulsed-laser photolyses with 347-<sup>1,2</sup> or 337-nm light.<sup>3</sup> Thus, while radical **2** has a strong, sharp band at 330 nm,<sup>1,5-7</sup> the electronically excited radical **2\*** exhibits an absorption at 355 nm of comparable intensity. Furthermore, upon irradiation of diarylmethyl halides with the combination of two pulsed lasers at 248 and 308 nm, excited diarylmethyl radicals and even diaryl carbocations were detected by UV spectroscopy.<sup>4</sup> The excited radical **2\*** fluoresces with a quantum yield of 0.31,<sup>8</sup> and this can be used as a standard to determine the fluorescence quantum yields for other radicals.<sup>9</sup> Scaiano<sup>3</sup> explored the chemistry of the excited radical **2\*** in  $\text{CCl}_4$  and showed that it gave essentially exclusively benzhydryl chloride as photolysis product by electron transfer. The tendency of the excited cyanodiphenylmethyl radical to undergo electron-transfer reactions has been claimed by Weir.<sup>10</sup>

The excited radical **2\*** was found to be unreactive in methanol.<sup>2</sup> On further excitation, the new transient decayed in a unimolecular reaction which did not lead to **2\***. Meisel proposed a hydrogen atom expulsion to form diphenylcarbene for this latter process. At the wavelength (337 nm) used by Scaiano,<sup>3</sup> further excitation of **2\*** to **2\*\*** was apparently very ineffective due to the low absorption of **2\*** at this wavelength.

The diphenylmethyl radical (**2**) seems to be ideal for a LJ experiment since the absorption characteristics of the intermediates **2** and **2\*** match optimally the available lines of the argon ion laser (333, 351, 364 nm). Moreover, the requisite that the lifetime of an intermediate for a LJ experiment should be greater than about

10 ns<sup>11</sup> is also fulfilled, since the lifetime of the excited radical **2\*** is about 250 ns<sup>2,3</sup> in several alcohols. We report herein our novel results on the formation of the benzhydryl cation (**2<sup>+</sup>**) by the photoionization of the benzhydryl radical (**2**) generated by the photolysis of the benzhydryl phenyl ketone (**1**) in the laser jet mode.

## Results

The photolysis products of ketone **1** in  $\text{CCl}_4$  as solvent show a strong dependence on the light intensity (Table I). Only small amounts of benzhydryl chloride were formed under lamp photolysis conditions, i.e. in the Rayonet irradiations (Table I, entry 1), which constitute the lowest light intensity. However, in the LJ photolysis experiment (Table I, entry 3) benzhydryl chloride was formed almost exclusively, which represents a dramatic change. Irradiation with the widened beam (Table I, entry 2) at exactly the same laser lines as in the LJ photolysis experiment afforded a product distribution more similar to the Rayonet experiment, as expected at the medium intensity supplied under these conditions. The products of the benzoyl radical, i.e. chlorobenzene, benzil, and benzoyl chloride, were detected but not quantified, and for this reason they are not explicitly stated in the table. In view of the facile solvolysis ( $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ) of the benzhydryl chloride, this product was quantitated after etherification with methanol and potassium carbonate.

In the Rayonet photolysis of methanol solutions of ketone **1** no products other than those of the normal Norrish type I process were detected, while in the LJ experiment ether **5** was formed in a considerable quantity (ca. 30%), as shown in Table II. A significant wavelength dependence was observed on the product distribution. Thus, irradiation with the 333-nm laser line (Table II, entry 3) was nearly as effective as that with all the available UV laser lines (Table II, entry 2), but photolysis at the 351-nm laser line gave only half as much (ca. 14%) ether **5** (Table II, entry 4). As expected, irradiation at the medium light intensity of the widened laser beam (Table II, entry 1) gave only traces of ether **5**.

A deuterium tracer experiment was conducted by running the LJ photolysis in deuterated methanol as trapping agent. By using 5% methanol-*d*<sub>1</sub> in benzene as the solvent system, the <sup>1</sup>H NMR spectrum revealed the formation of ether **5** but no **5-d**<sub>1</sub>.

