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Rate Constants for 1,2-Hydrogen Migration in Cyclohexylidene and in Substituted Cyclohexylidenes[1]

John Paul Pezacki,[†,‡] Philippe Couture, James A. Dunn,[†] and John Warkentin*

Department of Chemistry, McMaster University, 1080 Main Street West,
Hamilton, Ontario, Canada L8S 4M1

Paul D. Wood[⊥] and Janusz Lusztyk*

The Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive,
Ottawa, Ontario, Canada K1A 0R6

Francis Ford and Matthew S. Platz

Newman and Wolfrom Laboratory of Chemistry, The Ohio State University, 120 West 18th Avenue,
Columbus, Ohio 43210

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Laser flash photolysis (UV-LFP, 308 nm) of suitably substituted oxadiazolines leads to cyclohexylidene (**14a**), 4-*tert*-butyl-cyclohexylidene (**14b**), 2-trifluoromethylcyclohexylidene (**14d**), 8-aza-8-methyl[3.2.1]oct-3-ylidene (**14e**), diethylcarbene (**14f**), and ethyl(methyl)carbene (**14h**). Carbene intermediates were inferred from the products of steady state photolyses, and their pyridinium ylides were inferred from transient absorption spectra observed when pyridine was present. Yields of the pyridinium ylides **15a**−**h** as a function of pyridine concentration gave the lifetimes (τ) for carbenes **14a**−**h** in cyclohexane, cyclohexane-d_{12}, and benzene solutions, at 22 °C. The intermediacy of cyclohexylidene (**14a**) was inferred from the observation of cyclohexene formed in both the LFP and steady state (SS) experiments. The major products from dual wavelength irradiation of the oxadiazolines (at 254 and 300 nm) were those of 1,2-migration of hydrogen (1,2-H) in the corresponding carbenes. 2-Trifluoromethylcyclohexylidene gave 3-trifluoromethylcyclohexene and 1-trifluoromethylcyclohexene in a 9.8:1 ratio. The kinetic data support the conclusion that 1,2-H in the cyclohexylidenes is accelerated, relative to 1,2-H in dimethylcarbene. A 4-*tert*-butyl substituent has a negligible effect on the rate constant for 1,2-H, but the CF_3 group at the α-position decelerates 1,2-H by roughly 10-fold, as inferred from the distribution of products.

Introduction

The intra- and intermolecular reactivities of alkyl- and dialkylcarbenes have been actively studied in recent years.[2,3] For singlet dialkylcarbenes, 1,2-migration of hydrogen (1,2-H) is well-known[2,4] and is modulated by substitution at the carbene carbon.[2a] For example, dimethylcarbene has a lifetime (τ) of ∼7 ns[4] in perfluorohexane at ambient temperature which corresponds to $k_{1,2-\mathrm{H}} \cong 1.4 \times 10^8\ \mathrm{s}^{-1}$, while in chloro(methyl)carbene[5] and bromo(methyl)carbene,[6] $k_{1,2-\mathrm{H}} = (1-3) \times 10^6\ \mathrm{s}^{-1}$ and $(5-6) \times 10^6\ \mathrm{s}^{-1}$, respectively. By comparison, methoxy(methyl)carbene[7] must rearrange very slowly to methyl vinyl ether by 1,2-H at 25 °C, as that rearrangement barely competes with attack on precursor diazirine (azine formation) in dilute solutions of hydrocarbons.

Presumably modulation of rate constants for 1,2-H occurs through substituent effects on the stabilities of both the ground and transition states for intramolecular rearrangement. In some cases, 1,2-H in carbenes appears to be accelerated by polar solvents.[8] In other cases, the formation of π-complexes with arenes may affect the rate constants.[9]

The degree of overlap between the C−H bond orbital of the migrating hydrogen and the virtual p orbital of the carbene, in cases where conformational interconversion is restricted, is believed to affect the absolute rate constant for migration.[10] In conformationally restricted cyclohexylidenes, 1,2-H migrations could be separated into contributions from axial and equatorial hydrogens.[10−14] The ratio of rate constants at 120−160 °C (k_{ax}:k_{eq}) in

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[†] NSERC Scholar 1996−1998.

[‡] NRCC Visiting Scientist, summers, 1996−1998.

[⊥] NRCC Research Associate, 1996−1998.

[1] Issued as NRCC No. 42177.

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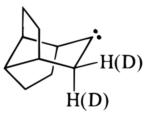
homobrexylidene (**1**)[10a,11] is 2.2:1 and in 2,2-dimethyl-4-*tert*-butylcyclohexylidene (**2**)[10a,12] it is 1.9:1 at 155 °C.



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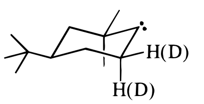
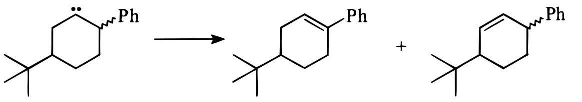


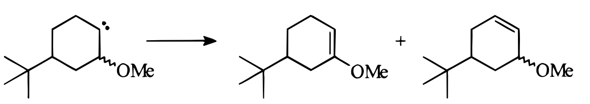
2

Substituents such as axial or equatorial 2-phenyl in 5-*tert*-butylcyclohexylidene (**3**)[13] or equatorial 2-methoxy in 4-*tert*-butylcyclohexylidene (**6**)[14] favor 1,2-H from the 2-position, leading preferentially to **4** and **7** (160 °C, eq 1; 190 °C, eq 2).[10b] Equatorial 2-methyl-4-*tert*-butylcyclohexylidene affords 79.7% 5-*tert*-butyl-1-methylcyclohexene and 20.3% 5-*tert*-butyl-3-methylcyclohexene.[10c]



	3	**4**	**5**
phenyl equatorial :		77.1%	21.6%
phenyl axial :		52.3%	41.3%

Eq. 1.



	6	**7**	**8**
methoxy equatorial :		95.1%	4.70%
methoxy axial :		29.4%	58.4%

Eq. 2.

Despite extensive studies of cyclohexylidenes, generated from precursors such as 1,2-diazaspiro[2.5]oct-1-ene (**9**) by laser flash photolysis (LFP), all attempts[15] to estimate rate constants for 1,2-H by means of the pyridine ylide trapping method[3,4] failed. Excited state reactions that mimic carbene reactions by forming the same products (not necessarily in the same ratios) have been found,[16] and it is possible that excited state chemistry minimizes carbene formation from precursors such as **9**. Having used oxadiazoline precursors successfully to study dialkylcarbenes,[17] we turned to them again to generate four different cyclohexylidenes. The photoproducts were determined from dual wavelength (254 and 300 nm) steady state (SS) photolysis experiments. Rate constants for rearrangement of the carbenes were estimated by intercepting them with pyridine in LFP experiments.

