5336 *J. Phys. Chem. A* **1999,** *103,* 5336−5342

Chemistry and Kinetics of Dipropylcarbene in Solution

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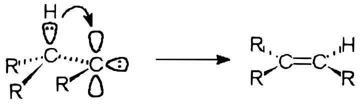
Received: January 19, 1999; In Final Form: April 19, 1999

The photochemistry of 2-methoxy-2-methyl-5,5-dipropyl-Δ^3-1,3,4-oxadiazoline (**1a**) and 2,2-dimethoxy-5,5-dipropyl-Δ^3-1,3,4-oxadiazoline (**1b**) was investigated. Photolysis (300 nm) of these compounds in solution leads to fragmentation to 4-diazoheptane (major), which slowly forms the corresponding azine. Fragmentation to form 4-heptanone is also observed. Yields of 4-diazoheptane in CH_2Cl_2 are much larger than those in pentane. 4-Diazoheptane can be trapped with 1-pentene to form a pyrazoline or with methanol to form 4-methoxyheptane. The pyrazoline can be decomposed photochemically to form 1,1,2-tripropylcyclopropane. In solution, 4-diazoheptane is inefficiently photolyzed to dipropylcarbene (DPC), which can be trapped with piperidine or with pyridine in laser flash photolysis experiments. Analysis of the piperidine and pyridine data indicates that the lifetime of DPC in cyclohexane, methylene chloride, or Freon-113 ($CF_2ClCFCl_2$) solution at ambient temperature is controlled by 1,2 hydrogen migration to form *Z*- and *E*-3-heptene. The lifetime deduced under these conditions is ≈300 ps, which is about 20-fold shorter than that of dimethylcarbene in perfluorohexane at ambient temperature. Upon photolysis (254 nm) of oxadiazoline **1a** in argon, 4-diazoheptane and 1-methoxydiazoethane are formed. These diazo compounds undergo subsequent photolysis that revealed the formation of methoxy(methyl)carbene and *E*- and *Z*-3-heptene. It was not possible to detect DPC in argon at 14 K.

I. Introduction

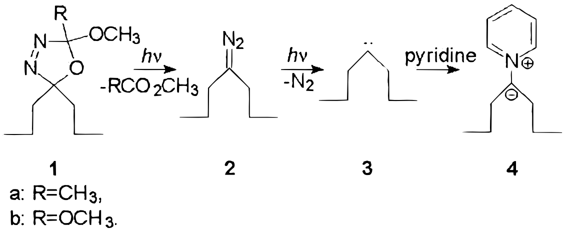
Dialkylcarbenes can undergo 1,2 hydride-like shifts to form alkenes.[1]



These reactions are very exothermic ($\Delta H \approx -60$ kcal/mol)[2] and for years the lifetimes of dialkylcarbenes were thought to be so short (femtoseconds) as to preclude their efficient bimolecular capture for preparative chemistry.

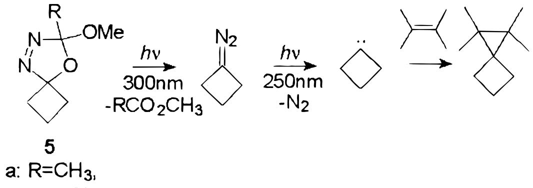
Recently, we have used the pyridine ylide method to demonstrate that dimethylcarbene has a nanosecond lifetime and large rate constants of intermolecular reactions. Intramolecular reactions of carbenes, in general, actually have larger enthalpic barriers than do intermolecular processes such as the addition to an alkene.[3,4]

Ab initio calculations indicate that the classical barrier to a 1,2 hydrogen shift is 5−7 kcal/mol for unbranched dialkylcarbenes.[2,5] Placement of an alkyl group at the carbon bearing the migrating hydrogen should accelerate the rearrangement by weakening the C−H bond and by stabilizing the positive charge developing in the transition state.[2−5]



To test that prediction,[2] we have investigated simple oxadiazoline **1a** in the hope that its photolysis would generate 4-diazoheptane (**2**) in situ[6] and that this species might then be photolyzed to form dipropylcarbene (**3**), which might be intercepted with pyridine to form ylide **4** and allow a measurement of its lifetime in solution.

This strategy has been used successfully with cyclobutyl compound **5** and other simple cyclic and acyclic oxadiazolines.[7]



10.1021/jp990198d CCC: $18.00

TABLE 1: Values of $k_{PYR}\tau$ Obtained by LFP of Precursor 1a, 1b, or 1b-d_3 in the Presence of Pyridine at Ambient Temperature

precursor	solvent	$k_{PYR}\tau$
1a	CH_2Cl_2	0.9 ± 0.1
1b	CH_2Cl_2	0.9 ± 0.2
1b-d_3	CH_2Cl_2	2.2 ± 0.2
1b	$CF_2ClCFCl_2$	0.5 ± 0.1
1b	c-C_6H_{12}	0.5 ± 0.1
1b	c-C_6D_{12}	0.5 ± 0.1

Herein we are pleased to report the results of this study, which include studies of the photochemistry of **1a** and **1b** by laser flash photolysis, classical chemical analysis, and argon matrix isolation techniques.

II. Experimental Section

Materials. Solvents (Aldrich) were used as received. 1-Pentene was passed through an alumina column immediately before use. Methanol, pyridine, and piperidine were purified by distillation. *E*- and *Z*-3-heptene were used as received from Aldrich.