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Table I. Product Studies of the Photolyses of Ketone 1 in CCl<sub>4</sub>

entry	mode	time	conv, <sup>a</sup> %	mb, <sup>b</sup> %	product distribution, <sup>c</sup> %			
					Ph <sub>2</sub> CHCl <sup>d</sup>	Ph <sub>2</sub> CH-) <sub>2</sub>	Ph <sub>2</sub> CHCCl <sub>3</sub>	Ph <sub>2</sub> CO
1	Rayonet	15 min	53	70	5	31	54	10
2	laser, <sup>e,f</sup> widened beam	20 s	17	>95	19	37	37	7
3	laser jet <sup>f,g</sup>	1 cycle	22	80	95	5	- <sup>h</sup>	- <sup>h</sup>

<sup>a</sup>  $c = 1.01 \times 10^{-2}$  M. <sup>b</sup> mb stands for mass balance. <sup>c</sup> Normalized to 100%, HPLC detection, error 5% of stated value, benzoyl-derived products are not listed. <sup>d</sup> Detected as Ph<sub>2</sub>CHOCH<sub>3</sub>. <sup>e</sup> Irradiation was carried out in a Schlenck tube. <sup>f</sup> All UV lines, 3.5 W. <sup>g</sup> 100- $\mu$ m capillary, flow rate of 0.60 mL/min. <sup>h</sup> Not detected, less than 0.5%.

Table II. Product Studies of the Photolyses of Ketone 1 in CH<sub>3</sub>OH

entry	mode	time	conv, %	mb, <sup>a</sup> %	product distribution, <sup>b</sup> %		
					Ph <sub>2</sub> CHOCH <sub>3</sub>	Ph <sub>2</sub> CHCHPh <sub>2</sub>	Ph <sub>2</sub> CO
1	laser, <sup>c</sup> widened beam	30 s	21	>95	<2	>98	<sup>f</sup>
2	laser jet, <sup>c,d</sup> all UV lines	1 cycle	27	90	34	59	7
3	laser jet, <sup>d,e</sup> 333 nm	1 cycle	13	70	32	68	<sup>f</sup>
4	laser jet, <sup>d,e</sup> 351 nm	1 cycle	7	>95	14	86	<sup>f</sup>

<sup>a</sup> mb stands for mass balance. <sup>b</sup> Normalized to 100%, HPLC detection, error 5% of stated value, benzoyl-derived products are not listed. <sup>c</sup> All UV lines, 3.5 W. <sup>d</sup> 100- $\mu$ m capillary, flow rate of 0.60 mL/min, 1 cycle. <sup>e</sup> Stated laser line was isolated by prism and slit. <sup>f</sup> Not detected.

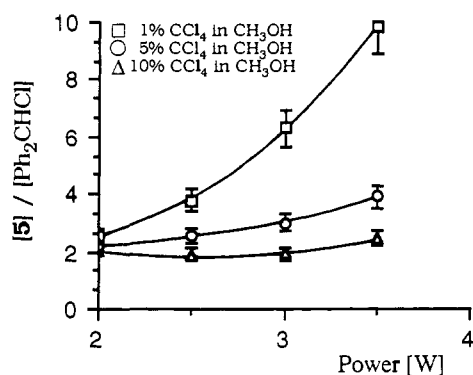


Figure 1. The ratio of ether 5 versus benzhydryl chloride as a function of the laser intensity at different CCl<sub>4</sub> concentrations.

Of mechanistic relevance in the LJ photolysis was a study of the influence of the intensity on the product distribution as a function of CCl<sub>4</sub>/MeOH ratios. At low concentrations of CCl<sub>4</sub> (1% CCl<sub>4</sub>, squares in Figure 1), the ratio of ether 5 versus benzhydryl chloride exhibited a pronounced increase at higher laser power, while at high concentrations (10% CCl<sub>4</sub>, triangles in Figure 1) a leveling effect was observed, i.e. the ratios of ether 5 versus benzhydryl chloride stayed essentially constant over the range of intensity variation.