Methods, Results, and Discussion

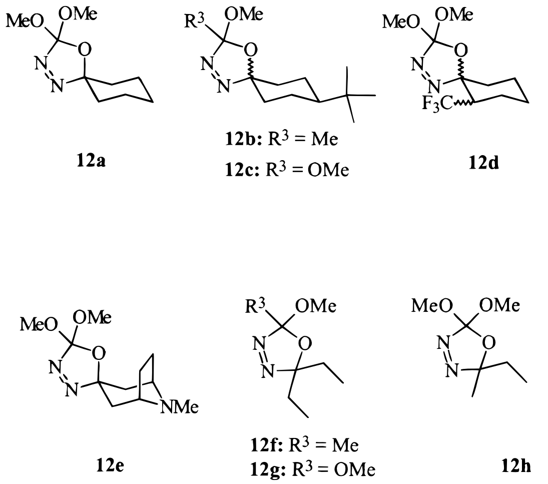
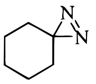


Figure 1.



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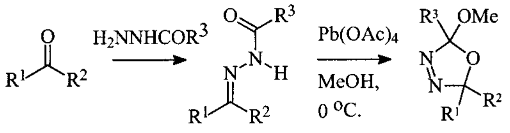
Oxadiazolines **12a**−**h** (Figure 1) served as precursors of cyclohexylidene (**14a**), 4-*tert*-butylcyclohexylidene (**14b**), 2-trifluoromethylcyclohexylidene (**14d**), 8-aza-8-methyl-[3.2.1]oct-3-ylidene (**14e**), diethylcarbene (**14f**), and ethylmethylcarbene (**14h**), Table 1. Oxadiazolines **12a**−**c**,**e**−**h** were prepared by oxidative cyclization (eq 3) of the corresponding acyl hydrazones with lead tetraacetate as described previously,[18] and **12d** was prepared by alkylation of the pyrrolidine enamine of cyclohexanone with CF_3I to give 2-trifluoromethylcyclohexanone (**10d**),[19] which was converted to **11d** and then to a mixture of diastereomeric oxadiazolines **12d**, Scheme 1.



10 **11** **12** Eq. 3.

Steady state and laser flash photolysis of oxadiazolines analogous to **12** gives diazoalkanes,[20] in contrast to the thermal reactions of Δ^3-1,3,4-oxadiazolines which lead to dialkoxycarbenes,[21] and dialkylcarbenes.[17,22] Diazoal-

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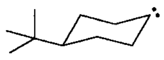
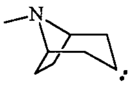
Table 1. Lifetimes of Carbenes from Oxadiazolines, Deduced with the Pyridine Ylide Technique

Carbene	Solvent	τ (ns)[a], double reciprocal	τ (ns)[a], curvefit[d]
 **(14a)**	Cyclohexane	0.1 - 0.7	(0.19 - 0.97) ± 9.2 %
	Cyclohexane-d$_{12}$	0.1 - 0.7	(0.24 - 1.2) ± 23 %
	Benzene	0.8 - 4	(0.60 - 3.0) ± 22 %
 **(14b)**	Cyclohexane	0.3 - 2	(0.17 - 0.86) ± 15 %
	Cyclohexane-d$_{12}$	0.2 - 1	(0.24 - 1.2) ± 26 %
	Benzene	1 - 5	(0.46 - 2.3) ± 20 %
 **(14d)**	Cyclohexane	1 - 5	(0.98 - 4.9) ± 12 %
	Cyclohexane-d$_{12}$	1 - 5	(0.74 - 4.7) ± 11 %
 **(14e)**	Cyclohexane	1.4 - 6.9	(1.7 - 8.3) ± 9.3 %
	Cyclohexane-d$_{12}$	1.5 - 7.6	(0.98 - 7.9) ± 9.1 %
	Benzene	0.6 - 3.0	(0.62 - 3.1) ± 9.8 %
 **(14f)**	$CF_2ClCFCl_2$	0.6 - 3	----
	Cyclohexane	1 - 5	
	Benzene	1 - 5	
 **(14h)**	$CF_2ClCFCl_2$	0.6 - 3	----
	Cyclohexane	1 - 5	
	Benzene	1 - 5	
	$CF_2ClCFCl_2$	4.2 - 21[b]	----
	Pentane	4.6 - 23[b]	
	C_6F_{14}	7[c]	

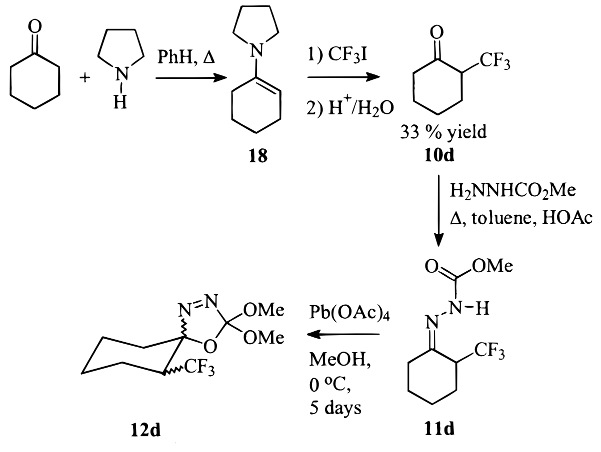
[a] Assuming k_{PYR} = (1-5) x 10^9 M^{-1} s^{-1}

[b] References 4a-c and 17.

[c] Reference 4d. Determined from the intercept of a plot of k_{obs} *vs.* [pyridine].

[d] Errors were determined directly from curve fitting of the data.

Scheme 1



kanes are the primary photoproducts in steady state photolyses with 300 nm light, and they may be photolyzed further with 254 nm light to generate dialkylcarbenes in steady state experiments. Such dual wavelength experiments were done here to determine product distributions. LFP of oxadiazolines at 308 nm, in the presence of pyridine, gives pyridinium ylides, and those ylides arise from the trapping of the corresponding dialkylcarbenes.[17] Indirect evidence for the formation of dialkylcarbenes from oxadiazolines was provided by comparison of carbene lifetimes and pyridinium ylide spectra derived from both an oxadiazoline and the diazirine precursor of dimethylcarbene.[17] However, LFP (308 nm) of 5,5-dialkyl-2-methoxy-2-methyl-Δ^3-1,3,4-oxadiazolines in the presence of pyridine affords two pyridinium ylides, one resulting from trapping of the dialkylcarbene (Scheme 2, upper path) and one resulting from trapping of methoxy(methyl)carbene (Scheme 2, R^3 = Me, lower path).[17] For kinetic work it is therefore better to use 2,2-dimethoxy-5,5-dialkyl-Δ^3-1,3,4-oxadiazolines, such as **12a**,**d**,**e**,**h**, because the reaction of dimethoxycarbene with pyridine is too slow to be observed by ns LFP.[23]

Laser Flash Photolysis of Oxadiazolines. LFP of oxadiazolines **12a**−**h** at 308 nm in the presence of pyridine[24] gave transient absorptions, all with λ_{max} ~360 nm. Examples of time-resolved pyridinium ylide spectra from carbenes **14a**−**h** are in Figure 2. The lifetimes of those carbenes were determined by Stern−Volmer analy-

