1,2-Hydrogen Migration and Alkene Formation in the Photoexcited States of Alkylphenyldiazomethanes

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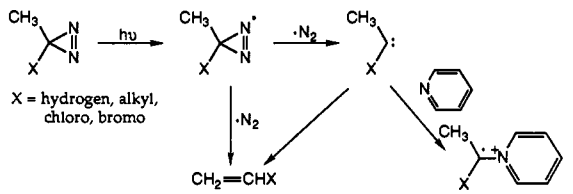
Abstract: Laser flash photolysis of alkylphenyldiazomethanes in the presence of pyridine produces easily detected ylides. The data indicate that photolysis of alkylphenyldiazomethanes leads to both carbene formation and direct formation of rearrangement products which do not derive from relaxed carbene intermediates.

Introduction

The 1,2-hydrogen migration reaction is a general reaction of alkylcarbenes.[1] These reactions are believed to be very rapid because it is usually difficult to intercept alkylcarbenes with external trapping agents. However, carbene chemists have long worried whether the alkenes formed on photolysis of diazo compounds derive entirely from carbene intermediates or in part from the photoexcited states of the nitrogenous precursors of carbenes or carbene excited states.[2] It is well-appreciated that the photochemical Wolff rearrangement of certain diazo ketones can bypass carbene intermediates in the formation of ketenes.[3]

We have recently demonstrated that pyridine reacts with carbenes at near diffusion-controlled rates to form long-lived ylides which are easily detected by laser flash photolysis (LFP) techniques[4] but that pyridine does not react with the excited states of nitrogenous carbene precursors.[5] This allowed us to demonstrate that photolysis of acyclic dialkyldiazirines[6] and alkylchloro[7] and alkylbromodiazirines[8] leads to nitrogen extrusion with carbene formation and, in parallel, to the formation of rearrangement products. There is a "nontrappable carbene" path to stable 1,2-hydrogen rearrangement products which bypasses relaxed carbene intermediates (Scheme I).

Scheme I



In the case of dimethyldiazirine,[6] we could demonstrate with isotope effects that the "nontrappable carbene" intermediate is the diazirine excited state. Identical isotope effects (dimethyldiazirine-d_0 vs -d_6) were observed for the diazirine fluorescence intensities and carbene yields. As alkylchloro- and alkylbromodiazirines fluoresce very weakly or not at all, we could not use this argument to establish the excited state of the precursor as the nonrelaxed carbene intermediate responsible for product formation. We could not rule out a short-lived, "nontrappable" excited state of the alkylchloro- or alkylbromocarbene as a second route to 1,2-hydrogen rearrangement products. However, as photolysis of alkylchloro- and alkylbromodiazirines *necessarily* produces an electronically excited state, and given the precedent of dimethyldiazirine, we postulated that it is the excited state of the alkylhalodiazirines that is the key, second product-forming intermediate. Similar conclusions have been reached by Moss and Ho[9] who also discovered 1,2-carbon migration in the excited state of cyclobutylchlorodiazirine. These issues are not restricted to photolysis of carbene precursors, however, as Jones and coworkers[10a] have discovered that there are mechanistic paths to rearrangement products that bypass relaxed carbene intermediates and are followed upon *pyrolysis* of aryldiazo compounds.

The low, isolated yields of intermolecular reaction products of alkylcarbenes either realized or anticipated with dialkyldiazirine precursors are due to inefficient formation of carbenes from these precursors rather than to prohibitively rapid intramolecular rearrangements. Alkylchlorocarbenes can be intercepted with alkene traps[11] despite the fact that alkylchlorodiazirine excited states suffer hydrogen migration in concert with nitrogen extrusion.

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‡ The Ohio State University.

(1) (a) Baron, W. J.; DeCamp, M. R.; Hendrick, M. L.; Jones, M., Jr.; Levin, R. H.; Sohn, M. B. *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1973; Vol. 1, p 1. (b) Nickon, A.; Huang, F.-Chich; Weglein, R.; Matsuo, K.; Yagi, H. *J. Am. Chem. Soc.* **1974**, *96*, 5264. (c) Kyba, E. P.; Hudson, C. W. *J. Org. Chem.* **1977**, *42*, 1935. (d) Kyba, E. P.; Hudson, C. W. *J. Am. Chem. Soc.* **1976**, *98*, 5696. Kyba, E. P.; John, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 8329. (e) Press, L. S.; Schechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 509. (f) Seghers, L.; Shechter, H. *Tetrahedron Lett.* **1976**, *23*, 1943. (g) Freeman, P. K.; Hardy, T. A.; Baleat, J. R.; Wescott, L. D., Jr. *J. Org. Chem.* **1977**, *42*, 3356. (h) Nickon, A. *Acc. Chem. Res.* **1993**, *26*, 84.

(2) For example, see: Chang, K. T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 5082 and references therein.

(3) (a) For reviews, see: ref 1a, p 117. Moss, R. A.; Jones, M. B., Jr. *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1985; Vol. 3, p 95–98. (b) Kaplan, F.; Meloy, G. R. *J. Am. Chem. Soc.* **1968**, *88*, 950. (c) Roth, H. D. *Acc. Chem. Res.* **1977**, *10*, 85.

(4) (a) Jackson, J. E.; Platz, M. S. *Advances in Chemical Applications of Lasers*; Brinker, U., Ed.; JAI Press: Greenwich, CT; in press. (b) Jackson, J. E.; Soundararajan, N.; Platz, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 5595. (c) Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Doyle, M. P.; Liu, M. T. H. *Tetrahedron Lett.* **1989**, *30*, 1335. (d) Jackson, J. E.; Soundararajan, N.; White, W.; Liu, M. T. H.; Bonneau, R.; Platz, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 6874. (e) Chateauneuf, J. E.; Johnson, R. P.; Kirchoff, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 3217. (f) Zugravescu, I.; Petrovanu, M. *N-Ylide Chemistry*; McGraw Hill: New York, 1976.

(5) (a) Morgan, S.; Jackson, J. E.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 2782. (b) LaVilla, J. A.; Goodman, J. *Tetrahedron Lett.* **1990**, *31*, 5109. (c) White, W.; Platz, M. S.; Chen, N.; Jones, M., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 7794. (d) Chen, N.; Jones, M., Jr.; White, W. R.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 4981. (e) Eaton, P. E.; Hoffman, K.-L. *J. Am. Chem. Soc.* **1987**, *109*, 5285. (f) Chen, N.; Jones, M., Jr. *J. Phys. Org. Chem.* **1988**, *1*, 305. (g) Chen, N.; Jones, M., Jr. *Tetrahedron Lett.* **1989**, 6969.

(6) Modarelli, D. A.; Morgan, S. C.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *116*, 7034.

(7) White, W. R.; Platz, M. S. *J. Org. Chem.* **1992**, *57*, 2841.

(8) Chidester, W.; Modarelli, D. A.; White, W. R.; Whitt, D.; Platz, M. S. *J. Phys. Chem.* **1993**, submitted for publication.

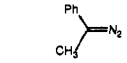
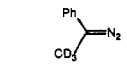
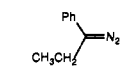
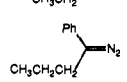
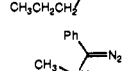
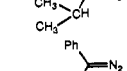
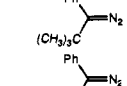
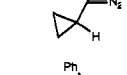
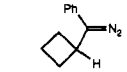
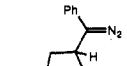
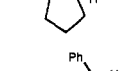
(9) Moss, R. A.; Ho, G.-J. *J. Phys. Org. Chem.* **1993**, *6*, 126.

(10) (a) Fox, J. M.; Scacheri, J. E. G.; Jones, K. G. L.; Jones, M., Jr.; Shevlin, P. B.; Armstrong, N.; Sztyrbicka, R. *Tetrahedron Lett.* **1992**, *33*, 5021. (b) Fox and Jones have found that some *trans*-cyclopropane product is formed on photolysis of isopropylphenyldiazomethane.