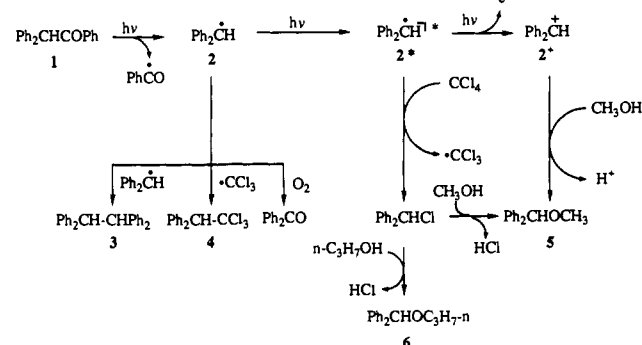
Since in CCl<sub>4</sub>/MeOH solvent mixtures the benzhydryl methyl ether (5) may arise also from dark methanolysis of the benzhydryl chloride, it was necessary to assess this possibility in the laser jet experiment. Immediately after the photolysis the reaction mixture was injected into *n*-PrOH and the amount of solvolysis during post-photolysis handling determined by monitoring the benzhydryl *n*-propyl ether product with the help of quantitative GC analysis. During the time interval of the laser jet photolysis the extent of dark methanolysis was ca. 60–70% of the benzhydryl chloride produced. This fact is displayed in the intercept in Figure 1, in which the intercept, ratio of ether 5 and Ph<sub>2</sub>CHCl, extrapolates to ca. 2:1 at zero laser power and thus represents the amount of dark methanolysis.

## Discussion

In CCl<sub>4</sub> as solvent, the ground-state reactions of the radical 2 are, as expected (low-intensity experiments under normal lamp photolysis), its dimerization to the hydrocarbon 3 and its reaction with oxygen to form benzophenone (Scheme 1). Furthermore, the halogenated product 4 is due to coupling of radical 2 with trichloromethyl radicals, which are formed from the reaction of benzoyl radicals with the solvent CCl<sub>4</sub>.

In contrast to this normal Norrish type I photochemistry of  $\alpha$ -cleavable ketones, for the high-intensity photolysis (multiple-photon chemistry) novel phototransformations of the intermediary

Scheme 1. Ground-State and Multiple-Photon Chemistry of the Diphenylmethyl Radical 2 in CCl<sub>4</sub> and Methanol



Ph<sub>2</sub>CH• radical can be witnessed. Thus, analogous to Scaiano's experiments (pulsed laser), also in the LJ photolysis benzhydryl chloride was observed as a two-photon product of benzhydryl phenyl ketone (1) in CCl<sub>4</sub>, except that under the continuous irradiation conditions of the LJ mode the benzhydryl chloride was observed essentially quantitatively. This is shown in Table I (entry 3), which underscores that the LJ photolysis is extremely efficient for such two-photon processes. The isolation and characterization of the two-photon products was possible in the LJ photolysis because highly concentrated solutions and high conversions can be achieved without problems.

Scaiano<sup>3</sup> found that the excited radical 2\* is quenched by CCl<sub>4</sub> with  $k_q = (1.6 \pm 0.1) \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>. Since CCl<sub>4</sub> is the only solvent in which this lifetime could not be measured on the nanosecond time scale, it was stated to be smaller than 5 ns. He proposed an electron transfer mechanism between the excited radical 2\* and CCl<sub>4</sub>, which leads to the benzhydryl cation 2+ and a CCl<sub>4</sub><sup>-</sup> radical anion pair. This pair is considered to be geminate as no spectroscopic evidence is found for free cation 2+. The tendency of 2\* to react in SET reactions was also shown by quenching with paraquat<sup>3</sup> and other substrates.<sup>10</sup>

In methanol as solvent, a much different spectrum of products is obtained because now electron transfer from 2\* as in the case of CCl<sub>4</sub> is not feasible. Although Meisel<sup>2</sup> showed that the electronically excited radical 2\* was photoactive only on further excitation (he postulated H-atom expulsion to produce the diphenylcarbene), in the LJ photolysis mode we observed efficient photochemistry of ketone 1 to afford ether 5.