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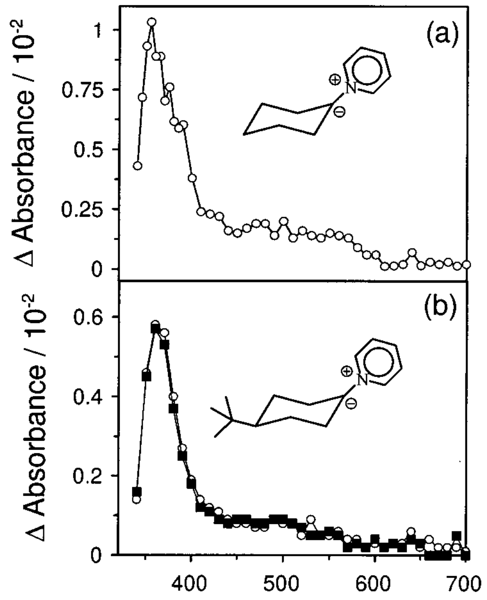
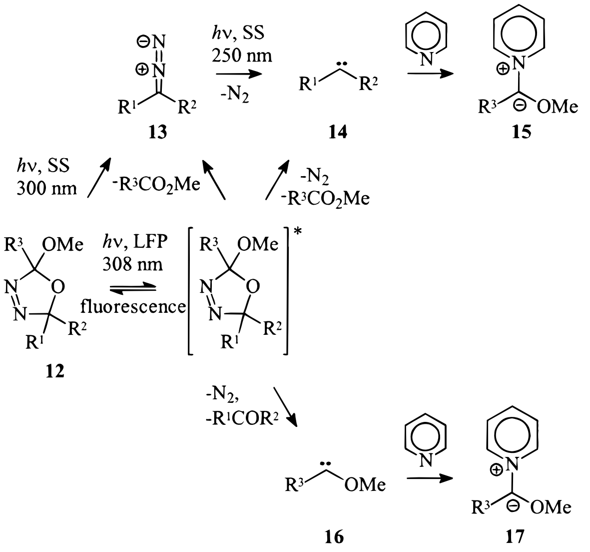


Figure 2. (a) Time-resolved UV−vis spectrum observed 380 ns after 308 nm LFP of 3,4-diaza-2,2-dimethoxy-1-oxa[4.3]-spirodec-3-ene in cyclohexane containing 2.0 M pyridine at 22 °C. (b) Time-resolved UV−vis spectrum observed following 308 nm LFP of 8-*tert*-butyl-3,4-diaza-2-methoxy-2-methyl-1-oxa-[4.3]spirodec-3-ene in cyclohexane containing 1.0 M pyridine at 22 °C. The data were collected at intervals of 460 ns (○) and 32.6 μs (■) after the laser pulse.

Scheme 2



sis of the maximum amplitudes of the ylide absorptions as a function of [pyridine], Figure 3. The data were analyzed by linear least-squares fitting of the curve to eq 4 and by double reciprocal treatment of the data.[3c] In eq 4, A_{YLIDE} is the amplitude of absorbance of the pyridinium ylide in the presence of various amounts of added pyridine, $A^{\infty}{}_{\mathrm{YLIDE}}$ is the amplitude of absorbance

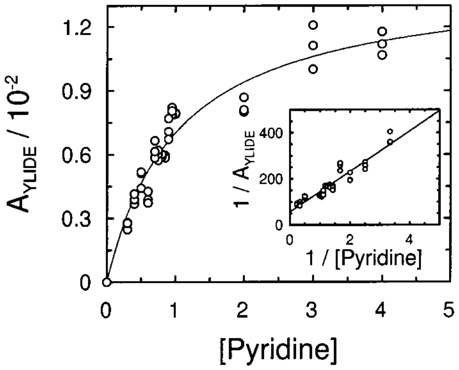


Figure 3. Absorbance of the pyridinium ylide of cyclohexylidene vs pyridine concentration in cyclohexane at 22 °C. Inset shows the double reciprocal plot of 1/absorbance of the pyridinium ylide of cyclohexylidene vs 1/pyridine concentration in cyclohexane at 22 °C.

of the pyridinium ylide at infinite [pyridine] and constant laser intensity, k_o is the sum of all the rate constants leading to the disappearance of the transient carbene, $\tau = 1/k_o$ is the lifetime of the transient carbene, and k_{pyr} is the bimolecular rate constant for the reaction of the carbene with pyridine. Fitting the data to a curve allows one to solve for the product $k_{\mathrm{pyr}}\tau$ without using double reciprocal plots.[25]

$$A_{\mathrm{YLIDE}} = A^{\infty}{}_{\mathrm{YLIDE}}\frac{k_{\mathrm{pyr}}[\mathrm{pyridine}]}{k_o + k_{\mathrm{pyr}}[\mathrm{pyridine}]} = A^{\infty}{}_{\mathrm{YLIDE}}\frac{k_{\mathrm{pyr}}\tau[\mathrm{pyridine}]}{1 + k_{\mathrm{pyr}}\tau[\mathrm{pyridine}]} \quad (4)$$

Results of lifetime measurements in cyclohexane, cyclohexane-d_{12}, and in benzene are summarized in Table 1. The lifetimes of carbenes **14a**,**b**,**d**,**e** do not depend significantly on the isotope (H or D) in the cyclohexane solvent, and the slightly longer lifetimes in solutions of benzene may be the result of the formation of π-complexes with these carbenes or to a slightly smaller value of k_{pyr} in benzene. Such π-complexes have been implicated as the cause of extended carbene lifetimes in benzene vs nonaromatic hydrocarbon solvents by as much as an order of magnitude.[9]

Cyclohexylidenes are likely to have singlet ground states with low-lying triplet states. Dimethylcarbene is believed to have a singlet ground state,[4] with $\Delta E_{\mathrm{S-T}} \sim 1.6$ kcal mol^{-1}.[26] Adamantylidene, with an angle constraint similar to that expected in cyclohexylidene, is also a singlet in the ground state, with $\Delta E_{\mathrm{S-T}} \sim 3$ kcal mol^{-1}.[27] In cyclohexylidenes, 1,2-H migration from the singlet dominates over triplet state chemistry, presumably because the barriers for triplet state reactions are higher.[28]

As expected, **12b** and **12f** also afforded the pyridinium ylide from methoxy(methyl)carbene in the LFP experiments. Kinetic traces obtained following LFP of **12b** at

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[24] Oxadiazoline precursors give the best signals for pyridinium ylides of dialkyl- and cycloalkylcarbenes when irradiated with 308 nm by LFP. For these experiments pyridine purity was extremely important as impurities (presumably the *N*-oxide) absorb at the excitation wavelength. In some cases it was necessary to purify pyridine by $ZnCl_2$ complexation and release to obtain solutions of pyridine which did not absorb light at 308 nm, see: Heap, J.; Jones, W. J.; Speakman, J. B. *J. Am. Chem. Soc.* **1921**, *43*, 1936. Very pure pyridine turns yellow over a period of 10−30 min at room temperature when exposed to oxygen.

[25] The major problem with the linearized functions is that they give excessive weighting to points which may be poorly defined.

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[27] (a) Morgan, S.; Jackson, J. E.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 2782. (b) Bally, T.; Matzinger, S.; Truttman, C.; Platz, M. S.; Morgan, S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1964.