Typical Procedure for Photolysis Experiments. Various amounts of carbene quenchers were added to each cuvette with maintenance of a constant concentration (typically 0.01 M) of carbene precursor. Solvent was then added to each cuvette in order to achieve a constant volume of sample (0.3 mL) for each experiment. Samples were degassed by purging with oxygen-free argon for 3 min before they were irradiated individually with sixteen 300 nm bulbs in a Ray-o-Net reactor for 2 h. The yields of products were then determined by integration of peaks in gas chromatograms using analytical GC, with decane as internal standard. Analytical gas chromatography was performed on a Perkin-Elmer 8500 gas chromatograph equipped with a flame ionization detector, using a Supelco fused silica capillary column cross-linked with methylsilicone (i.d. 0.32 mm, length 30 m, film thickness 3 μm). GC/MS analyses were performed on a HP-6890 Series GC System with an HP-1 methylsiloxane capillary column (40.0 m × 100 μm × 0.20 μm). Compounds giving rise to those peaks were identified from their mass spectral fragmentation patterns and by comparison with authentic samples.

2-Methoxy-2-methyl-5,5-dipropyl-Δ^3-1,3,4-oxadiazoline (1a). 4-Heptanone (2.7 g, 11.8 mmol) and acetylhydrazine (0.87 g, 11.8 mmol) were refluxed in benzene; water was removed with a Dean–Stark trap. The solvent was removed from the resultant mixture to yield crude 1-acetyl-2-(4-heptylidene)hydrazine, which was purified by column chromatography (silica, 50% EtOAc in hexane, 85% yield). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ 9.58 (s, 1H), 2.11 (m, 7H), 1.42 (m, 4H), 0.86 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ 173.8, 155.1, 38.5, 31.7, 21.5, 19.5, 18.9, 14.0, 13.5. Mp: 38–39 °C. A solution of the 1-acetyl-2-(4-heptylidene)hydrazine in methanol was added dropwise to a solution of lead tetraacetate (5.7 g, 12.9 mmol) in methanol cooled with an ice bath. After 4 h at room temperature, the yellow color of the mixture disappeared. Potassium hydroxide (0.66 g, 11.8 mmol) in methanol (10 mL) was added, and the resultant mixture was stirred overnight under argon. The mixture was extracted with dichloromethane (3 × 70 mL), the combined organic layers were dried ($MgSO_4$), the solvent was evaporated, and the residue was chromatographed (silica, 5% EtOAc in hexane). The yield was 79%. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ 3.16 (s, 3H), 1.60 (s, 3H), 1.70–1.58 (m, 8H), 0.85 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ 132.2, 125.2, 50.7, 38.1, 37.7, 21.9, 17.2, 16.8, 14.3, 14.2. UV (pentane): 235, 321 nm. HRMS (EI): calcd for $C_{10}H_{21}N_2O_2$ (M + 1) 201.1604, found 201.1617.

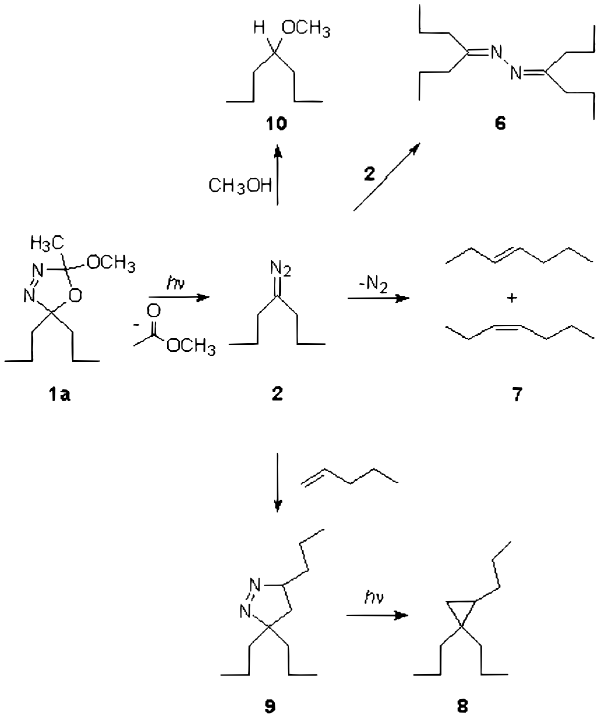
2,2-Dimethoxy-5,5-dipropyl-Δ^3-1,3,4-oxadiazoline (1b). Compound **1b** was prepared using the procedure of El-Saidi et al.[8] 4-Heptanone (2.7 g, 11.8 mmol) and methyl hydrazinecarboxylate (1.07 g, 11.8 mmol) were refluxed in benzene. Water was removed with a Dean–Stark trap. Rotary evaporation removed solvent and generated the methoxycarbonyl hydrazone of 4-heptanone (99%), which was used without purification in the next step. It could be recrystallized after drying under vacuum. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ 3.78 (s, 3H), 3.69 (s, 1H), 2.15 (m, 4H), 1.49 (m, 4H), 0.89 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ 157.5, 128.0, 52.5, 38.5, 30.5, 20.0, 18.5, 14.0, 13.7. Mp: 73–74 °C. A solution of 1-methoxycarbonyl-2-(4-heptylidene)hydrazine in methanol was added dropwise to a solution of lead tetraacetate (5.7 g, 12.9 mmol) in methanol cooled with an ice bath. After 4 h at room temperature, potassium hydroxide (0.66 g, 11.8 mmol) in methanol (10 mL) was added and the solution was stirred overnight under argon. The mixture was extracted with dichloromethane (3 × 50 mL), the combined dichloromethane extracts were dried ($MgSO_4$), the solvent was evaporated, and the residue was chromatographed (silica, 10% EtOAc in hexane). The yield was 89%. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ 3.52 (s, 6H), 1.78 (m 4H), 1.35 (m, 4H), 0.91 (t, 6H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ 136.5, 124.7, 52.0, 38.2, 17.5, 14.4. HRMS: calcd for $C_{10}H_{20}N_2O_3$ 216.1474, found 216.1510.