(11) Moss, R. A.; Munjah, R. C. *J. Chem. Soc., Chem. Commun.* **1978**, *775*.

0002-7863/93/1515-8613$04.00/0

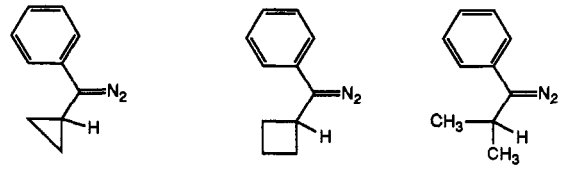
Table I. Pyridine Ylide Formation from Alkyl Aryl Diazo Compounds

precursor no.	precursor structure	A_{ylide}^{Sat}	ylide	abs λ_{max} (nm)	rel intensity (carbene, % yield)
5a		0.280	**5c**	450	72
6a		0.300	**6c**	450	77
7a		0.0568	**7c**	450	14
8a		0.043	**8c**	450	11
9a		0.028	**9c**	450	7
10a		0.373	**10c**	360	96
11a		0.389	**11c**	450	100
12a		0.023	**12c**	450	6
13a		0.108	**13c**	420	28
14a		0.096	**14c**	430	25
15a		0.344	**15c**	460	88

Herein, we are pleased to report our studies of a series of 11 alkyl aryl diazo compounds (Table I). The data demonstrate that the excited states of these precursors suffer hydrogen migration and direct alkene formation in a manner reminiscent of diazirine photochemistry.

Results

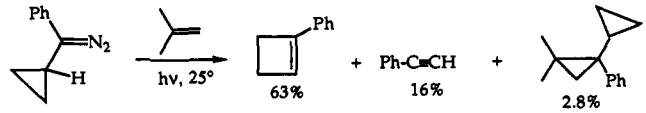
1. Chemical Analysis of Reaction Mixtures. The stable products formed on photolysis of three alkylphenyldiazomethanes in acetonitrile and methanol were identified. All three compounds



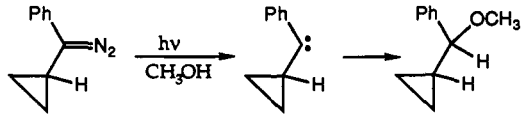
possess a secondary carbon atom adjacent to the diazo group, but they differ with respect to the strength of the adjacent, secondary C–H bond. They also differ in the ability of the alkyl group to interact electronically with the diazo group and carbene center.

Photolysis of cyclopropylphenyldiazomethane in isobutylene has been investigated by Moss and Wetter.[12] The yield of cyclopropane adduct is low at 25 °C but increases to 42% upon lowering the temperature of photolysis to −128 °C. We find that photolysis of this compound in acetonitrile produces phenylcyclobutene and phenylacetylene as the only volatile products, in agreement with the earlier study of Moss.[12] Phenylcyclobutene and phenylacetylene are formed in a 2.3:1 ratio in acetonitrile at ambient temperature. However, we find that photolysis of

(12) Moss, R. A.; Wetter, W. P. *Tetrahedron Let.* **1981**, *22*, 997.

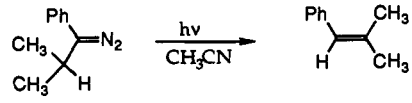


cyclopropylphenyldiazomethane in methanol gives the ethereal product of OH insertion in quantitative yield. One interpretation

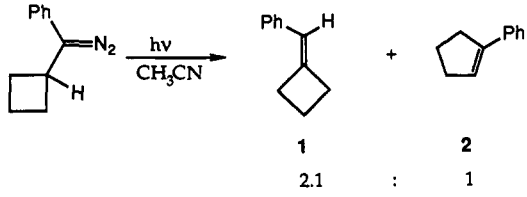


of this data is that cyclopropylphenyldiazomethane cleanly decomposes upon photolysis to form cyclopropylphenylcarbene which is sufficiently long-lived to be completely captured by methanol and give the observed ethereal product (as per Scheme II for methylphenylcarbene).

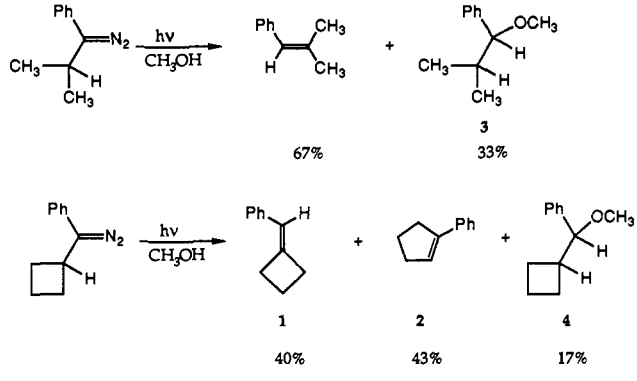
Photolysis of isopropylphenyldiazomethane in acetonitrile gives largely β,β-dimethylstyrene,[10b] and photolysis of the cyclobutyl



analog in the same solvent produces isomeric alkenes **1** and **2** as the only volatile products. Alkenes **1** and **2** are formed in a ratio of 2.1:1 in acetonitrile.



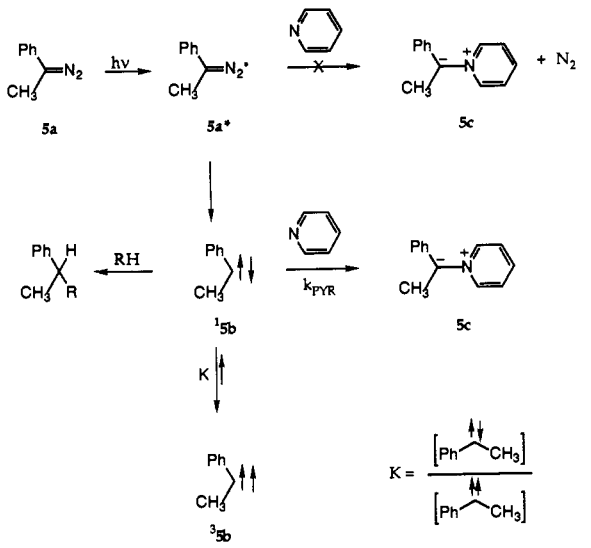
Unlike that of the cyclopropyl compound, however, photolysis of isopropylphenyldiazomethane and cyclobutylphenyldiazomethane in methanol produces the corresponding ether as only a minor product. Olefinic products β,β-dimethylstyrene and **1** and **2** still predominate in methanol upon photolysis of isopropylphenyldiazomethane and cyclobutylphenyldiazomethane, respectively.



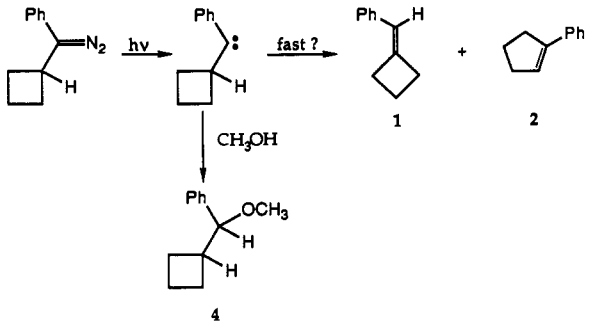
A preliminary interpretation of the data to this point, within the constraints of Scheme II (RH = CH_3OH), is that isopropylphenylcarbene and cyclobutylphenylcarbene rearrange much faster than does cyclopropylphenylcarbene and, thus, are less efficiently trapped by methanol.