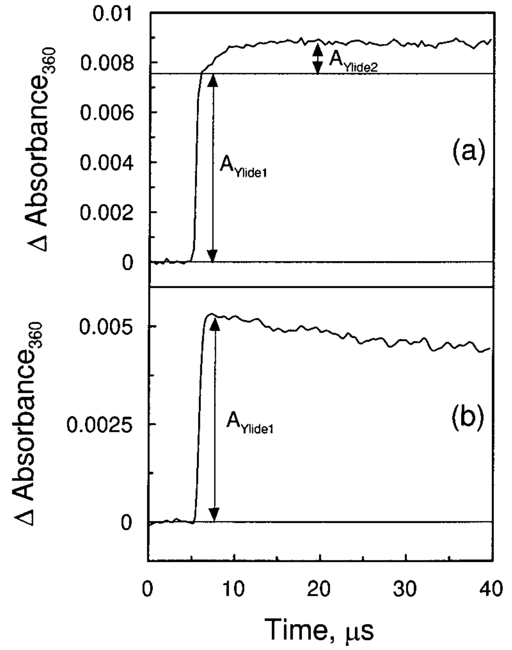
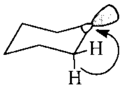


Figure 4. (a) Trace obtained upon 308 nm LFP of 8-*tert*-butyl-3,4-diaza-2-methoxy-2-methyl-1-oxa[4.3]spirodec-3-ene (**12b**) in the presence of 0.4 M pyridine in cyclohexane at 22 °C. (b) Trace obtained upon 308 nm LFP of 8-*tert*-butyl-3,4-diaza-2,2-dimethoxy-1-oxa[4.3]spirodec-3-ene (**12c**) in the presence of 0.4 M pyridine in cyclohexane at 22 °C.

308 nm in the presence of pyridine, observed at 360 nm, showed "instantaneous" growths which varied in amplitude as a function of pyridine concentration (A_{ylide1}, Figure 4) and a slow growth the kinetics of which also varied with pyridine concentration (A_{ylide2}, Figure 4). For methoxy(methyl)carbene $k_{\mathrm{pyr}} = 5.5 \times 10^5$ M^{-1} s^{-1} [29] and the slow growth could easily be distinguished from the "instantaneous" growths of signals for the pyridinium ylides **15b** and **15e**. Linear least-squares fitting of the rate constants for formation of the pyridinium ylide of methoxy(methyl)carbene as a function of pyridine concentration gave $k_{\mathrm{pyr}} = 6.4 \pm 0.9 \times 10^5$ M^{-1} s^{-1}, in reasonable agreement with the literature value.[29] LFP (308 nm) of oxadiazolines **12c** and **12g** in the presence of pyridine led to only one observable ylide in each case; the ylides of **14b** (4-*tert*-butylcyclohexylidene) and **14f** (diethylcarbene), respectively. The lifetimes of carbenes **14b** and **14f**, derived from Stern–Volmer analyses of data obtained from dimethoxyoxadiazolines **12c** and **12g**, were the same as those from monomethoxy analogues **12b** and **12f**, but analyses of the data from the dimethoxy precursors were more straightforward (Figure 4).

1,2-Hydrogen Migration in Cyclohexylidene and 4-*tert*-Butylcyclohexylidene. The lifetimes of **14a** and **14b**, in both cyclohexane and benzene solutions, were the same within experimental error, although the 4-*tert*-butyl substituent should raise the energies of twist boat transition states for the H-migrations. The fact that the *tert*-butyl group has an effect that is too small to be detected by the method could mean that both **14b** and **14a** prefer 1,2-H from the chair conformation (**19**)[30] or that their lifetimes are too short for conformational change to occur. A model for cyclohexylidene is cyclohexanone, which undergoes conformational change[31] over a barrier of <2.3 kcal/mol. At 25 °C, the rate constant must be $>10^9$ s^{-1} and it is likely then that cyclohexylidenes do undergo conformational change during their lifetimes and that the method used here is not sensitive enough to detect small substituent effects. The 1,2-H shift reaction is very exothermic. Thus it will have a very early TS and may not feel small substituent and conformational effects. Also the alkyl substituent may weaken the migrating CH bond and thus accelerate the rearrangement.



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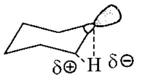

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The lifetimes of carbenes **14a**,**b**,**e** in benzene, relative to that of dimethylcarbene, are between (~0.1–0.3):1 although they should be somewhat longer if statistics were dominant. Presumably the increase in rates of 1,2-H in the former carbenes is a "bystander effect" [10b] resulting mainly from increased substitution at the α-carbon, which would stabilize positive charge there in the transition state (**20**). Analysis of the products of photolysis of **12a** (hexadecane, 308 nm LFP, and 254 + 300 nm SS) by GC-MS showed that cyclohexene is the major product in both experiments. Analyses (^{1}H NMR, 500 MHz) of the products of photolysis of **12a**–**c**, **12f**, and **12h** (cyclohexane-d_{12}, 254 + 300 nm SS) showed that 1,2-H migration is also the major reaction pathway of carbenes **14a**, **14b**, **14f**, and **14h**. From diethylcarbene (**14f**), the three major products were (*E*)-2-pentene, (*Z*)-2-pentene, and 1,2-dimethylcyclopropane (~15:10:1 (58%, 38%, 3.8%), while ethyl(methyl)carbene (**14h**) gave (*E*)-2-butene, (*Z*)-2-butene, 1-butene, and methylcyclopropane (~45:34:20: 1, respectively). Similar ratios of products have been reported from ethyl(methyl)carbene generated from other nitrogenous precursors.[32] The barriers for migrations in ethyl(methyl)carbene leading to (*E*)- and (*Z*)-2-butene, 1-butene, and methylcyclopropane have recently been computed to be 5.2, 5.9, 8.5, and 8.3 kcal/mol, respectively.[33] It is likely that excited state migrations in the diazo precursors of carbenes **14a**–**h** also yield the alkene products derived from 1,2-H in the carbenes.[16,17] Therefore, the ratios of products from dual wavelength irradiations most likely reflect a composite of carbene and excited state rearrangements. Contributions of each process to the overall yield from a given carbene can sometimes be estimated by increasing the concentration of a suitable trap. When all the carbene can be trapped, the yields of alkenes represent the contribution of the excited state rearrangements. Attempts to reach satura-

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[28] It is most likely that vertical transitions lead to the formation of singlet carbenes ^{1}**14a**–**h** in photolyses of oxadiazolines **12a**–**h**. The rate constants for reactions proceeding through the triplet state manifold are then the products of the equilibrium constant for intersystem crossing (ISC), K_{ISC}, and the rate constants for the reactions of triplet carbenes ^{3}**14a**–**h**, k_t (assuming that the preequilibrium approximation applies) according to the scheme below.

$$\mathbf{12a{-}h} \xrightarrow{h\nu} {}^1\mathbf{14a{-}h} \overset{K_{\mathrm{ISC}}}{\rightleftharpoons} {}^3\mathbf{14a{-}h} \xrightarrow{k_t} \text{triplet derived products}$$

[29] Ge, C. S.; Jang, E. G.; Jefferson, E. A.; Liu, W.; Moss, R. A.; Wostowska, J.; Xue, S. *J. Chem. Soc., Chem. Commun.* **1994**, 1479.

[30] We prefer not to draw a virtual (unreal) p orbital, to which migration formally occurs, at the carbene carbon.