2,2-Dimethoxy-5,5-dipropyl-Δ^3-1,3,4-oxadiazoline (1b-d_3). 4-Heptanone (5.4 g, 23.8 mmol) was stirred with a trace amount of sodium methoxide in CD_3OD overnight under argon. After CD_3OD was evaporated, water was added to quench the sodium methoxide and the resulting mixture was extracted with dichloromethane (3 × 50 mL). The combined dichloromethane extracts were evaporated, generating 4-heptanone-d_3. The product was used without purification in the next step. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ 2.31 (m, 1H), 1.55 (q, 4H, J = 10.5 Hz), 0.88 (t, 6 H). MS (EI), m/z (rel intensity): 117 (28), 73 (100), 61 (10), 45 (93). This deuterated ketone was used to prepare **1b-d_3** by the method already described for **1b**. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ 3.50 (s, 6H), 1.74 (m, 1H), 1.35 (m, 4H), 0.88 (t, 6H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ 136.4, 124.5, 51.7, 37.4 (m), 16.4, 16.3, 14.0. HRMS: calcd for $C_{10}D_3H_{17}N_2O_3$ 219.1662, found 219.1641. Using a Kratos MS-25 with direct cold probe injection, **1b** and **1b-d_3** were analyzed for their isotopic composition. For **1b-d_3**, the relative ratios of d_0, d_1, d_2, d_3, and d_4 were determined to be 3:14:53:100:77. This analysis was performed on the intense peaks with m/z = 185–189, which correspond to loss of CH_3O from the molecular ion.

Azine of 4-Heptanone (6). 4-Heptanone (5.4 g, 0.6 mmol) and hydrazine (0.38 g, 11.8 mmol) in benzene (120 mL) were refluxed overnight. Water was removed with a Dean–Stark trap. The crude product was purified on a column of silica gel by elution with 50% EtOAc in hexane (yield 87%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.26 (m, 8H), 1.61 (m, 4H), 1.45 (m, 4H), 0.97 (m, 6H), 0.91 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ 165.3, 39.0, 33.1, 20.2, 19.8, 14.8, 14.5. MS (EI), m/z (rel intensity): 224 (M, 4), 181 (100), 140 (92), 112 (55), 70 (86).

1,1,2-Tripropylcyclopropane (8). Oxadiazoline **1a** (0.14 g, 0.70 mmol) and neat 1-pentene (5.5 mL) were irradiated (300 nm) for 16 h after bubbling with dry Ar for several minutes. The remaining 1-pentene was removed by rotary evaporation, and the mixture was chromatographed (silica, 7.5% EtOAc in

SCHEME 1



petroleum ether). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ 1.35 (m, 12H), 0.85 (m, 9H), 0.45 (m, 1H), 0.35 (dd, 1H, $J = 10.0$, 6.0 Hz), −0.15 (dd, 1H, $J = 10.0$, 6.0 Hz). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ 33.0, 31.5, 29.5, 24.0, 23.6, 23.5, 20.0, 19.5, 18.5, 14.8, 14.5, 14.0. MS (EI), m/z (rel intensity): 168 (M, 6), 125 (20), 83 (68), 69 (100), 55 (66).

3,3,5-Tripropylpyrazoline (9). Oxadiazoline **1a** (0.0154 g) and 1-pentene (0.2 mL) in pentane (0.8 mL) were photolyzed with 300 nm light for 40 min before the solution was kept in the dark at RT until the orange color disappeared. After the solvent was evaporated, the product was purified on a column of silica gel by elution with 2% EtOAc in hexane. ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ 4.38 (m, 1H), 2.05 (m, 1H), 1.90−0.80 (series of m, 22H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ 95.0, 88.1, 44.0, 38.0, 34.1, 29.0, 20.1, 16.9, 16.2, 14.0, 13.9, 12.7. MS (EI), m/z (rel intensity): 196 (M, 1), 168 (4), 125 (11), 83 (68), 69 (100), 55 (74).

4-Heptyl Methyl Ether (10).[9] 4-Heptanol (0.824 g, 6.54 mmol) was added to a solution of NaH (0.45 g, 7.85 mmol) in diethyl ether (30 mL) under argon. After stirring for 1 h, methyl iodide (0.5 mL, 7.85 mmol) was added and the solution was stirred for an additional 2 h at room temperature. The remaining NaH was quenched with water (30 mL), and the solution was extracted with diethyl ether (3 × 30 mL). The combined ether extract was dried ($MgSO_4$), the solvent was evaporated, and the residue was chromatographed (silica, 5% EtOAc in hexane).^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ 3.30 (s, 3H), 3.10 (t, 1H, $J = 6$ Hz), 1.33 (m, 4H), 1.23 (m, 4H), 0.9 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ 76.0, 55.1, 49.1, 37.0, 33.0. MS (EI), m/z (rel intensity): 129 (M − 1, 5), 87 (100), 55 (20), 45 (66).

***N*-4-Heptylpiperidine (11).** Compound **11** was prepared using the general procedure of Barney et al.[10] Titanium tetrachloride (1.12 g, 5.9 mmol) was added dropwise to a stirred solution of 4-heptanone (1.5 g, 11.8 mmol), piperidine (1.0 g, 11.8 mmol), and triethylamine (3.56 g, 35.4 mmol) in dichloromethane. The mixture was stirred for 18 h at room temperature. After the solvent was evaporated, sodium cyanoborohydride in methanol was added to the enamine-containing solution and stirring was continued for 1 h. The excess borohydride was quenched with 5% NaOH, and the solution was extracted with dichloromethane. The combined organic layers were dried ($MgSO_4$), the solvent was evaporated, and the residue was chromatographed (silica, 10% EtOAc in hexane).^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ 2.40 (t, 4H, $J = 6$ Hz), 2.25 (m, 1H), 1.1−1.6 (m, 14H), 0.85 (t, 6H, $J = 10$ Hz). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ 84.0, 69.1, 52.1, 47.0, 45.1, 40.0, 34.0. MS (EI), m/z (rel intensity): 183 (M, 1), 140 (100), 98 (3), 84 (3), 55 (3), 41 (4). HRMS (EI): calcd for $C_{12}H_{25}N$ 183.1988, found 183.1981.