Laser flash photolysis experiments to be presented demonstrate that this explanation is not correct. Cyclopropyl- and cyclobutylphenylcarbene have nearly identical lifetimes in pentane solution at ambient temperature and comparable absolute reactivity to methanol. We have not been able to study the lifetime and reactivity of isopropylphenylcarbene (*vide infra*).

Scheme II

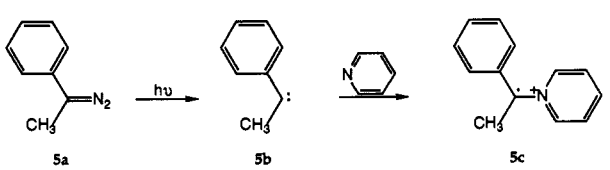


Flaws in the preliminary interpretation are also obvious in the cyclobutylphenylcarbene data. The ratio of methylenecyclo-



butane **1** to cyclopentene **2** is significantly different in acetonitrile (2.1:1) and in methanol (~1:1). Barring an enormous solvent effect on the partitioning of cyclobutylphenylcarbene, the data require that there are two pathways to the olefinic product and that the two pathways respond differently to the presence of a carbene trap. We will conclude that hydrogen migration and alkene formation proceed in concert in the excited state of isopropylphenyldiazomethane as per dialkyl- and alkylchlorodiazirines.[6,7] We will agree with Jones and Chen,[5g] Eaton and Hoffmann,[5e] and Moss and Ho[9] that carbon migrations proceed in the excited states of cyclobutylcarbene precursors.

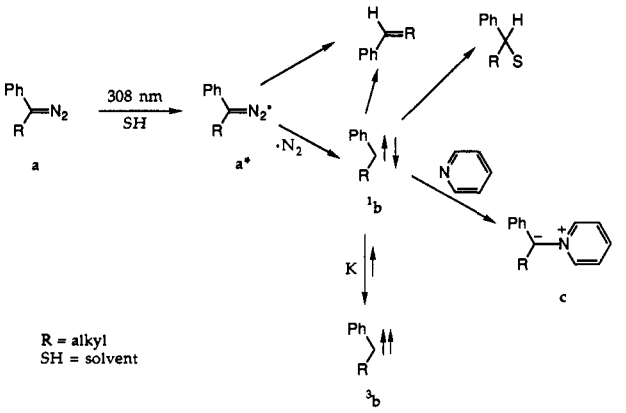
2. Laser Flash Photolysis Studies. We have previously reported that laser flash photolysis (LFP) of methylphenyldiazomethane (**5a**, Table I) produces methylphenylcarbene (**5b**) which can be intercepted with pyridine to form ylide **5c**.[13] It is difficult to observe triplet arylcarbenes directly by optical methods because their absorption spectra severely overlap those of their diazo precursors. Thus, it is easier to monitor the ylide than the carbene itself.[4]



The lifetime of the growth of ylide **5c** (and of the decay of the *immediate* precursor of the ylide) is on the order of several hundred nanoseconds when [pyridine] ≈ 0.1–0.4 M. This lifetime is far too long for the nonfluorescent excited state of diazo compound

(13) Sugiyama, M.; Celebi, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 966.

Scheme III

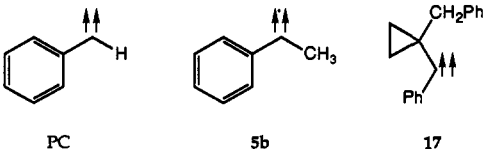


5a* to be reacting with pyridine and to function as the *immediate* ylide precursor. Thus we conclude, as before, that it is carbene **5b** which is trapped by pyridine and not the excited state of diazo compound **5a**.

Solvent isotope effects reveal that the lifetime of **5b** is controlled by reaction of the carbene with alkane solvent and not by 1,2-hydrogen migration to form styrene.[13] It was possible to accelerate the 1,2-hydrogen shift reaction rate by using a more polar solvent (e.g., acetonitrile).[13]

LFP (XeCl) excimer laser, 308 nm, 150 mJ, 18 ns) of diazo compounds **5a–15a** (A_{308} = 1) in deoxygenated pentane fails to produce any measurable transient absorption between 300–700 nm. However, LFP of **5a–15a** in pentane containing pyridine produces intense transient absorptions (Table I) attributed to ylides **5c–15c**.[4,14]

The Role of Spin Multiplicity. Phenylcarbene (PC), methylphenylcarbene (**5b**), and 1-(benzylcyclopropyl)phenylcarbene (**17**) have triplet ground states.[15] We suspect that this is true as



well for carbenes **6b–14b**. Benzocyclohexenylidene **15b** will have a smaller bond angle than phenylcarbene and thus theory[16] suggests that it may have a singlet ground state.

All of the available chemical and kinetic evidence is consistent with a small singlet–triplet energy gap in phenylcarbene[17] and methylphenylcarbene,[13,18] and this equilibrium is established rapidly in alkane solvents. Thus, the low-lying singlet states of **5b–15b** are accessible at equilibrium and react with pyridine to form the ylides detected in this work (Scheme III).

According to Scheme III, the observed rate constant of formation of ylide **5c** following the laser pulse is given in eq 1

(14) The transient spectra of the ylides of Table I are virtually identical to the spectrum of the ylide formed between phenylcarbene and pyridine. A. Admasu and M. S. Platz, unpublished research at The Ohio State University.

(15) (a) McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1987**, *109*, 683. (b) Chapman, O. L.; Johnson, J. W.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.* **1988**, *110*, 50. (c) Barcus, R. L.; Palik, E. C.; Platz, M. S. *Tetrahedron Lett.* **1982**, *23*, 1323.

(16) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485.

(17) (a) Gutsche, C. D.; Bachman, G. L.; Coffee, R. S. *Tetrahedron* **1962**, *18*, 617. (b) Closs, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042. (c) Dietrich, H.; Griffin, G. W.; Petterson, R. C. *Tetrahedron Lett.* **1968**, 153. (d) Closs, G. L. *Top. Stereochem.* **1968**, *3*, 193. (e) Baer, T. A.; Gutsche, C. D. *J. Am. Chem. Soc.* **1971**, *93*, 5180. (f) Moss, R. A.; Dolling, U.-H. *J. Am. Chem. Soc.* **1971**, *93*, 954.

(18) (a) Closs, G. L.; Coyle, J. J. *J. Org. Chem.* **1966**, *31*, 2759. (b) Moritani, I.; Yamamoto, Y.; Murahashi, S.-I. *Tetrahedron Lett.* **1968**, *54*, 5697. (c) Abelt, C. J.; Pleier, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 1796. (d) Overberger, C. G.; Anselme, J.-P. *J. Org. Chem.* **1964**, *29*, 1188. (e) Moss, R. A.; Joyce, M. A. *J. Am. Chem. Soc.* **1977**, *99*, 7399. (f) Yamamoto, Y.; Murahashi, S.-I.; Moritani, I. *Tetrahedron* **1975**, *31*, 2663.

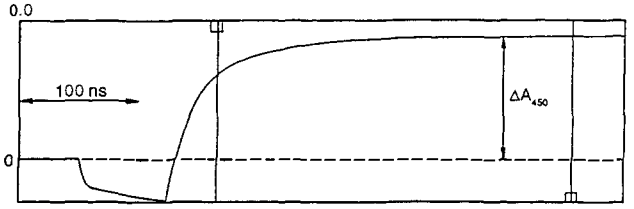


Figure 1. Absolute rate of formation of ylide **4c** following LFP of 1-phenyldiazobutane (**8a**) in *n*-pentane at 25 °C, monitored at 450 nm. The initial negative readings are due to the fluorescence of styrene-type impurities and scattered light.