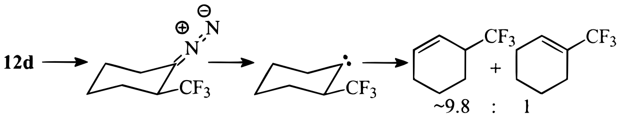
[31] Oki, M. Applications of Dynamic NMR Spectroscopy to Organic Chemistry. In *Methods of Stereochemical Analysis*; Marchand, A. P., Ed.; Vol. 4, VCH: Deerfield Beach, FL, 1985; pp 297–298.

[32] Mansoor, A. M.; Stevens, I. D. R. *Tetrahedron Lett.* **1966**, 1733.

[33] Sulzbach, H. M.; Platz, M. S.; Schaefer, H. F., III; Hadad, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 5682.

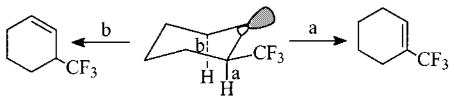
tion with tetramethylethylene as the trap for **14a** were not successful, and excited state rearrangements could not be separated from carbene rearrangements.

Modulation of Reactivity by an α-Trifluoromethyl Substituent. Previous studies of substituted cyclohexylidenes have shown that electron-donating substituents at the α-position favor 1,2-H from that site, as inferred from product ratios.[10c,34,35] 2-Trifluoromethylcyclohexylidene (**14d**) was therefore expected to undergo 1,2-H preferentially from C6. In practice, photolysis (254 + 300 nm SS) of **12d** in benzene and in hexadecane gave 3-trifluoromethyl- (**21**) and 1-trifluoromethylcyclohexene (**22**) in a 9.8:1 ratio, according to ^{1}H NMR, ^{19}F NMR, and GC-MS.[36] Although rearrangement of diazoalkane **13d** in its excited state may have contributed to the formation of **21** and **22**, it is unlikely that hydrogen migration would be more selective in the excited state than in the carbene.[16,17] Thus, the CF_3 substituent in **14d** favors migration from the C6 position. The result could be a composite of electronic and stereochemical effects, since the substituent at C2 of cyclohexylidenes can affect product ratios.[10b,c,13,14] If the CF_3 group were in the axial position, then the geminal equatorial H could migrate more slowly than an axially oriented counterpart. Fortunately, it was possible to assign the conformation of diazo compound **13d** and, by extrapolation, that of carbene **14d** as described below.



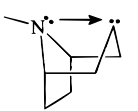
13d **14d** **21** **22**

Although **12d** was obtained as a mixture of diastereomers, diazoalkane **13d** was stable enough to be analyzed by spectroscopy. The infrared spectrum recorded following the photolysis of **12d** in a SS experiment with 300 nm light (30 min) showed a diazo stretching band at 2052 cm^{-1} corresponding to **13d**, a broad C−F stretching band centered at 1282 cm^{-1}, and a carbonyl band at 1756 cm^{-1} assigned to dimethyl carbonate. The COSY spectrum of the photolysis mixture indicated that the two major products were dimethyl carbonate (^{1}H NMR 500 MHz, C_6D_6, δ 3.38 ppm) and diazoalkane **13d**, as a single conformer. Cross-peaks in the COSY spectrum showed that all peaks assigned to **13d** are correlated with each other and therefore originate from the same molecule. Coupling constants for the CF_3CH group of **13d** (δ 2.37) were 10.0 Hz, due to coupling to F of the CF_3 group, as well as 7.1 and 3.3 Hz from axial/axial and axial/equatorial coupling to protons at C3. It follows that C2-H and CF_3 in **13d** must be axial and equatorial, respectively. Since 2-trifluoromethyldiazocyclohexane is generated initially in the SS experiment and is subsequently converted to the carbene, the product ratio (~9.8:1) presumably reflects reactions of the carbene with the CF_3 group in the equatorial position. Thus, migration of H from C2 is that of axially oriented H (normally favored) and its retardation, relative to migration from C6, must reflect an electronic effect of the CF_3 group. This first ever observation of retardation is in accord with the view that 1,2-H in singlet carbenes involves a transition state in which the migrating H is hydride-like and, consequently, the migration origin is cation-like. The analysis is, of course, predicated upon the assumption that the 1,2-H from the excited state of **13d** causes only minor skewing of the product distribution.



Although the CF_3 substituent affects the distribution of products from carbene **14d** substantially, the lifetime of **14d** is not significantly longer than that of the parent cyclohexylidene, because the dominant reaction of **14d** is migration from C6, which is presumably not strongly affected by the CF_3 group at C2. Carbene **14d** did not show a significant solvent kinetic isotope effect (C_6H_{12} vs C_6D_{12}), and it is therefore assumed that it is a ground state singlet and that its chemistry in solution is predominantly that of the singlet state.

Dative Stabilization in 8-Aza-8-methylbicyclo[3.2.1]oct-3-ylidene (14e). Photolysis of **12e** (LFP, 308 nm) in the presence of pyridine also gave a pyridinium ylide. The lifetimes of **14e**, which were determined as described above, are given in Table 1. Although dative stabilization of the carbenic center of **14e** by the neighboring amino group, in a pseudo-boat conformation (**24**), might have enhanced its lifetime, the effect, if any, is small. Moreover, the enhanced lifetime may not be real, because k_{pyr} may be reduced by steric hindrance, thereby giving the appearance of a longer lived carbene. The same qualifier applies to the other cyclohexylidenes that have some hindrance to the approach of pyridine to the carbene site.



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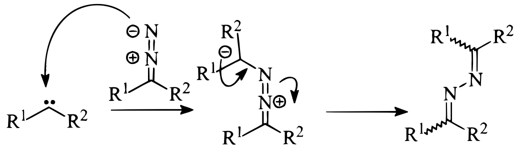
Azine Formation. Steady state irradiations of oxadiazolines **12a**−**h** with 300 nm light led to diazoalkanes (as evidenced by the pink color of the resulting solutions and the characteristic CNN band in IR spectra) in high yield as determined spectroscopically (see Experimental Section). The slow thermal decomposition of these diazo compounds at room temperature gave the corresponding azines with little (0−2%) or no products of rearrangement of the corresponding carbene, even at concentrations of 10^{-3} M. This suggests that a mechanism other than the reaction of carbenes **14a**−**h** with their corresponding diazoalkanes **13a**−**h** (eq 5) is responsible for the formation of azines. For example, if cyclohexylidene has a lifetime of ~1 ns in a hydrocarbon solvent at room temperature, then $k_{1,2-H}$ is ca. 1×10^9 s^{-1}. Assuming that cyclohexylidene traps diazocyclohexane, as in eq 5, with



Eq. 5.

a rate constant of 5×10^9 M^{-1} s^{-1}, then, at concentrations

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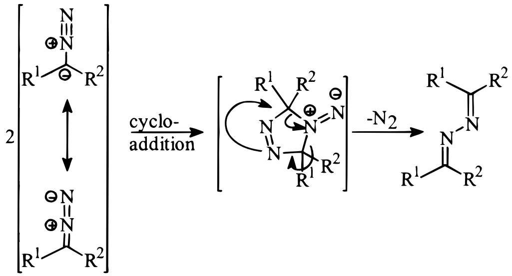
[34] Seghers, L.; Shechter, H. *Tetrahedron Lett.* **1976**, 1943.

[35] Press, L. S.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 509.