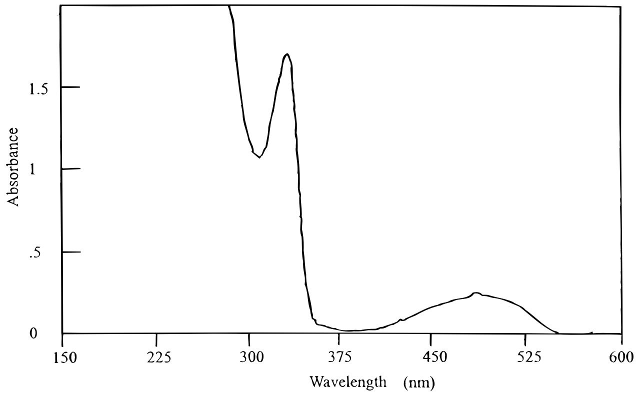


Figure 1. UV/vis spectrum of diazo compound **2** produced upon 300 nm photolysis of **1a** in pentane at 4 °C. The spectrum was recorded at ambient temperature.

Typical Procedure for Laser Flash Photolysis Experiments. The LFP apparatus in use at OSU has been described previously.[11] Reactions were run in quartz cuvettes containing a carbene precursor (always at 0.01 M), pyridine in various amounts, and solvent to make a total volume of 1 mL. Samples were degassed by purging with oxygen-free argon for 5 min. Three or four transient spectra were recorded for each cuvette. Average values of A_{ylide} were used in the data analysis.

Matrix-Isolation Spectroscopy. The colorless oxadiazoline **1a** was placed in a U-type glass tube cooled to −16 °C with a dry ice−acetone bath. The tube was connected to a closed cycle cryogenic system cooled by helium (Air Products). Argon gas flowed over the sample, which sprayed onto a round KBr window at 18 K to generate a transparent matrix. Subsequently, the matrix was cooled to 14 K and maintained at this temperature during the remainder of the experiment. UV/vis spectra were measured with an HP 8452 diode array spectrophotometer from 200 to 550 nm, and infrared spectra were recorded with an FT-IR 2000 spectrometer (Perkin-Elmer) with 2 cm^{-1} resolution. Either a bank of 254 nm Ray-o-Net lamps or a 1000 W mercury lamp with a band-pass filter were used to photolyze the sample in the argon matrix. UV/vis and IR spectra were recorded before and after irradiating the sample.

III. Results and Discussion

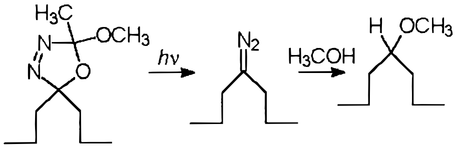
III.1. Chemical Analysis of Photolyzate Mixtures. Oxadiazoline **1a** was photolyzed in quartz cells in pentane using 300 nm Ray-o-Net lamps at 4 °C. GC/MS analysis of a solution photolyzed for 2 h revealed the presence of azine **6**, *E*- and *Z*-3-heptene (**7**), and 4-heptanone (Scheme 1). The ratio of 3-heptenes was $E{:}Z = 2.6{:}1$. During the photolysis the solution turned pink in color and the UV/vis (Figure 1) and IR (2033 cm^{-1}) spectra taken at this time are consistent with the presence of 4-diazoheptane.[12]

In the presence of 1-pentene, photolysis of **1a** again afforded a pink color that persisted for several hours before the solution again turned colorless. GC/MS analysis revealed the formation of azine **6** and cyclopropane **8** (Scheme 1). Cyclopropane **8** can be formed in 8% absolute yield (0.05 M [**1a**], 7.5 M 1-pentene, 300 nm, 2 h, 4 °C).

When the photolysis of **1a** was interrupted, pyrazoline **9** could be detected by GC/MS (Scheme 1). This intermediate was isolated and characterized by spectroscopic methods. Photolysis (300 nm) converted **9** smoothly to cyclopropane **8**. Thus we are forced to conclude that although a "carbene" addition product is formed upon photolysis of **1a** in the presence of 1-pentene, the adduct is derived from thermal cycloaddition chemistry of **2** rather than from dipropylcarbene **3**.

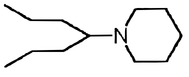
It is clear that only a modest amount of diazo compound **2** is photolyzed under the reaction conditions. To enhance the photochemistry of **2**, the sample was simultaneously exposed to 300 and 254 nm radiation. Although this strategy was successful with cyclobutyl oxadiazoline **5** and its related diazo compound,[7] the yield of **8** actually decreased under the conditions of this study.

Upon photolysis of **1a** (0.03 M) (300 nm, 2 h) in pentane, diazo compound **2** was captured with methanol (2.47 M) to give 4-methoxyheptane (**10**) in 20% yield,



1a **2** **10**

Oxadiazoline **1a** was then photolyzed in the presence of a trap expected to react very slowly with diazo compound **2** and to give a product that is more likely to originate from the carbene than the diazo compound. Photolysis of **1a** (0.06 M) in pentane (300 nm, 2 h, 4 °C) in the presence of piperidine (1 M) gives azine **6** (4%), 3-heptenes **7** (24%), 4-heptanone (4%), and a small amount (<1% yield) of adduct **11**. No adducts of DPC with pentane were observed in the presence or absence of piperidine.