The formation of ether 5 can be rationalized in terms of insertion of the diphenylcarbene into the O–H bond of methanol, which would confirm Meisel's hypothesis that the upper excited radical 2\*\* expels an H-atom to produce the carbene Ph<sub>2</sub>C:. However, the photoionization of aryl-substituted methyl radicals has recently been reported,<sup>12</sup> so that a possible route for the

formation of ether **5** could be nucleophilic trapping of the diphenylmethyl cation **2<sup>+</sup>** by methanol.

To resolve this mechanistic problem, we carried out the LJ photolysis in deuterated methanol (CH<sub>3</sub>OD) as trapping agent. The carbene route should afford monodeuterated ether **5-d<sub>1</sub>**, while the photoionization process should form the undeuterated ether **5**. Since the <sup>1</sup>H NMR spectrum of the crude LJ photolysate revealed no deuterium incorporation, photoionization of **2<sup>\*</sup>** (Scheme I) to generate the cation **2<sup>+</sup>** is therewith mechanistically established.

An important question is whether the ether **5** is formed in an overall (counting from the starting ketone **1**) two- or three-photon process. In view of the spectral characteristics of the ground-state radical **2** and its first excited state **2<sup>\*</sup>**, a wavelength-dependent experiment seemed necessary to assess the number of photons involved in the production of ether **5** during the LJ photolysis. In the experimental UV absorption spectra sharp bands for **2** ( $\lambda_{\text{max}} = 330$  nm) and **2<sup>\*</sup>** ( $\lambda_{\text{max}} = 355$  nm) were reported. Moreover, in the OD difference spectrum of **2** and **2<sup>\*</sup>**, which corresponds to the UV spectrum of **2<sup>\*</sup>**, a  $\Delta\text{OD}$  of zero was assumed at 330 nm, which suggests that the electronically excited radical **2<sup>\*</sup>** does not appreciably absorb at this wavelength. If excitation of **2** is carried out at the 333- or 351-nm laser lines, it would be expected that the amount of ether **5** product should change. In particular with excitation at 351 nm, the excitation step **2**  $\rightarrow$  **2<sup>\*</sup>** should be disfavored due to the low absorption of the ground-state radical **2** at this wavelength. However, any electronically excited **2<sup>\*</sup>** that is generated should be photoionized efficiently to its cation **2<sup>+</sup>** because of its strong band at 355 nm. Indeed, the results (Table II, entry 4) show a significant reduction (nearly by half) of the yield of ether **5** compared to the irradiation at all laser lines (Table II, entry 2), which strongly supports the mechanism proposed in Scheme I.

On the other hand, on 333-nm irradiation the excitation step **2**  $\rightarrow$  **2<sup>\*</sup>** should be efficient, whereas the photoionization step **2<sup>\*</sup>**  $\rightarrow$  **2<sup>+</sup>** should not proceed due to the reportedly negligible absorption of **2<sup>\*</sup>** at this wavelength.<sup>1</sup> Since the formation of ether **5** is not significantly altered in the 333-nm LJ photolysis experiment (Table II, entry 3), these results contradict the mechanism proposed in Scheme I.

Two alternatives shall be considered to explain these results: either the cation **2<sup>+</sup>** is formed directly from radical **2** by photoionization or the assumption<sup>1</sup> of negligible absorption of **2<sup>\*</sup>** at 330 nm does not apply and a three-photon process (by counting from the starting ketone **1**, cf. Scheme I) is involved. It would require a third photon to execute the ionization of the electronically excited radical **2<sup>\*</sup>** to produce the cation **2<sup>+</sup>**.