[36] (a) Haas, A.; Plümer, R.; Schiller, A. *Chem. Ber.* **1985**, *118*, 3004. (b) Bouillon, J.-P.; Maliverny, C.; Merènyi, R.; Viehe, H. G. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2147.

Scheme 3



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of 10^{-3} M diazoalkane, intramolecular rearrangement rather than intermolecular capture of cyclohexylidene should dominate. Therefore, a bimolecular reaction of diazoalkanes **13a**−**h**, such as that in Scheme 3, must be responsible for the high yields of azines. The lack of significant yields of azines from dual wavelength irradiations, where dialkyl- and cycloalkylcarbenes are generated photochemically, supports this conclusion. Dimerization of diazo compounds has been proposed previously to explain stereoselective azine formation in the decomposition of phenyldiazomethanes.[37]

Conclusions

Three substituted cyclohexylidenes and the parent, generated photochemically from oxadiazolines by LFP, could be trapped as the corresponding pyridinium ylides to yield the first absolute rate constants for 1,2-H migrations in cyclohexylidenes. Those rate constants, which are about 10-fold larger than those of acyclic analogues, show that the effect of a 4-*tert*-butyl substituent is small and that an amino group, which could stabilize the carbene intermediate by intramolecular electron donation, does not have a large effect. 2-Trifluoromethyl is the first substituent shown to decrease the rate constant for 1,2-H migration from the 2-position, by roughly 10-fold, as inferred from the product distribution.

Diethylcarbene and ethyl(methyl)carbene can also be generated by means of the oxadiazoline approach. Those carbenes undergo 1,2-H migrations about 8-fold more slowly than cyclohexylidene, ca. 1.7×10^8 s^{-1} vs ca. 1.4×10^9 s^{-1} in hydrocarbon solvent, assuming that k_{pyr} is invariant at 1×10^9 M^{-1} s^{-1} . Previous failures to trap cyclohexylidenes with pyridine can probably be attributed to low yields of the carbenes (e.g., from diazirines), rather than to extraordinarily fast 1,2-H migrations.

Steady state photolysis of the oxadiazolines leads to the same carbenes, via diazoalkane intermediates. With a suitable choice of wavelength, the diazoalkanes can be accumulated and characterized. The steady state photolysis makes it possible to characterize carbene-derived products under conditions that roughly simulate LFP conditions.

Experimental Section

General Information. GC-MS analyses were carried out with a gas chromatograph equipped with a mass selective detector and a DB-1 capillary column (12 m × 0.2 mm). UV−visible spectra were measured with a double-beam spectrophotometer, and mass spectra were obtained with a double-focusing mass spectrometer. Infrared (FT) spectra are from samples in KBr windows.

Materials. Pyridine (Aldrich) was distilled from either calcium hydride or barium oxide and stored under nitrogen over potassium hydroxide. In some cases it was necessary to purify pyridine by Zn complexation.[24] Cyclohexane and benzene (BDH Omnisolv) were distilled from sodium prior to use. All other solvents and reagents were of the highest purity commercially available and were used as received.

Δ^3-1,3,4-Oxadiazolines (12). Oxadiazolines were prepared by oxidative cyclization of the appropriate hydrazones using lead tetraacetate as described previously.[18] The products were purified by radial chromatography on silica gel with hexane/ethyl acetate (9:1) as the eluent. Yields were determined from hydrazones. In a number of cases oxadiazoline structures were confirmed using COSY, HSQC, and HMBC 2-dimensional NMR techniques.

Carbomethoxyhydrazone of cyclohexanone (11a):[38] yield 91%; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.5−1.8 (m, 6H), 2.20 (dd, J = 5.4, 6.4 Hz, 2H), 2.34 (dd, J = 5.5, 6.3 Hz, 2H), 3.80 (s, 3H), 7.5−7.7 (br s, 1H).

3,4-Diaza-2,2-dimethoxy-1-oxa[4.3]spirodec-3-ene (12a): yield 66%; clear oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47−2.01 (m, 10H), 3.42 (s, 6H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 22.7 (+), 24.6 (+), 33.5 (+), 51.8 (−), 121.0 (+), 136.1 (+); IR (neat, KBr) 3003, 2945, 2862, 1576, 1447, 1226 cm^{-1}; UV $\lambda_{\max}$ = 328 nm (ϵ = 400); MS (EI) *m*/*z* (molecular ion not obsd), 169 [M − OMe]$^+$, 113, 91, 90, 81, 67, 59 (100%); MS (CI, NH_3) *m*/*z* 218 [M + NH_4]$^+$, 201 [M + H]$^+$. Anal. Calcd for $C_9H_{16}N_2O_3$: C 53.99, H 8.05, N 13.99. Found: C 53.75, H 8.18, N 13.40.

Acetylhydrazone of 4-*tert*-butylcyclohexanone (11b): yield 95%; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.86 (s, 9H), 1.5−1.8 (m, 6H), 2.02 (dd, J = 5.5, 6.4 Hz, 2H), 2.23 (dd, J = 5.5, 6.4 Hz, 2H), 2.15 (s, 3H), 8.4−8.6 (br s, 1H).

8-*tert*-Butyl-3,4-diaza-2-methoxy-2-methyl-1-oxa[4.3]-spirodec-3-ene (12b): yield 71%; 4 diastereomers (10:10:1:1, estimated by integration of the minor (mi.) and major (ma.) methoxy signals); white solid, mp 15−20 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83 (s, mi.), 0.87 (s, mi.), 0.89 (s, ma.), 0.92 (s, ma.), 1.21−2.25 (m) overlapping with 1.60 (s) and 1.62 (s), 3.08 (s, mi.), 3.10 (s, mi.), 3.12 (s, ma.), 3.17 (s, ma.); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 23.1, 23.3, 23.6, 23.8, 24.0, 25.1, 27.5, 27.7, 32.4, 32.8, 33.1, 34.2, 35.2, 36.9, 46.8, 47.3, 50.3, 50.5, 120.1, 133.8; UV $\lambda_{\max}$ = 328 nm (ϵ = 300); MS (EI) *m*/*z* (molecular ion not obsd), 209 [M − OMe]$^+$, 167, 155, 139, 123, 75, 59, 43 (100%); MS (CI, NH_3) *m*/*z* 258 [M + NH_4]$^+$, 241 [M + H]$^+$. Anal. Calcd for $C_{13}H_{24}N_2O_2$: C 64.97, H 10.06, N 11.66. Found: C 64.72, H 9.76, N 11.46.

Carbomethoxyhydrazone of 4-*tert*-butylcyclohexanone (11c):[38] yield 81%; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (s, 9H), 1.5−1.8 (m, 6H), 2.19 (dd, J = 5.5, 6.3 Hz, 2H), 2.35 (dd, J = 5.5, 6.3 Hz, 2H), 3.80 (s, 3H), 7.5−7.7 (br s, 1H).