11

The low yield of **11** in pentane suggests that piperidine does not react rapidly with diazo compound **2**. Furthermore, oxadiazoline **1a** (0.01 M) was photolyzed (300 nm) in CH_2Cl_2 to produce a pink solution of 4-diazoheptane, to which piperidine (2 M) was added, and the solution was allowed to stand in the dark for 5 h. GC analysis did not reveal the formation of even traces of **11** under these conditions. Thus, 4-diazoheptane does not react with piperidine; adduct **11** must be derived from dipropylcarbene.

Upon photolysis of **1a** in CH_2Cl_2 (300 nm, 2 h, 4 °C), a 20% yield of **11** can be realized (1 M piperidine) with a reduction in yield of 3-heptene **7** (11%), 4-heptanone (2%), and azine **6** (<1%).

The data suggest that the ratio of $k_{pip}/k_{1,2H}$ (Scheme 2) is significantly larger in CH_2Cl_2 than in pentane. However, it is not clear whether the solvent effects only one or both rate constants.

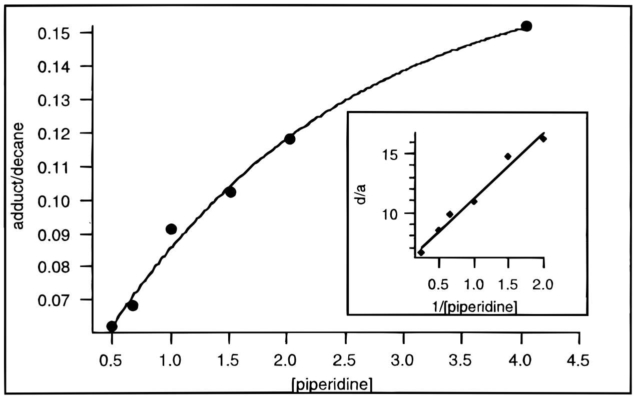
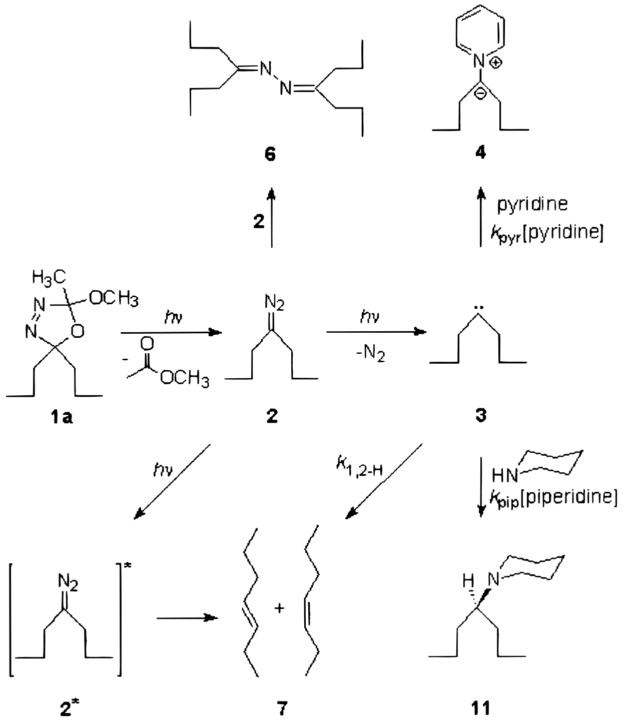


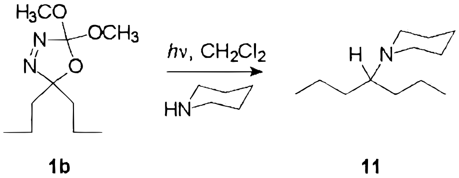
Figure 2. Yield of amine **11** formed upon photolysis of **1a** in pentane as a function of [piperdine]. The inset shows a double reciprocal treatment of the data.

SCHEME 2



A plot of [decane]/[**11**] versus 1/[piperidine] is linear (Figure 2). The ratio of the intercept to the slope of this plot ($k_p\tau$) was 1.01 where k_p is the absolute rate constant of reaction of carbene **3** with piperidine. Assuming $k_p = (1-5) \times 10^9$ M^{-1} s^{-1}, we deduce that τ for dipropylcarbene in pentane at 4 °C is 0.2−1 ns. This is about 7−35 times shorter than the lifetime of dimethylcarbene in perfluorohexane at ambient temperature.[5]

Precursor **1b**, upon photolysis in the presence of 1 M piperidine, gave **11** in 1% and 25% yields in pentane and CH_2Cl_2, respectively.



1b **11**

A plot of the yield of **11** (from **1b**) versus [piperidine] in dichloromethane gave a $k_P\tau$ value of 1.04, in excellent agreement with that obtained with precursor **1a** in pentane.

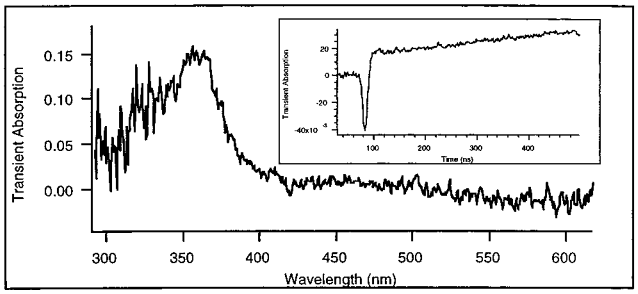


Figure 3. Transient spectrum of ylide **4** produced by LFP (XeCl excimer, 308 nm, 150 mJ, 20 ns) of **1a** in CH_2Cl_2 at ambient temperature. The transient spectrum was recorded over a window of 300 ns, 200 ns after the laser pulse. Inset: Growth of transient absorption at 360 nm following the laser pulse.