The results of the following competition experiment strongly support the latter alternative, in which the proportion of the multiple-photon products, i.e. benzhydryl chloride and benzhydryl methyl ether (**5**), was determined as a function of laser intensity using all UV lines (333, 351, and 364 nm) at different concentrations of CCl<sub>4</sub> in MeOH (Figure 1). If the ether **5** and benzhydryl chloride were to be formed from the same intermediate, e.g. the electronically excited radical **2<sup>\*</sup>**, irradiation of ketone **1** in mixtures of CCl<sub>4</sub> and methanol at different laser intensities should yield a constant ratio of the two multiple-photon products benzhydryl chloride and ether **5**. However, at low CCl<sub>4</sub> concentrations a strong dependence of the product ratio on the laser power was observed (Figure 1), which indicates a competition of photons and CCl<sub>4</sub> for the excited radical **2<sup>\*</sup>**. Thus, at high photon densities photoionization of **2<sup>\*</sup>** dominates and the three-photon product **5** is favored, whereas at low intensities the electron transfer reaction of **2<sup>\*</sup>** with CCl<sub>4</sub> prevails and benzhydryl chloride is preferred. The constant ratios of the two products at higher CCl<sub>4</sub> concentrations (10% CCl<sub>4</sub>) show that under these conditions the electron transfer reaction between **2<sup>\*</sup>** and CCl<sub>4</sub> occurs more efficiently and faster than photoionization. The data by Meisel<sup>2</sup> and Scaiano,<sup>3</sup> who found **2<sup>\*</sup>** to be unreactive in ROH solvents and showed that an additional photon is required for irreversible

bleaching, also support the three-photon process to generate cation **2<sup>+</sup>** from ketone **1**. On the basis of the pulsed-laser photolysis these authors had advanced spectroscopic evidence to confirm the multiple-photon process, while our LJ experiments provide a chemical proof for the three-photon process.

The time-resolved spectroscopic method with pulsed lasers offers valuable mechanistic data in terms of absorption spectra, lifetimes, and rate constants of short-lived transients, but normally insufficient amounts of products are formed to conduct detailed product studies. The LJ technique fills this gap in that sufficient quantities of multiple-photon products can be prepared for isolation, purification, and complete characterization (new compounds) or identification (known compounds). Thus, the LJ mode of operation constitutes a valuable complementary technique for time-resolved laser flash photolysis with pulsed lasers.

## Experimental Section

**Materials and General Techniques.** Benzhydryl phenyl ketone (**1**) was prepared and purified according to the literature.<sup>13</sup> Methanol and tetrachloromethane were reagent grade, and methanol-*d*<sub>1</sub> was 99.9% D (Fluka).

The HPLC analyses were carried out on a Kontron analytical system (T-414 pumps, Uvikon 720LC spectrometer, and an Anacomp 220 integrator) equipped with a RP-8 reversed phase column by using ternary solvent mixtures of acetonitrile, methanol, and water as eluent. Detection of the products was performed at 215 nm. The Uvikon spectrometer was also used for the determination of the spectra by HPLC/UV. GC analyses were carried out on a Carlo Erba HRGC, equipped with a SE 54 fused silica column (30 m). NMR spectra were recorded on a Bruker AC 200 or a Bruker AC 250 spectrometer.

**Low-Intensity Photolyses.** Irradiations were carried out in Schlenk tubes. The solutions were degassed by purging with a slow stream of dry argon gas for 20 min and irradiated in a Rayonet photochemical reactor [RPR(75W, 110V)] from the Southern England UV Co. equipped with 300-nm lamps. Higher light intensities were obtained by irradiation 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. The 2-mL samples were irradiated for the time stated in the tables.

**High-Intensity Photolyses.** The experimental setup is described in detail in two recent publications.<sup>11</sup> The beam of the argon ion laser was focussed by means of a quartz lens (*f* = 80 mm) onto a free-falling liquid stream of the photolysis solution. When monochromatic light was needed, the laser beam was split by an external quartz prism and the desired line was isolated by a razor blade as slit. The free-falling liquid stream was maintained by a Bischoff 2200 HPLC pump and passed through a 100- $\mu\text{m}$  capillary. The samples were degassed by purging with a slow stream of dry argon gas for 20 min. The irradiation chamber was kept under a positive argon gas pressure and the substrate solutions were passed once through the focal point. The collecting flask was washed twice with 1 mL of photolyzed solution and afterwards a 1-mL aliquot was withdrawn by means of a syringe for HPLC analysis.