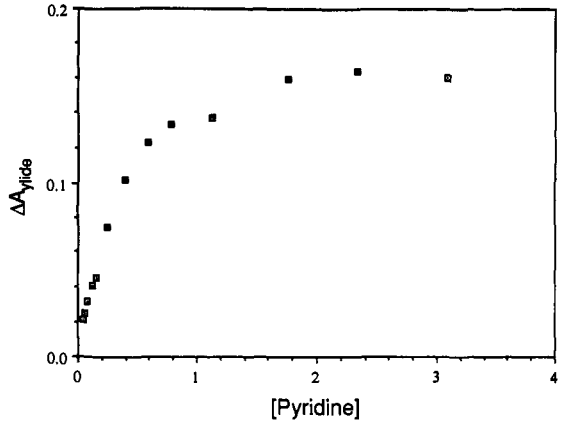
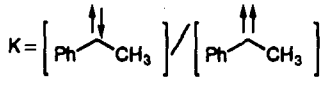


Figure 2. Yield of ylide **11c** (ΔA_{ylide}), as defined in Figure 1, following LFP of cyclopropylphenyldiazomethane (**11a**) in pentane as a function of pyridine concentration.

$$k_{obs} = k_T + k_{PYR}K[PYR] \quad (1)$$

where K is the singlet–triplet equilibrium constant



and k_T is the total of all first-order and pseudo-first-order processes which consume the singlet and triplet carbene in the absence of pyridine. These processes include intramolecular rearrangement and bimolecular reactions with solvent, impurities, and precursor. For methylphenylcarbene (**5b**) in heptane, we found[13] that $k_T = 1.2 \times 10^6$ s^{-1} and that $k_{PYR}K = 2 \times 10^7$ M^{-1} s^{-1}. We deduced[13] that $K = 0.02$ in heptane and 0.03 in acetonitrile by assuming that $k_{PYR} = 1 \times 10^9$ M^{-1} s^{-1}, as is common for other singlet carbenes.[4-6]

It was difficult to resolve the growth of ylides **6c–15c** because of small signals with some precursors and severe fluorescence from trace amounts of styrene impurities (Figure 1). However, it was possible to measure the optical yield of ylide by measuring the change in absorbance (ΔA_{ylide}) following the laser pulse as a function of [pyridine]. Of course, $\Delta A_{ylide} = 0$ when [pyridine] = 0. ΔA_{ylide} increases steadily until typically [pyridine] $\approx$ 1 M. A_{ylide} is invariant (ΔA^{Sat}_{ylide}) when [pyridine] > 1.5 M (Figure 2). Thus, all of the alkylphenylcarbene produced in a laser pulse must be completely converted into ylide when [pyridine] > 1.5 M.

Inspection of Table I reveals wide variation in the magnitude of ΔA^{Sat}_{ylide} as a function of diazo precursor. The C–H bond dissociation energies of C–H bonds adjacent to a diazo group are not known. Thus, for the sake of discussion, we will assume that a diazo group and a methyl group have similar effects on adjacent C–H bond dissociation energies. We find that *the optical yield of pyridine ylide increases with increasing bond dissociation energy of the C–H bond adjacent to the diazo group* (Figure 3).[19]

(19) Griller, D.; Kanabus-Kaminska, J. M. *Handbook of Photochemistry Vol. II*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; p 259.

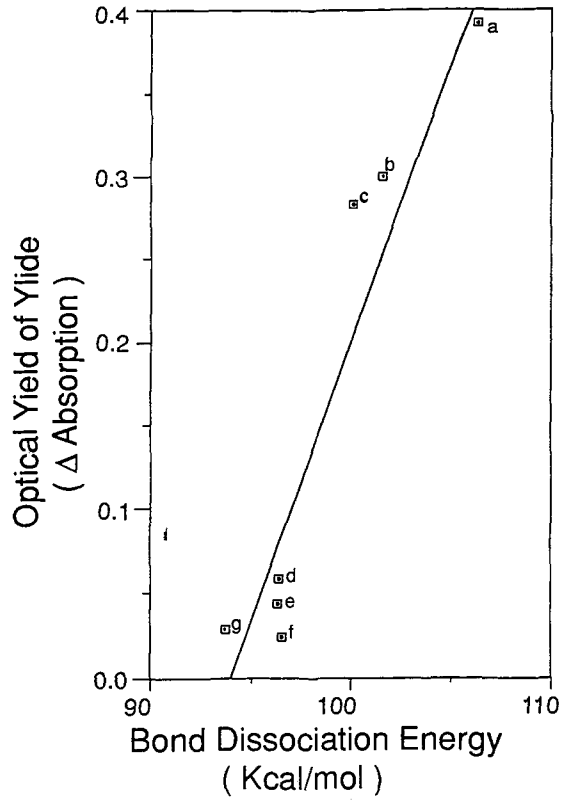


Figure 3. Yield of ylides (ΔA^{Sat}_{ylide}), as defined in Figure 1, as a function of α-C–H bond dissociation energy using BDE data for the corresponding hydrocarbon (e.g., assuming that a diazo group and a methyl group have the same effect on the strength of adjacent C–H bonds): (a) cyclopropyl ylide **11c**, (b) trideuteriomethyl ylide **6c**, (c) methyl ylide **5c**, (d) ethyl ylide **7c**, (e) *n*-propyl ylide **8c**, (f) cyclobutyl ylide **12c**, and (g) isopropyl ylide **9c**.

The difference in ΔA^{Sat}_{ylide} between carbene **11b** with its unusually strong cyclopropyl C–H bond dissociation energy (106.3 kcal/mol) and **12b** with a much smaller cyclobutyl C–H bond dissociation energy (96.5 kcal/mol)[20] is particularly striking. A very large optical yield of ylide is also obtained with *tert*-butylphenylcarbene (**10b**), a system in which there is no C–H bond adjacent to the diazo moiety. However, the absorption maximum of this ylide is severely displaced from that of the other ylides that are detected, perhaps as a consequence of a wide bond angle at the ylide carbon due to the steric bulk of the *tert*-butyl group.

We see no compelling reason to believe that there is a large variation in the extinction coefficients of ylides **5c–9c** and **11c–15c** with the nature of the alkyl group; thus, it appears that *the optical yield of ylide tracks the chemical yield of ylide and ultimately that of the alkylarylcarbene that is produced photochemically* (Scheme III). The only exception to this rule is *tert*-butylphenylcarbene (**10b**) which, as stated previously, has an unusual pyridine ylide absorption maximum.

We suspect that the presence of a relatively weak C–H bond adjacent to the diazo group lowers the yield of carbene by increasing the importance of hydrogen migration and alkene formation in the excited state of the diazo precursor (Scheme III). However, our data are also permissive of formation and rearrangement of carbene excited states.

The data indicate that hydrogen migrates much more rapidly than does alkyl carbon in the excited states of acyclic alkyl aryl diazo compounds or carbene excited states. If we assume there

(20) (a) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465. (b) Benson, S. W. *J. Chem. Ed.* **1965**, *42*, 502. (c) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 492. (d) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. S.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

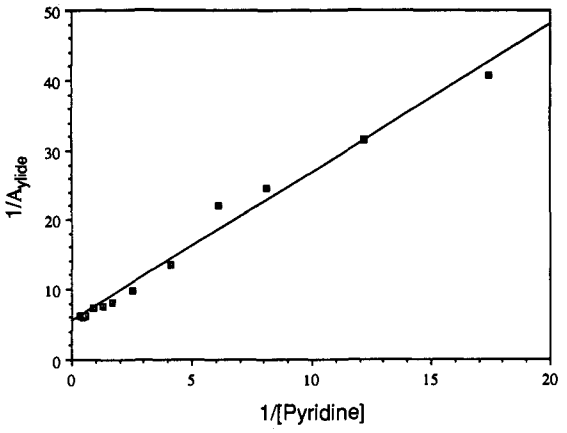


Figure 4. Plot of the inverse yield ($1/A_{ylide}$) of cyclopropylphenylpyridine ylide **11c** vs 1/[PYR].

is no rearrangement in the excited state of cyclopropyl phenyl diazo compound **11a*** (or in **11b***), then the percentage yield of carbene produced from a given alkyl aryl diazo compound can be quantified (Table I). The data demonstrate that *relaxed carbene formation is only a minor process in the photochemistry of certain alkyl phenyl diazo compounds.* The facility of the 1,2-hydrogen shift reaction in diazo or carbene excited states and the consequent inability to intercept alkylcarbenes with olefinic traps may have led to an overestimation of the rates of the 1,2-hydrogen shift reactions in alkylcarbenes. In fact, the rates of isomerization of singlet alkylarylcarbenes[13] may resemble those of alkylhalocarbenes.[21]

3. Carbene Lifetimes. Styrene-type impurities fluoresce strongly and prevent accurate measurement of the rates of formation of ylides **6b–15b**. However, it is possible to deduce approximate carbene lifetimes again by considering the optical yield of ylide (A_{ylide}) as a function of pyridine concentration.