8-*tert*-Butyl-3,4-diaza-2,2-dimethoxy-1-oxa[4.3]spirodec-3-ene (12c): yield 77%, 2 diastereomers (1.3:1 estimated by integration of the methoxy signals); viscous liquid; ^{1}H NMR (500 MHz, $CDCl_3$, integrations normalized for minor (mi.) and major (ma.) isomers) δ 0.86 (s, mi., 9 H), 0.91 (s, ma., 9 H), 1.12−2.15 (m), 3.44 (s, mi., 6 H); 3.46 (s, ma., 6 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 23.3, 24.8, 27.5, 27.6, 32.4, 33.2, 35.2, 46.5, 47.1, 51.9, 120.9, 136.4; UV $\lambda_{\max}$ = 328 nm (ϵ = 300); MS (EI) *m*/*z* (molecular ion not obsd), 225 [M − OMe]$^+$, 204, 167, 109, 101, 75, 57, 43 (100%); MS (CI, NH_3) *m*/*z* 257 [M + H]$^+$. Anal. Calcd for $C_{13}H_{24}N_2O_3$: C 60.91, H 9.44, N 10.93. Found: C 60.56, H 9.66, N 10.32.

6-Trifluoromethyl-3,4-diaza-2,2-dimethoxy-1-oxa[4.3]-spirodec-3-ene (12d). A two-necked, 500 mL round-bottom flask was fitted with an acetone−dry ice condenser, and CF_3I, ca. 6 g, was transferred into the flask. Pentane (75 mL) was added, followed by 9.0 g (60 mmol, 0.5 equiv) of the pyrrolidine enamine of cyclohexanone (**18**) in 75 mL of pentane. The solution was stirred at room temperature for 3 h. The precipitate was then filtered off and washed with pentane, and

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[37] Abelt, C. J.; Pleier, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 1795.

[38] Okimoto, M.; Chiba, T. *J. Org. Chem.* **1990**, *55*, 1070.

the solvent was removed with a rotary evaporator. The resulting oil was acidified with 5 M H_2SO_4 and stirred at room temperature for another 3 h. Extraction with ether (3 × 50 mL) was followed by washing of the organic layer with water (20 mL), 5% sodium bicarbonate (3 × 25 mL), and brine (25 mL). After the solution had been dried over magnesium sulfate it was filtered, and the solvent was removed by rotary evaporation. The product, 2-trifluoromethylcyclohexanone (**10d**), was purified by fractional distillation at ca. 25 Torr. The fraction collected at 85−87 °C (2.0 g) consisted of 85% **10d** and 15% cyclohexanone as determined by GC; overall yield 33%. A solution of benzene (50 mL) containing 2-trifluoromethylcyclohexanone (**10d**, 1.77 g, 9 mmol, weight adjusted for cyclohexanone impurity), methyl hydrazinocarboxylate (1.24 g, 13.8 mmol), and acetic acid (2 drops) was refluxed for 24 h in a Dean−Stark apparatus. The crude product containing **11d** was isolated as an oil, and attempts to crystallize **11d** from it (various solvent mixtures) failed: ^1H NMR (500 MHz, $CDCl_3$) δ 1.2−2.1 (m, 8H), 2.1−2.3 (m, 3H), 3.80 (s, 3H), 7.6−7.8 (br s, 1H). Hydrazone **11d** (2.92 g, 1.23 mmol, weight adjusted for carbomethoxyhydrazone of cyclohexanone) dissolved in 20 mL of methanol under N_2 was added from a dropping funnel during 30 min to an ice-cold solution of lead tetraacetate (LTA, 5.55 g, 12.5 mmol) in 25 mL of methanol. The solution was kept at ca. −10 °C for 5 days with occasional stirring before the solvent was removed by rotary evaporation and methylene chloride (50 mL) was added to the residue. The solution was filtered to remove inorganic salts, and it was washed with 5% sodium bicarbonate (4 × 25 mL) before the organic layer was dried over magnesium sulfate. Removal of the solvent left oxadiazoline **12d** which was purified from minor amounts of oxadiazoline **12a** by repeated radial chromatography on silica, eluting with 5−20% ethyl acetate in hexane. Yield of **12d**, 12%, a 2:1 mixture of diastereomers; clear liquid: ^1H NMR (500 MHz, $CDCl_3$, integrations normalized for minor (mi.) and major (ma.) isomers) δ 1.42−2.03 (m), 2.05−2.15 (m), 2.25−2.40 (m), 3.45 (s, ma., 3H), 3.52 (s, mi., 3H), 3.54 (s, mi., 3H), 3.55 (s, ma., 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.8, 22.9, 23.3, 23.4, 24.1, 24.8, 33.7, 36.1, 46.0 (q, $J = 26.3$ Hz), 48.2 (q, $J = 26.0$ Hz), 51.9, 52.0, 52.1, 118.1, 118.6, 120.3 (q, $J = 299$ Hz), 125.4 (q, 280 Hz), 136.2, 137.4; ^{19}F NMR (470 MHz, $CDCl_3$ referenced to $CFCl_3$) δ −64.9 (ma., d, $J = 7.5$ Hz), −66.3 (mi., d, $J = 7.5$ Hz); UV $\lambda_{max} = 328$ nm ($\epsilon = 300$); MS (EI) m/z (molecular ion not obsd), 237 $[M - OMe]^+$, 219, 169, 150, 131, 119, 100, 69 (100%). Anal. Calcd for $C_{10}H_{15}F_3N_2O_3$: C 44.78, H 5.64, N 10.44. Found: C 44.67, H 5.53, N 10.05.

Carbomethoxyhydrazone of tropinone (11e): yield 91%; ^1H NMR (200 MHz, $CDCl_3$) δ 1.4−1.6 (m, 2H), 1.9−2.1 (m, 4H), 2.40 (s, 3H), 2.62 (dd, $J = 4.4, -14$ Hz, 4H), 3.3−3.5 (m, 2H), 3.80 (s, 3H), 7.5−7.7 (br s, 1H).

(1α,3β,5α)-5′,5′-Dimethoxy-8-methylspiro[8-azabicyclo-[3.2.1]octane]-3,2′-[Δ^3-1,3,4-oxadiazoline] (12e): yield 32%, one diastereomer, presumably because of participation of the amino group during oxidative cyclization, clear liquid; ^1H NMR (500 MHz, $CDCl_3$) δ 1.23 (d, $J = 13.8$ Hz, 1H), 1.35 (d, $J = 13.9$ Hz, 1H), 1.76−1.91 (m, 4H), 2.08 (s, 3H), 2.09 (s, 3H), 2.10−2.17 (m, 1H), 2.65 (dd, $J = 13.9, 3.5$ Hz, 1H), 2.82−2.89 (m, 2H) 3.24 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.5, 25.8, 26.9, 37.7, 38.8, 39.3, 39.7, 51.3, 51.5, 59.4, 59.9, 118.8, 138.9; UV $\lambda_{max} = 328$ nm ($\epsilon = 400$); MS (EI) m/z (molecular ion not obsd), 210 $[M - OMe]^+$, 198, 162, 155, 138, 108, 95, 82 (100%); MS (CI, NH_3) m/z 259 $[M + NH_4]^+$, 242 $[M + H]^+$. Anal. Calcd for $C_{11}H_{19}N_3O_3$: C 54.76, H 7.94, N 17.41. Found: C 54.38, H 8.23, N 17.20.

Carbomethoxyhydrazone of 3-pentanone (11f):[38] yield 82%; ^1H NMR (200 MHz, $CDCl_3$) δ 1.06 (t, $J = 7.5$ Hz, 6H), 2.32 (q, $J = 7.5$ Hz, 4H), 3.80 (s, 3H), 7.5−7.7 (br s, 1 H).