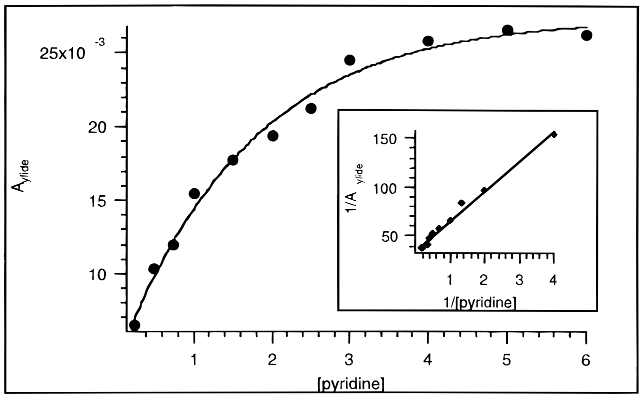
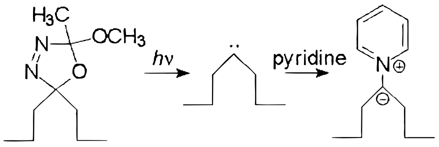


Figure 4. Yield of transient absorption of **4** following LFP of **1a** in CH_2Cl_2 as a function of pyridine concentration. Inset: Double reciprocal treatment of the data.

III.2. Laser Flash Photolysis Studies. Laser flash photolysis (LFP, XeCl excimer, 308 nm, 150 mJ, 20 ns) of either **1a** or **1b** failed to produce a transient with significant absorption between 300 and 700 nm. However, LFP of **1a** or **1b** in the presence of pyridine produced the transient spectrum of Figure 3. It was not possible to resolve the growth of the transient ylide. As methoxy(methyl)carbene and dimethoxycarbene react slowly with pyridine and have microsecond lifetimes, the species detected can be confidently attributed to ylide **4**, from capture of dipropylcarbene with pyridine.[13,14]



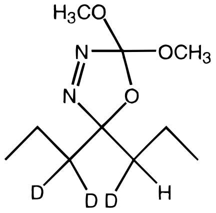
1a 3 4

We posit that precursors **1a** and **1b** fragment to form 4-diazoheptane, which in turn is photolyzed with low, but not zero, efficiency to produce dipropylcarbene within the excimer laser pulse. Control experiments, described below, demonstrated that 4-diazoheptane does not react with pyridine. Oxadiazoline **1a** was photolyzed (300 nm) in CH_2Cl_2 to produce a pink solution of 4-diazoheptane. The half-life of the diazo compound in CH_2Cl_2 at ambient temperature is approximately 4 h. This half-life is not shortened by the presence of pyridine nor is any ylide formed (as monitored by UV/vis spectroscopy) under these conditions.

Although 4-diazoheptane photolyzes inefficiently to form dipropylcarbene, it is too unstable to isolate. Generating the diazo precursor, in situ, and photolyzing it is the most convenient method of studying the dialkylcarbene.

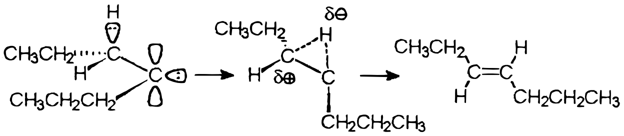
The optical yield of ylide **4** was measured as a function of pyridine concentration. Double reciprocal plots of the data were linear, in agreement with the chemical (GC) study discussed previously (Figure 4). Values of $k_{pyr}\tau$ (0.86−0.93) determined by LFP in CH_2Cl_2 were very similar to the values of $k_p\tau$ (1.01−1.04) determined by analytical gas chromatography. This gave us confidence that the same species, dipropylcarbene, was being studied by both chemical and physical methods.

The value of $k_{pyr}\tau$ determined in cyclohexane and cyclohexane-d_{12} are the same within experimental error. This is consistent with product studies that failed to detect any adducts formed between DPC and pentane. Thus, unlike dimethylcarbene (DMC)[5] the lifetime of DPC is scarcely influenced by reaction with solvent ($\tau \approx 1/k_R$, Scheme 2). LFP of **1b-d_3** in CH_2Cl_2 again produced a transient ylide. Analysis as before revealed that the lifetime of DPC-d_3 is roughly 2.4 times longer than that of DPC. Thus, the pattern of isotope effects indicates that the lifetime of DPC in CH_2Cl_2 and cyclohexane is largely controlled by 1,2 migration of hydrogen to form *E*- and *Z*-3-heptene.[3]



1b-d$_3$

The absolute rate constant for reaction of dimethylcarbene with pyridine is about 3×10^9 M^{-1} s^{-1}, and the lifetime of DMC in perfluorohexane at ambient temperature is 7 ns.[5] If we assume that DPC also reacts with pyridine with absolute rate constant 3×10^9 M^{-1} s^{-1}, we deduce that the lifetime of this carbene is ≈0.3 ns. Thus, the lifetime of DPC in dichloromethane and in cyclohexane is about 20 times shorter than that of DMC in perfluorohexane at ambient temperature. The 1,2 migration of hydrogen is 20 times faster (30 times after statistical correction) in DPC than in DMC because alkyl groups on the carbon bearing the migrating hydrogen atom weaken the C−H bond that breaks in this rearrangement. Furthermore, the alkyl group helps to accommodate the positive charge that develops in the transition state on the carbon bearing the migrating hydrogen.[2]



III.3. Photolysis of 1a in an Argon Matrix. *320 nm Photolyses of 1a.* The UV/vis spectrum of **1a** in an argon matrix is shown in curve a of Figures 5 and 6. After exposure of **1a** to 320 nm radiation, its absorption at 320 nm gradually decreased, as shown in curves a and d. New bands in the UV or visible region concurrent with the disappearance of **1a** were not observed. This is not the case in the corresponding IR spectra (Figure 7), as strong new bands at 2040 and 1755 cm^{-1} were formed as the IR absorption bands of **1a** disappeared. We were able to attribute the species with a 2040 cm^{-1} absorption to a diazo compound and the species absorbing at 1755 cm^{-1} to