The quantum yield of ylide formation ϕ_{ylide} is given in eq 2

$$\phi_{ylide} = \phi_c\left(\frac{k_{PYR}[PYR]}{k_{PYR}[PYR] + k_T}\right) \quad (2)$$

where ϕ_c is the quantum yield of carbene formation and k_{PYR} and k_T are as defined earlier. The measurable quantity A_{ylide} is related to ϕ_{ylide} by eq 3

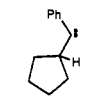
$$A_{ylide} = \phi_{ylide}A^{Sat}_{ylide} \quad (3)$$

Equations 1 and 2 can be combined and rearranged to (4)

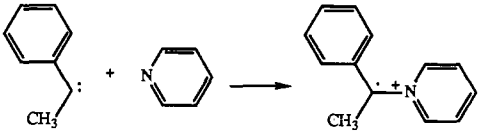
$$\frac{1}{A_{ylide}} = \frac{1}{\phi_c A^{Sat}_{ylide}} + \left(\frac{k_T}{k_{PYR}K}\right)\left(\frac{1}{\phi_c A^{Sat}_{ylide}}\right)\left(\frac{1}{[PYR]}\right) \quad (4)$$

Thus, a plot of $1/A_{ylide}$ vs 1/[PYR] should be linear (Figure 4), and division of the slope by the intercept yields ($k_T/k_{PYR}K$). Assuming that the value of $k_{PYR}K$ of 2×10^7 M^{-1} s^{-1} of methylphenylcarbene is valid for carbenes **6b–15b** yields the values of k_T and the lifetimes ($\tau = 1/k_T$) of the carbenes listed in Table II.

Table II. Lifetimes of Alkylarylcarbenes in Pentane at 25 °C Determined by the Double-Reciprocal Method[a]

carbene no.	carbene structure	$k_T/k_{PYR}K$	τ (ns)
5b		*d*	595–833[e]
6b		*d*	535–885[e]
7b		0.421	119
8b		0.437	114
9b		*b*	*b*
10b		0.111	*c*
11b		0.392	128
12b		0.374	134
13b		0.207	241
14b		0.156	320
15b		0.110	454

[a] Assuming $k_{PYR}K = 2 \times 10^7$ M^{-1} s^{-1}. [b] Ylide signal too weak for an accurate determination of the carbene lifetime. [c] Assuming $k_{PYR}K = 2 \times 10^7$ M^{-1} s^{-1} is unrealistic due to steric retardation and decreasing K due to opening of the angle at the carbene center. [d] Not determined, see reference 12. [e] Reference 12; note, τ varies with solvent (heptane, α,α,α-trifluorotoluene, and benzene).



The assumption of a constant value of $k_{PYR}K$ is surely flawed for *tert*-butylphenylcarbene (**10b**). However, we expect that $k_{PYR}K$ is similar for cyclopropyl- and cyclobutylphenylcarbene which were also studied by chemical analysis of product mixtures. There is no reason to postulate that $k_{PYR}K$ is substantially smaller for cyclopropylphenylcarbene (**11b**) than for its cyclobutyl analogs **12b**. This unsupported assumption would require that singlet cyclopropylphenylcarbene is either *less* accessible at equilibrium (small K) or less reactive toward pyridine (small k_{PYR}) than singlet cyclobutylphenylcarbene. Recall that this explanation is needed to explain the quantitative capture of cyclopropylphenylcarbene (**11b**) with methanol and the apparent inefficient capture of isopropyl- and cyclobutylphenylcarbene with methanol in a manner consistent with the mechanism of Scheme II. In fact, if the cyclopropyl group stabilizes singlet carbene **11b** by overlap with a Walsh-type orbital, then K will *increase* in **11b** relative to **12b**. Furthermore, $k_{PYR}K$ and k_T will then increase and τ will shorten, which is *opposite* to the direction of the change in τ needed to explain the carbene trapping data in methanol. Thus, the data show that the lifetimes of these two carbenes are rather similar despite the great disparity in the yield of ylide obtained

(21) (a) Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1990**, *112*, 3915. (b) Liu, M. T. H.; Murray, S. K.; Zhu, J. *Chem. Commun.* **1990**, 1650. (c) Stevens, I. D. R.; Liu, M. T. H.; Soundararajan, N.; Paike, N. *Tetrahedron Lett.* **1989**, *30*, 48. (d) Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1989**, *111*, 6873. (e) Liu, M. T. H.; Subramanian, R. *J. Phys. Chem.* **1986**, *90*, 75 (benzylbromo). (f) Liu, M. T. H.; Bonneau, R.; Raypz, M. *J. Am. Chem. Soc.* **1989**, *111*, 5973. (g) Moss, R. A.; Ho, G.-J. *J. Am. Chem. Soc.* **1990**, *112*, 5642. (h) Moss, R. A.; Ho, G.-J.; Shen, S.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1990**, *112*, 1638 (cyclopropylchloro). (i) LaVilla, J. A.; Goodman, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 712. (j) Du, X.; Fan, H.; Goodman, J. L.; Kesselmayer, M. A.; Krogh-Jespersen, K.; LaVilla, J. A.; Moss, R. A.; Shen, S.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 1920. (k) Bonneau, R.; Liu, M. T. H.; Rayez, M. T. *J. Am. Chem. Soc.* **1989**, *111*, 5973. (l) Ho, G. J.; Krogh-Jespersen, K.; Moss, R. A.; Shen, S.; Sheridan, R. S.; Subramanian, R. *J. Am. Chem. Soc.* **1989**, *111*, 6875. (m) Liu, M. T. H.; Bonneau, R. *J. Phys. Chem.* **1989**, *93*, 7298. (n) Moss, R. A.; Ho, G.-J.; Shen, S.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1990**, *112*, 1638.

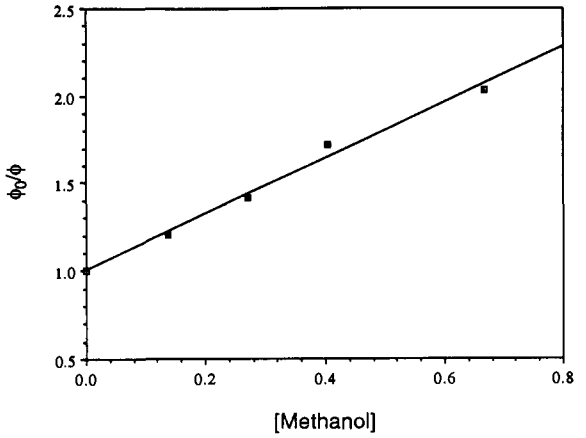
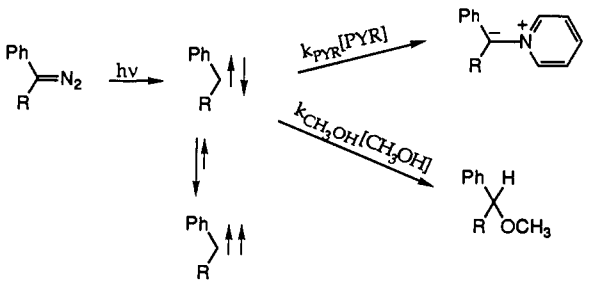


Figure 5. Plot of $A^{Sat}_{ylide}/A_{ylide}$ vs [methanol] at constant [PYR] (1.8 M).

by LFP of cyclopropylphenyldiazomethane (**11a**) and cyclobutylphenyldiazomethane (**12a**).