**Competition Experiments.** Three methanol solutions ( $1.00 \times 10^{-2}$  M of ketone **1**) with 1, 5, and 10% CCl<sub>4</sub> were irradiated in the LJ at different light intensities. After one pass through the focal point, 1.2 mL of the photolysis solution was injected into a flask containing 3 mL of 1-propanol kept at -78 °C. The photolysate samples were stored under liquid N<sub>2</sub> until all samples had been collected, the methanol and most of the propanol were evaporated (ca. 20 °C/15 Torr), and the photolyses solutions were analyzed by GC.

**Product Studies.** Quantitative product studies were performed by HPLC with the help of 1,2-dicyanobenzene as internal standard. The benzhydryl chloride was detected as ether **5** after etherification with CH<sub>3</sub>OH/K<sub>2</sub>CO<sub>3</sub> at 20 °C for 1.5 h. Tetraphenylethane (**3**) and the trichlorodiphenylethane<sup>14</sup> (**4**) were isolated from an irradiated CCl<sub>4</sub> solution of ketone **1** by employing the widened-beam mode of the laser and characterized on the basis of their <sup>1</sup>H and <sup>13</sup>C NMR spectra. The ether **5** was isolated from the laser jet experiment (see below) and was characterized by its <sup>1</sup>H and <sup>13</sup>C NMR spectra. Benzophenone and benzil were identified by coinjection and comparison of their UV spectra with those of the authentic materials. The other products, e.g. benzene, benzaldehyde, chlorobenzene, and benzoyl chloride (benzoyl radical chemistry), were identified but not quantified.

To obtain sufficient amounts of the deuterated ether **5-d<sub>1</sub>** for <sup>1</sup>H NMR analysis, a  $1.11 \times 10^{-2}$  M solution of ketone **1** in benzene with 5%

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CH<sub>3</sub>OD was passed once through the focal point of the laser jet (flow 0.60 mL/min, 100- $\mu$ m capillary, 3.0 W over all UV lines). The solvent was evaporated and the <sup>1</sup>H NMR spectrum (250 MHz, CDCl<sub>3</sub>) revealed ethane **3** and ether **5** in a ratio of 72:28. For the ether **5** the integration of the signals at 3.26 ppm (OCH<sub>3</sub>) and at 5.20 ppm (CH) gave a 3:1 ratio within the error limits.

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**Registry No.** 1, 1733-63-7; benzhydryl, 4471-17-4; benzhydryl cation, 709-82-0.

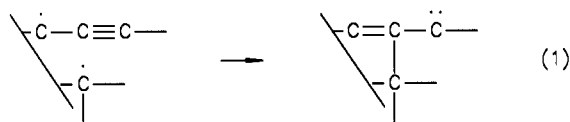
## Thermal and Photochemical Decomposition of *N*-[2-(3,3-Dimethyl-1-butynyl)-2,5,5-trimethyl-1-pyrrolidinyl]nitrene

M. G. Horner, M. J. Rudolph, Steven Wolff, and William C. Agosta\*

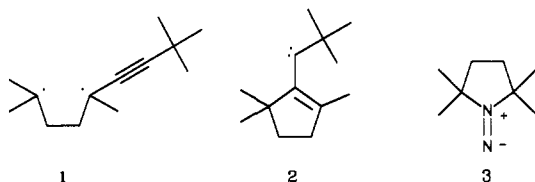
Contribution from the Laboratories of The Rockefeller University, New York, New York 10021-6399. Received January 31, 1992

**Abstract:** Oxidation of *N*-aminopyrrolidine **5** with *tert*-butyl hypochlorite at -130 °C yields the 1,1-disubstituted diazene **4**, which is stable in dimethyl ether solution at this temperature. Thermal (-90 °C) or photochemical (-130 °C,  $\lambda > 330$  nm) decomposition of **4** furnishes singlet alkyl propargyl biradical **1**, which undergoes fragmentation to **16**, cyclization to **17**, and disproportionation to **18** and **19** (Table I). The absence of products attributable to the cyclization of **1** to vinyl carbene **2** (cf. eq 1) is interpreted as evidence that cyclization according to eq 1, when observed, occurs directly from the triplet biradical in competition with intersystem crossing.