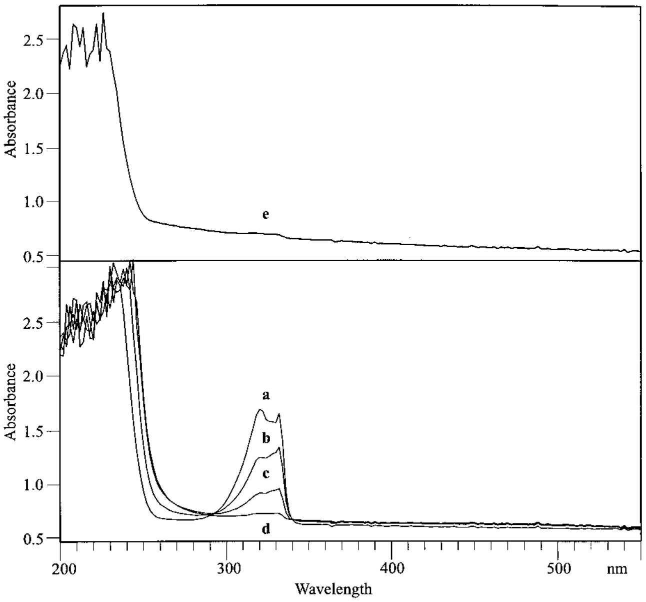


Figure 5. UV/vis spectra of **1a** in an argon matrix: (a) before the photolysis; (b), (c), (d) after 320 nm photolysis at 120, 270, and 540 min, respectively; (e) after photolysis at 254 nm.

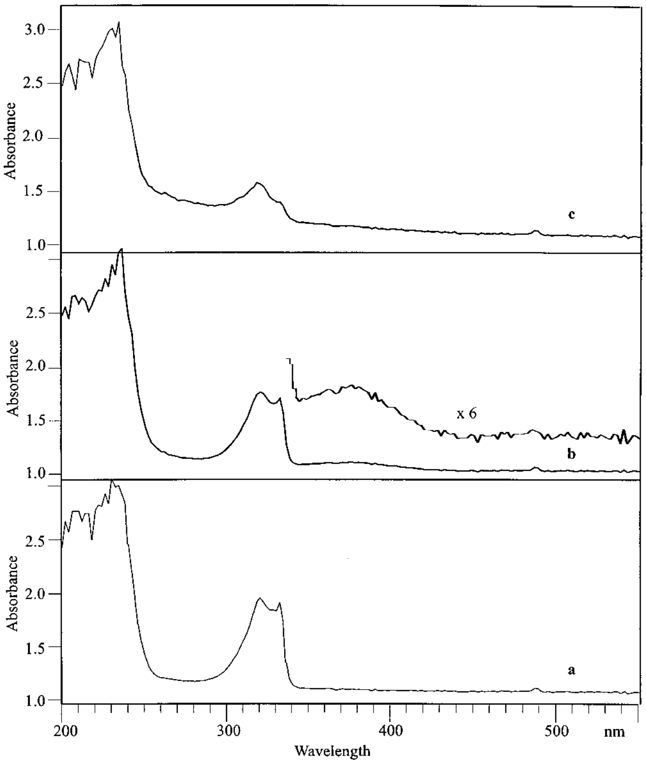


Figure 6. UV/vis spectra: (a) before photolysis of **1a**; (b) after 10 min photolysis at 254 nm; (c) after 280 min photolysis at 254 nm.

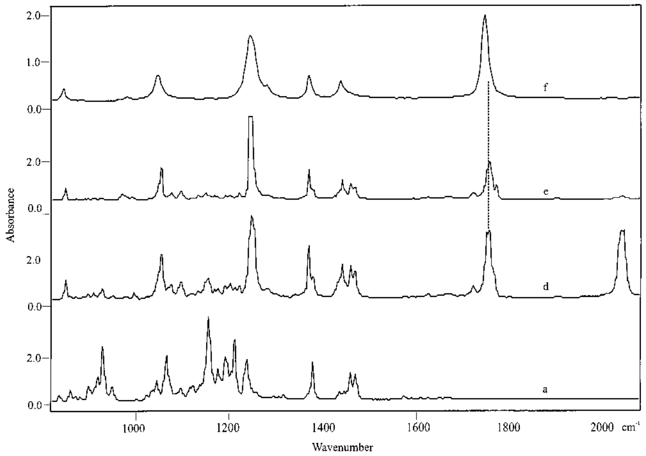


Figure 7. IR spectra of **1a** during photolysis with 320 nm light: (a) before the photolysis; (d) after photolysis for 540 min at 320 nm; (e) after photolysis at 254 nm. (f) Spectrum of methyl acetate.

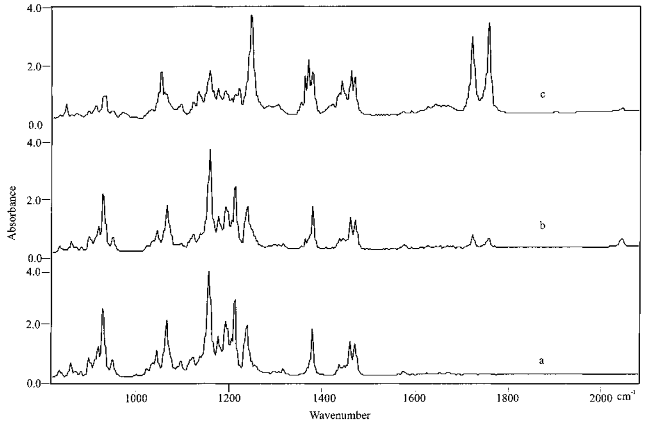
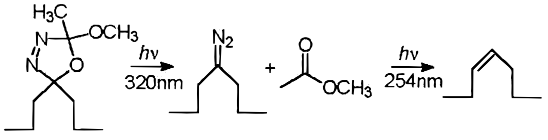


Figure 8. IR spectra: (a) before the photolysis of **1a**; (b) after 10 min photolysis at 254 nm; (c) after 280 min photolysis at 254 nm.