We believe that the excited state of isopropylphenyldiazomethane largely experiences 1,2-hydrogen migration. However, the excited state of cyclobutylphenyldiazomethane migrates both carbon and hydrogen with almost equal facility. Carbon migrations are more facile in the excited states of cyclobutylphenyldiazomethane than in those of cyclopropylphenyldiazomethane because of the greater release of strain in the ring enlargement of the former system. Rearrangement of methylcyclobutane to cyclopentene relieves more strain than rearrangement of methylcyclopropane to cyclobutene, which actually leads to a small increase in strain energy.[20]

4. Kinetics of Reaction of Carbenes with Methanol. LFP of isopropyl-, cyclobutyl-, and cyclopropylphenyldiazomethane in pentane in the presence of 1.8 M pyridine leads to capture of every alkylarylcarbene generated in the laser pulse. If methanol is present in solution, the ylide yield is reduced relative to A^{Sat}_{ylide} in alcohol-free pentane because of competitive capture of the carbene. (Note that the pyridine ylides are stable in methanol on the time scale of the LFP experiment).



The ratio of $(A^{Sat}_{ylide}/A_{ylide})$ is given by eq 5

$$\frac{A^{Sat}_{ylide}}{A_{ylide}} = \frac{k_{CH_3OH}[CH_3OH]}{k_{PYR}[PYR]} \quad (5)$$

where A_{ylide} is the yield of ylide at saturating pyridine concentration in the presence of methanol, (A^{Sat}_{ylide}) is the yield of ylide at constant saturating pyridine concentration in the absence of methanol, and k_{CH_3OH} is the absolute rate constant for the reaction of the singlet carbene with methanol. A plot of $(A^{Sat}_{ylide}/A_{ylide})$ vs methanol is predicted and found (Figure 5) to be linear at constant pyridine concentration with slopes of k_{CH_3OH}/k_{PYR}[PYR] which are listed in Table III. If we again assume that $k_{PYR} = 1 \times 10^9$ M^{-1} s^{-1}, values of k_{CH_3OH} can be deduced. It is not necessary to assume that K is constant in isopropylphenyl-, cyclopropylphenyl-, and cyclobutylphenylcarbene to deduce the values of Table III. It is clear that the small variation in k_{CH_3OH} with carbene can not explain the greater yield of ethereal trapping product obtained with cyclopropylphenylcarbene (**11b**) relative to that obtained with cyclobutylphenylcarbene (**12b**) and isopropylphenylcarbene (**9b**) in methanol, without recourse to 1,2-hydrogen migration in the excited states of alkyl aryl diazo compounds or in the excited states of the carbenes (Scheme III).

Table III. Methanol Quenching of Ylide Yields, [Pyr] = 1.8 M, in Pentane at Ambient Temperature

carbene		k_{CH_3OH}/k_{PYR}[PYR]	k_{CH_3OH} ($\times 10^9$ M^{-1} s^{-1})[a]
no.	structure		
11b		0.9	1.6
12b		1.6	2.9
9b		1.2	2.2

[a] Assuming $k_{PYR} = 1 \times 10^9$ M^{-1} s^{-1}.

Conclusions

Photolysis of alkylarlydiazomethanes produces excited diazo compounds which partition between carbene formation and hydrogen migration to directly form styrene-type products. The efficiency of styrene formation is a sensitive function of the strength of the C–H bond of the migrating hydrogen. The lifetimes of ethyl-, propyl-, cyclopropyl-, and cyclobutylphenylcarbene are similar and in the range of 110–130 ns. An excited state of cyclobutylphenylcarbene or cyclobutylphenyldiazomethane migrates both carbon and hydrogen with almost equal facility at ambient temperature. Relaxed carbene formation is a minor process in this system.

Experimental Section

General. NMR spectra were recorded on a Varian AM-250 instrument in $CDCl_3$ or DMSO-d_6 and are reported in ppm (δ) downfield from TMS. Infrared spectra were measured on a Perkin-Elmer 457 FT-IR spectrometer. Absorbance spectra were recorded on a Hewlett-Packard 845a Diode Array spectrophotometer. Product analyses by gas chromatography were performed on a Perkin-Elmer 8500 GC equipped with a 30-ft × 0.245-mm fused silica capillary column (5% DB-1741 0.25 mm) and a flame ionization detector using helium as the carrier gas. Identification of compounds in mixtures was accomplished by coinjecting the mixtures with authentic samples and observing the corresponding peak area enhancements and by GC/MS. Yields of photolysis products were quantified through the use of GC response factors. Separation and isolation of some of the photolysis products were performed using a Varian Aerograph Series 1400 gas chromatograph equipped with a thermal conductivity detector. GC/MS data relating to photolysis product mixtures and pure compounds were obtained on a Hewlett-Packard 5995A GC/MS. Melting points were obtained on an Electrothermal melting point apparatus in open capillary tubes and are uncorrected.

Materials. Solvents (Aldrich, reagent grade) were used as received unless otherwise specified. Tetrahydrofuran was distilled from sodium/benzophenone immediately prior to use. Acetonitrile was distilled from calcium hydride immediately prior to use. HPLC grade pentane was stirred over concentrated sulfuric acid several times followed by an acid/permanganate solution before being distilled from P_2O_5. HPLC grade methanol was distilled from a small amount of sodium. Spectroscopic grade pyridine was distilled from BaO and stored over KOH pellets. Benzaldehyde was distilled immediately before use. All starting materials were obtained from Aldrich.

Typical Procedure for Laser Flash Photolysis Experiments. The LFP apparatus in use at OSU has been described previously.[22] Stock solutions of the diazo compounds were typically prepared in dry pentane to an optical density (OD) at 308 nm of between 0.5 and 0.9 for lifetime and

(22) The LFP apparatus in use at Ohio State is described in Soundararajan, N.; Platz, M. S.; Jackson, J. E.; Doyle, M. P.; Oon, S.-M.; Liu, M. T. H.; Anand, S. M. *J. Am. Chem. Soc.* **1988**, *110*, 7143.

Stern–Volmer quenching experiments. The stock solutions were deoxygenated by bubbling with dry, oxygen-free argon for 5 min and transferring to deoxygenated Suprasil quartz cuvettes by syringe. To each cuvette containing 1.5 mL of the solution of diazo compound in pentane were added varying amounts of pyridine until [pyridine] ≈ 0–2 M (typically 12–15 cuvettes were used). Three transient spectra were recorded for each cuvette, with the average value of A_{ylide} used in the data analysis.

Stern–Volmer experiments were also performed in multiple cuvettes, typically 10–12 per experiment. The samples were prepared by adding a fixed amount of the stock solution to each of the cuvettes followed by the addition of the quencher and a constant volume of pyridine. Solvent was then added to each cuvette in order to maintain a constant volume of the sample throughout the experiment.

Three samples of each diazo compound were prepared for the ylide yield experiments with identical absorbances of 0.8 (±0.02) at 308 nm. Three transient spectra were recorded for each cuvette, with the average value of A_{ylide} used in the data analysis.