Alkyl propargyl biradicals can cyclize (eq 1) to vinyl carbenes whose subsequent fate depends on their specific structure. There

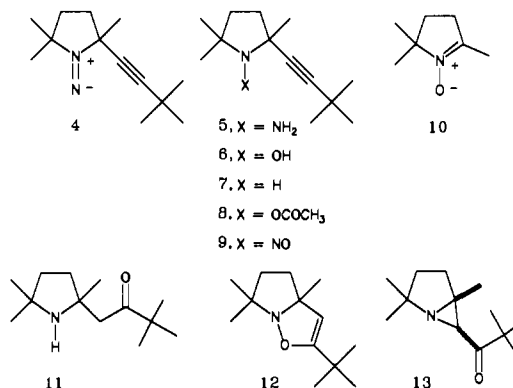


are now examples of this process in 1,4 biradicals created by several different photochemical routes,<sup>1</sup> along with evidence suggesting that the biradical cyclizes specifically from its triplet state in competition with the intersystem crossing to the singlet that precedes its other possible reactions.<sup>1,2</sup> In the present work, we have prepared the simple alkyl propargyl biradical **1** specifically in its singlet state in order to examine products formed under such defined conditions of biradical spin. We were particularly interested in learning whether products resulting from cyclization of **1** to carbene **2** according to eq 1 were formed under these conditions.



For this study we required a precursor that would reliably furnish **1** in its singlet state. The 1,1-disubstituted diazene **3** and diazenes from related pyrrolidines thermally decompose to hydrocarbon products at -20 °C and also decompose on direct irradiation at -78 °C, where they are thermally stable. These two reactions, which have been the object of careful study, lead to a very similar distribution of products, and both processes are believed to involve singlet 1,4 biradicals.<sup>3</sup> With this earlier work

in mind, we chose 1,1-disubstituted diazene **4** as a suitable precursor for **1**, in part because it offers these two independent routes, by way of both **4**(S<sub>0</sub>) and **4**(S<sub>1</sub>), to singlet **1** under mild conditions. We have prepared and purified diazene **4**, decomposed it thermally at -90 °C and by direct irradiation at -130 °C, and identified the products formed in these reactions. Our results are reported below.



**Preparative Chemistry.** The relatively stable precursor for **4** was hydrazine **5**. The earlier preparation of **3**<sup>3</sup> provided a model for the synthesis of **4**, but two steps in this sequence required modification to avoid undesirable attack on the triple bond. Addition of (*tert*-butylethynyl)magnesium chloride to nitrene **10**<sup>3</sup> furnished hydroxylamine **6**. Attempts to reduce **6** to the secondary amine **7** with zinc dust in acetic acid<sup>3</sup> failed. Concomitant hydration of the triple bond took place under these conditions, and the product obtained was amino ketone **11**. Treatment of **6** with zinc dust in methanol containing a drop of concentrated hydrochloric acid gave instead the cyclization product **12**. This result suggests that in hot acetic acid **12** is also formed and that subsequent reduction of the N-O bond under these more vigorous conditions then leads to **11**. Isoxazoline **12** was thermally unstable,

(1) Rathjen, H.-J.; Margaretha, P.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* 1991, 113, 3904. This report contains complete references to earlier work.

(2) Saba, S.; Wolff, S.; Schröder, C.; Margaretha, P.; Agosta, W. C. *J. Am. Chem. Soc.* 1983, 105, 6902.

(3) Schultz, P. G.; Dervan, P. B. *J. Am. Chem. Soc.* 1982, 104, 6660 and earlier papers cited therein.