5,5-Diethyl-2,2-dimethoxy-Δ^3-1,3,4-oxadiazoline (12f): yield 66%; clear oil; ^1H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, $J = 7.5$ Hz, 6H), 1.86 (q, $J = 7.5$ Hz, 4H), 3.53 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.3, 28.3, 51.6, 124.9, 136.6; UV $\lambda_{max} = 328$ nm ($\epsilon = 500$); MS (EI) m/z (molecular ion not obsd), 157 $[M - OMe]^+$, 129, 91, 75, 59 (100%), 43; MS (CI, NH_3) m/z 206 $[M + NH_4]^+$, 189 $[M + H]^+$. Anal. Calcd for $C_8H_{16}N_2O_3$: C 51.05, H 8.57, N 14.88. Found: C 50.96, H 8.27, N 14.80.

Acetylhydrazone of 3-pentanone (11g):[20b] yield 93%; ^1H NMR (200 MHz, $CDCl_3$) δ 1.02 (t, $J = 7.5$ Hz, 6H), 1.95 (q, 4H), 2.14 (s, 3H) 8.2−8.4 (br s, 1H).

5,5-Diethyl-2-methoxy-2-methyl-Δ^3-1,3,4-oxadiazoline (12g): yield 68%; clear oil; ^1H NMR (500 MHz, $CDCl_3$) δ 0.86 (t, $J = 7.5$ Hz, 6H), 0.95 (t, $J = 7.5$ Hz, 6H), 1.59 (s, 3H), 1.65−2.05 (m, 4H), 3.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 8.1, 14.4, 22.1, 29.4, 29.6, 50.3, 122.8, 133.1; UV $\lambda_{max} = 328$ nm ($\epsilon = 500$); MS (EI) m/z (molecular ion not obsd), 141 $[M - OMe]^+$, 113, 91, 75, 59 (100%), 43; MS (CI, NH_3) m/z 190 $[M + NH_4]^+$,173 $[M + H]^+$.

Carbomethoxyhydrazone of 2-butanone (12h): yield 88%; ^1H NMR (200 MHz, $CDCl_3$) δ 1.08 (t, $J = 7.5$ Hz, 3H), 1.78 (s, 3H), 2.31 (q, $J = 7.5$ Hz, 2H), 3.80 (s, 3H), 7.5−7.7 (br s, 1H).

5-Ethyl-2,2-dimethoxy-5-methyl-Δ^3-1,3,4-oxadiazoline (12h): yield 70%; clear oil; ^1H NMR (500 MHz, $CDCl_3$) δ 0.81 (dd, $J = 7.6$ Hz, 3H), 1.36 (s, 3H), 1.69 (ABX_3, $J = 7.6, -14.3$ Hz, 1H), 1.79 (ABX_3, $J = 7.6, -14.3$ Hz, 1H), 3.44 (s, 3H), 3.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.4, 21.4, 30.3, 51.4, 51.6, 121.8, 136.7; IR (neat, KBr) 2982, 2949, 2887, 2847, 1577, 1459, 1448, 1376, 1137, 1078, 930, 862 cm^{-1}; UV $\lambda_{max} = 328$ nm ($\epsilon = 500$); MS (EI) m/z (molecular ion not obsd), 143 $[M - OMe]^+$, 91, 74, 59 (100%); MS (CI, NH_3) m/z 192 $[M + NH_4]^+$, 175 $[M + H]^+$. Anal. Calcd for $C_7H_{14}N_2O_3$: C 48.26, H 8.10, N 16.08. Found: C 48.20, H 8.14, N 15.79.

Laser Flash Photolysis. The nanosecond laser flash photolysis system at NRC has been described.[39] A Lumonics EX-530 excimer laser (XeCl, 308 nm, 6 ns pulses, ≥40 mJ/pulse) was used for photolyses of oxadiazoline precursors. Sample solutions with absorbances (A) of 0.3−0.6 at the excitation wavelength (308 nm) were prepared as described below. These solutions were irradiated in 7 × 7 mm quartz cells. The nanosecond laser flash photolysis system at Ohio State has been described.[40] An excimer laser (Lambda Physic LPX-100) was used for photolysis of an oxadiazoline precursor. Stock solutions of oxadiazolines **12a−h** were prepared in freshly distilled benzene or cyclohexane containing various concentrations of pyridine (typically between 0.1 and 5.0 M) so that the values of A_{308} were approximately 0.4−0.6. Typical concentrations of oxadiazolines required to accomplish this were $\sim(2-3) \times 10^{-3}$ M. For each oxadiazoline, solutions without pyridine were degassed with N_2, and the time-resolved UV−vis spectra for each were acquired (300−700 nm) after 308 nm LFP to ensure that signals assigned to pyridinium ylides did not arise from intermediates other than pyridinium ylides. Stern−Volmer kinetics were obtained from values of A_{360} of solutions of oxadiazolines **12a−h** containing various amounts of pyridine, after 308 nm LFP.

For each pyridine quenching experiment, UV−visible spectra were taken of each solution prior to LFP, to ensure that the absorbances of the solutions at the excitation wavelength remained constant. Residual absorption of impurities in pyridine at the excitation wavelength can lead to errors in Stern−Volmer quenching, and the stock solutions of pyridine and LFP solutions were carefully monitored to eliminate this possibility.

Steady State Photolysis. Steady state photolyses were carried out in a Rayonet photochemical reactor equipped with a “merry-go-round” apparatus. Photolytic conversions of oxadiazolines to diazo compounds were performed by irradiating 0.001 M solutions of oxadiazolines **12a−h** in deoxygenated (N_2 or argon) benzene-d_6 in Pyrex reaction vessels (NMR tubes in some cases) with 10−14 300 nm lamps. Irradiation for 15−45 min was sufficient to convert each oxadiazoline completely to its corresponding diazoalkane. Diazoalkanes **13a−h** were stable for several hours at room temperature in dilute solution, but thermal azine formation occurred at room temperature over a period of 4−5 days, after which the solutions were analyzed by ^1H NMR and GC-MS. Conversions of oxadiazolines **12a−h** to cyclohexylidene (**14a**), substituted cyclohexylidenes

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14b,**d**,**e**, and dialkylcarbenes **14f**,**h** were done by irradiating 0.01 M solutions of oxadiazolines **12a**−**h** in deoxygenated (N_2 or argon) cyclohexane-d_{12} in quartz reaction vessels (NMR tubes in some cases) with 8−12 254 nm lamps and 1−2 300 nm lamps. Dual wavelength irradiation was required to convert each oxadiazoline to the corresponding carbene efficiently, and typical reaction times for complete conversion of the starting materials were 2−4 h. The reaction times were shortest when 12 254 nm lamps were used in conjunction with 2 300 nm lamps. Short reaction times were preferable to minimize azine formation. Dual wavelength irradiations of solutions of oxadiazolines in hexadecane allowed for GC and GC-MS analyses of reaction mixtures. Compounds **12a**,**c**−**e**,**g**,**h** afforded dimethyl carbonate as a coproduct, whereas compounds **12b**,**f** afforded methyl acetate as a coproduct. The steady state photolysis results have been deposited as Supporting Information.

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Supporting Information Available: Experimental data pertaining to steady state photolyses, infrared and COSY spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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