Typical Procedure for Photolysis Experiments. Photolysis of diazo samples or sodium salts of (*p*-toluenesulfonyl)hydrazones was performed in a Rayonet photochemical reactor equipped with five 350-nm lamps. *Pyrex tubes of the diazo samples were prepared by dissolving 20–27 mg* of the diazo compound in 1.0 mL of acetonitrile or anhydrous methanol. Solutions were degassed by bubbling argon through the solution for 30 min prior to irradiation. The conditions for the photolysis of the salts of the (*p*-toluenesulfonyl)hydrazone salts were similar to those described above, the only difference being the concentration of the salts (50 mg of salt in 1.0 mL of acetonitrile or anhydrous methanol).

General Procedure for Tosylhydrazone Preparation. The ketone was added to a magnetically stirred slurry of 1.0 equiv of (*p*-toluenesulfonyl)-hydrazine in absolute ethanol. The mixture was allowed to stir overnight at room temperature or at reflux under nitrogen. The white solid was collected by suction filtration and recrystallized from absolute ethanol.

Propiophenone tosylhydrazone was prepared from propiophenone (Aldrich) in 51% yield as white crystals (mp 115–116 °C): ^{1}H NMR ($CDCl_3$) δ 1.05 (3H, two t), 2.4 (3H, two s), 2.5 (2H, two g), 7.05 (1H, m), 7.3 (5H, m), 7.4 (1H, m), 7.6 (2H, m), 7.8 (1H, d), 7.9 (2H, d) (two isomers seem to exist); ^{13}C NMR ($CDCl_3$) δ 10.236, 10.583, 19.988, 21.545, 31.446, 126.308, 126.700, 127.931, 128.021, 128.346, 128.504, 129.444, 129.492, 129.532, 129.559, 129.694, 132.914, 135.446, 136.173, 143.868, 144.045, 156.944, 159.141; MS *m/e* 302 (10), 147 (100), 132 (15), 119 (60), 91 (40), 77 (17), 65 (18), 51 (12), 39 (16). Anal. Calcd for $C_{16}H_{18}N_2O_2S$: C, 63.55; H, 5.99; N, 9.26; S, 10.60. Found: C, 63.55; H, 6.01; N, 9.28; S, 10.93.

***n*-Butyrophenone Tosylhydrazone** was prepared from *n*-butyrophenone (Aldrich) in 76% yield as white crystals (mp 119–120 °C): ^{1}H NMR ($CDCl_3$) δ 0.8 and 0.9 (3H, two t), 1.5 (2H, m), 2.4 (3H, two s), 2.6 (2H, two t), 7.0 (1H, m), 7.20 (5H, m), 7.45 (2H, m), 7.65 (2H, m), 7.80 (1H, d), 7.90 (2H, d), 8.25 (1H, s); ^{13}C NMR ($CDCl_3$) δ 13.379, 13.955, 18.377, 19.274, 19.326, 21.509, 28.618, 126.334, 126.607, 127.833, 127.978, 128.260, 129.379, 129.433, 129.509, 129.628, 132.932, 135.466, 136.518, 143.827, 143.975, 155.897, 158.123; MS *m/e* 316 (5), 161 (53), 132 (3), 117 (50), 105 (13), 91 (50), 77 (28), 65 (20), 51 (12), 45 (100). Anal. Calcd for $C_{17}H_{20}N_2O_2S$: C, 64.53; H, 6.37; N, 8.85; S, 10.13. Found: C, 64.48; H, 6.44; N, 8.86; S, 10.23.

Isobutyrophenone tosylhydrazone was prepared from isobutyrophenone (Aldrich) in 34% yield (mp 105–106 °C): ^{1}H NMR ($CDCl_3$) δ 1.0 (6H, d), 2.45 (3H, s), 2.70 (1H, m seven lines), 6.95 (2H, m), 7.15 (1H, s), 7.30 (2H, d), 7.40 (3H, m), 7.80 (2H, m); ^{13}C NMR ($CDCl_3$) δ 19.755, 21.556, 36.254, 127.004, 127.920, 129.355, 129.437, 129.549, 132.293, 135.400, 143.827, 162.284; MS *m/e* 316 (5), 161 (26), 132 (40), 119 (100), 91 (40), 77 (12), 65 (16), 51 (10), 43 (15). Anal. Calcd for $C_{17}H_{20}N_2O_2S$: C, 64.53; H, 6.37; N, 8.85; S, 10.13. Found: C, 64.41; H, 6.37; N, 8.86; S, 10.23.

2,2-Dimethylpropiophenone tosylhydrazone was prepared from 2,2-dimethylpropiophenone (Aldrich) in 53% yield as white crystals (mp 156–158 °C): ^{1}H NMR ($CDCl_3$) δ 1.05 (9H, s), 2.45 (3H, s), 6.85 (3H, m), 7.35 (2H, d), 7.43 (3H, m), 7.80 (2H, d); ^{13}C NMR ($CDCl_3$) δ 21.582, 28.029, 38.530, 127.462, 127.906, 129.232, 129.325, 131.713, 135.461, 143.820, 165.408; MS *m/e* 330 (1), 175 (25), 159 (10), 146 (62), 131 (52), 119 (100), 105 (10), 91 (40), 77 (25), 57 (40), 41 (15). Anal. Calcd for $C_{18}H_{22}N_2O_2S$: C, 65.43; H, 6.71; N, 8.48; S, 9.70. Found: C, 65.07; H, 6.69; N, 8.45; S, 10.03.

Cyclopropyl phenyl ketone (*p*-toluenesulfonyl)hydrazone was prepared from cyclopropyl phenyl ketone in 56.6% yield: mp 131–132 °C; ^{1}H NMR ($CDCl_3$) δ 8.71 (br s, 1H, exchangeable), 7.95–7.91 (2H, d, J = ~6.18 Hz), 7.76–7.60 (1H, dd, J_{ortho} = ~6.18 Hz, J_{meta} = ~3 Hz), 7.33–7.67 (5H, m), 2.40 (3H, s), 1.57–1.46 (1H, m), 1.15–1.06 (2H, m), 0.52–0.43 (2H, m).

Cyclobutyl phenyl ketone(*p*-toluenesulfonyl)hydrazone was prepared from cyclobutyl phenyl ketone in 59.6% yield: mp 118–119 °C; ^{1}H NMR (CD_3SOCD_3) δ 9.91 (1H, br s, exchangeable), 7.74–7.70 (2H, d, J = 7.76 Hz), 7.46–7.38 (5H, m), 7.25–7.22 (2H, d, J = 7.76 Hz), 2.37 (3H, s), 2.07–1.14 (6H, m), 1.68–1.61 (1H, m).

Cyclopentyl phenyl ketone tosylhydrazone was prepared from phenyl cyclopentyl ketone (Aldrich) in 45% yield as white crystals (mp 94–96 °C): ^{1}H NMR ($CDCl_3$) δ 7.8 (2H, d), 7.4 (3H, m), 7.3 (2H, d), 7.2 (1H, s), 7.0 (2H, m), 2.9 (1H, m), 2.4 (3H, s), 1.6 (8H, m); ^{13}C NMR ($CDCl_3$) δ 21.574, 24.739, 29.910, 47.563, 126.869, 127.902, 129.374, 129.464, 132.983, 135.437, 143.818, 160.897.

Cyclohexyl phenyl ketone tosylhydrazone was prepared from phenyl cyclohexyl ketone (Aldrich) in 58% yield as white crystals (mp 95–96 °C): ^{1}H NMR ($CDCl_3$) δ 7.7 (2H, d), 7.4 (3H, m), 7.3 (2H, d), 7.2 (1H, s), 7.1 (1H, m), 6.95 (2H, m), 2.4 (3H, s), 2.35 (1H, m), 1.7 (5H, m), 1.2 (5H, m); ^{13}C NMR ($CDCl_3$) δ 21.582, 25.878, 30.036, 45.748, 126.947, 127.873, 129.377, 129.400, 129.487, 132.481, 135.425, 143.800, 162.184.