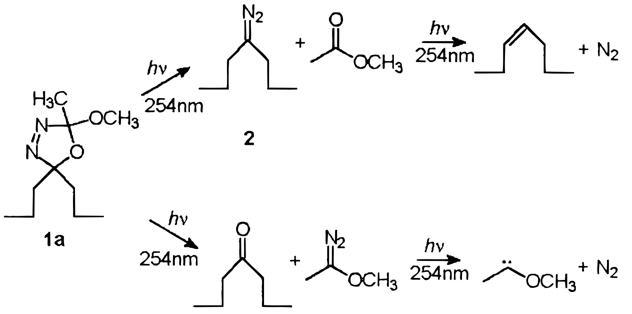
methyl acetate, by comparison with its authentic IR spectrum (curve f of Figure 7). The concentration of **2** was too low to detect by UV/vis spectroscopy due to the weakness of the chromophore. The diazo stretching frequency in argon is shifted by 7 cm^{-1} relative to its value in pentane solution.

Exposure of the sample of diazo compound to 254 nm radiation for 60 min, as shown in curve e of Figure 5, did not cause much change in the UV/vis spectrum during the photolysis. However, the 2040 cm^{-1} IR band disappeared almost completely (curve e of Figure 7). Decomposition of the diazo compound, using a 254 nm light source, was followed, but dipropylcarbene **3** could not be detected in the matrix isolation experiments. This is not a surprise because the barrier for hydrogen migration in alkylcarbenes is small and rearrangement may proceed rapidly, even at 14 K, by a quantum mechanical tunneling mechanism.[15] On the other hand we observed the formation of bands at 970 and 1470 cm^{-1}, which can be associated with the formation of the isomeric 3-heptenes. The photochemical transformations are summarized below.



1a **2**

*254 nm Photolyses of **1a**.* An argon matrix containing **1a** (curve a of Figure 6) was exposed to 254 nm radiation for 10 min. The 320 nm band of **1a** decreased and a weak and broad band centered near 390 nm was formed as shown in curve b of Figure 6. The related IR spectrum (curve b of Figure 8) demonstrated the formation of new absorption bands between 1700 and 2040 cm^{-1}. By analogy with the 320 nm photolysis of **1a**, the species absorbing at 2040 and 1755 cm^{-1} were assigned to diazo compound **2** and methyl acetate, respectively. There is another new band formed at 1720 cm^{-1}, typical of a saturated ketone, which was assigned to 4-heptanone. After careful inspection of the diazo group absorption region, we discovered a weak band at 2020 cm^{-1}. This species was assigned to methylmethoxydiazomethane on the basis of the reports of Moss et al.[14] This convinced us to assign the species absorbing at 390 nm to methoxy(methyl)carbene. This assignment is in good agreement with the reported spectrum of this carbene generated from the corresponding diazirine.[14] Prolonged exposure of the sample to 254 nm radiation led to a decrease of the diazo group absorption band and an increase of the ketone absorption band (curve c). Meanwhile, the 390 nm band of methoxy(methyl)carbene was bleached. The photochemical reactions initiated with 254 nm radiation are summarized below.



At present, we cannot explain the wavelength dependence of the photochemistry of **1a** in argon at 14 K.

IV. Conclusion

The photochemistry of 2-methoxy-2-methyl- 5,5-dipropyl-Δ^3-1,3,4-oxadiazoline (**1a**) and 2,2-dimethoxy-5,5-dipropyl-Δ^3-1,3,4 oxadiazoline (**1b**) was investigated. Photolysis (300 nm) of these compounds in solution leads to fragmentation to 4-diazoheptane (major), which slowly forms the corresponding azine. Fragmentation to form 4-heptanone is also observed. Yields of 4-diazoheptane in CH_2Cl_2 are much larger than in pentane. 4-Diazoheptane can be trapped with 1-pentene to form a pyrazoline or with methanol to form 4-methoxyheptane. The pyrazoline can be decomposed photochemically to form 1,1,2-tripropylcyclopropane. In solution, 4-diazoheptane is inefficiently photolyzed to dipropylcarbene (DPC), which can be trapped with piperidine to give an adduct or with pyridine in laser flash photolysis experiments. Analysis of the piperidine and pyridine data indicates that the lifetime of DPC in cyclohexane, methylene chloride, or Freon-113 ($CF_2ClCFCl_2$) solution at ambient temperature is controlled by 1,2 hydrogen migration to form *Z*- and *E*-3-heptene. The lifetime deduced under these conditions is $\approx$300 ps, which is about 20-fold shorter than that of dimethylcarbene in perfluorohexane at ambient temperature. Upon photolysis (254 nm) of oxadiazoline **1a** in argon, 4-diazoheptane and 1-methoxydiazoethane are formed. These diazo compounds undergo subsequent photolysis, which revealed the formation of methoxy(methyl)carbene and *E*- and *Z*-3-heptene. It was not possible to detect DPC in argon at 14 K.

Acknowledgment. Support of this work by the National Science Foundation (NSF CHE-9613861) is gratefully acknowledged. J.P.P. and J.W. thank NSERC of Canada for a grant in aid. The authors gratefully acknowledge the assistance of Dr. Isabelle Merdrignac and Dr. Johnny Brown in the determination of the isotopic composition of **1b-*d*$_3$**.

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