α-Tetralone tosylhydrazone was prepared from freshly distilled α-tetralone (bp 78 °C at 0.25 mm*Hg*) in 76% yield as white crystals (mp 176–178 °C): ^{1}H NMR ($CDCl_3$) δ 1.85 (2H, m), 2.40 (3H, s), 2.50 (2H, t), 2.70 (2H, t), 7.05 (1H, d), 7.20 (2H, m), 7.35 (2H, d), 7.95 (4H, m); ^{13}C NMR ($CDCl_3$) δ 21.377, 21.569, 25.427, 29.256, 125.033, 126.443, 128.130, 128.312, 129.566, 131.570, 135.524, 139.733, 144.085, 152.708; MS *m/e* 314 (20), 159 (100), 130 (55), 115 (32), 91 (30), 77 (12), 65 (8), 51 (8). Anal. Calcd for $C_{17}H_{18}N_2O_2S$: C, 64.94; H, 5.77; N, 8.91; S, 10.20. Found: C, 64.98; H, 5.83; N, 9.00; S, 9.75.

1-Benzosuberone tosylhydrazone was prepared from 1-benzosuberone (Aldrich) in 61% yield as white crystals (mp 145–146 °C): ^{1}H NMR ($CDCl_3$) δ 1.60 (2H, m), 1.80 (2H, m), 2.40 (5H, m and s), 2.70 (2H, t), 7.05 (1H, d), 7.25 (5H, m), 7.90 (2H, d), 8.10 (1H, s); ^{13}C NMR ($CDCl_3$) δ 20.829, 21.567, 25.396, 27.392, 31.200, 126.475, 127.961, 128.091, 128.470, 129.472, 129.532, 135.499, 137.280, 138.720, 144.027, 160.342; MS *m/e* 328 (8), 173 (100), 156 (8), 144 (35), 131 (50), 115 (20), 91 (28), 77 (8), 65 (18), 51 (10), 39 (12). Anal. Calcd for $C_{18}H_{20}N_2O_2S$: C, 65.83; H, 6.14; N, 8.53; S, 9.76. Found: C, 65.83; H, 6.20; N, 8.61; S, 9.30.

General Procedure for (Toluenesulfonyl)hydrazone, Sodium Salt Preparation. (*p*-Toluenesulfonyl)hydrazone (ca. 7 mmol) was dissolved in 80 mL of dry THF while being magnetically stirred and cooled to 0 °C in an ice bath. A 1.0-equiv portion of NaH was slowly added to the cooled solution, and the solution was stirred for 2 h under a nitrogen atmosphere in the dark. The resulting solid was collected by suction filtration, washed with dry THF, and dried *in vacuo* (65–93%).

General Procedure for Diazo Compound Preparation. Diazo compounds were prepared in one of two ways. Method A: Two milliliters of 1,1,3,3-tetramethylguanidine was added to ~100 mg of tosylhydrazone, and the solution was stirred under N_2 and heated in an oil bath (65–90 °C depending on the diazo compound) until the color turned red (ca. 30 min). The solution was poured into 25 mL of pentane and extracted twice with 10 mL of 10% Na_2CO_3 solution and twice with 10 mL of saturated NaCl solution before being dried over anhydrous Na_2SO_4. Method B: (Toluenesulfonyl)hydrazone, sodium salt (ca. 0.10 g) and a magnetic stir bar were placed in a 25-mL round-bottom flask. A short condenser allowed the diazo compound to distill from the flask directly into a receiving flask. The apparatus was evacuated to 0.01 Torr. The receiver was cooled with a dry ice–acetone bath, and the magnetically stirred salt was heated to 90–100 or 125–130 °C over a 30–45-min time period. The apparatus was vented with dry nitrogen, and the red diazo compound was diluted with pentane. In either procedure, the diazo compound was then stored at −15 °C in the dark.

Ethylphenyldiazomethane (7a) was prepared by method A and method B: IR (pentane) 2025 cm^{-1}; UV (pentane) 232, 286 nm; ^{1}H NMR ($CDCl_3$) δ 1.25 (3H, t), 2.55 (2H, g), 6.9 (2H, d), 7.05 (1H, m), 7.35 (2H, m); ^{13}C NMR ($CDCl_3$) δ 11.211, 17.142, 121.368, 123.243, 127.975, 128.959, 131.870.

***n*-Propylphenyldiazomethane (8a)** was prepared by method B: IR (pentane) 2025 cm^{-1}; UV (pentane) 230, 284 nm; ^{1}H NMR ($CDCl_3$) δ 1.05 (3H, t), 1.70 (2H, m), 2.50 (2H, t), 6.95 (2H, d), 7.05 (1H, m), 7.35 (2H, m); ^{13}C NMR ($CDCl_3$) δ 13.625, 20.296, 25.979, 121.412, 123.201, 128.031, 128.944.

Isopropylphenyldiazomethane (9a) was prepared by method B: IR (pentane) 2025 cm^{-1}; UV (pentane) 228, 283 nm; ^{1}H NMR ($CDCl_3$) δ 1.30 (6H, d), 2.85 (1H, septet), 7.00 (3H, m), 7.35 (2H, m); ^{13}C NMR ($CDCl_3$) δ 20.315, 22.757, 121.647, 123.179, 129.018.

tert-**Butylphenyldiazomethane (10a)** was prepared by method B: IR (pentane) 2025 cm^{-1}; UV (pentane) 224, 288 nm; ^1H NMR ($CDCl_3$) δ 1.40 (9H, s), 7.05 and 7.15 (3H, m), 7.40 (2H, m); ^{13}C NMR ($CDCl_3$) δ 23.372, 29.559, 123.752, 124.455, 127.363, 127.802, 128.696.

Cyclopropylphenyldiazomethane (11a) was prepared from its sodium salt in 52.2% yield: IR (pentane) 2025 cm^{-1}; UV (pentane) 226, 282 nm; ^1H NMR ($CDCl_3$) δ 7.41–7.35 (2H, m), 7.14–7.05 (3H, m), 1.87–1.74 (1H, m), 1.09–1.02 (2H, m), 0.67–0.59 (2H, m).

Cyclobutylphenyldiazomethane (12a) was prepared from the sodium salt of cyclobutyl phenyl ketone (*p*-toluenesulfonyl)hydrazone in 43.7% yield: IR (pentane) 2025 cm^{-1}; UV (pentane) 226, 282 nm; ^1H NMR ($CDCl_3$) δ 7.38–7.30 (2H, td, J = ~6.18 Hz), 7.08–7.00 (2H, td, J = ~6.18 Hz), 6.94–6.89 (2H, dd, J = ~6.18 Hz), 3.50–3.34 (1H, quintet), 2.57–2.36 (2H, m), 2.15–1.95 (4H, m).

Cyclopentylphenyldiazomethane (13a) was prepared by method A: IR (pentane) 2025 cm^{-1}; UV (pentane) 226, 292 nm.

Cyclohexylphenyldiazomethane (14a) was prepared by method A: IR (pentane) 2025 cm^{-1}; UV (pentane) 226, 292 nm.

1,2,3,4-Tetrahydro-1-diazonaphthalene (15a) was prepared by method A and method B: IR (pentane) 2025 cm^{-1}; UV (pentane) 227, 293 nm.

2,3-Benzodiazocycloheptane (16a) was prepared by a modification of method A. Tosylhydrazone (1.0 g, 3.0 mmol) was dissolved in 30 mL of dry THF and cooled in an ice bath under N_2. One equivalent of NaH/oil was added, and the mixture was allowed to stir at room temperature for 1 h. A reflux condenser was attached, and the mixture was refluxed overnight under N_2. The resulting, white precipitate was filtered and the THF evaporated under reduced pressure. The residual, red oil was dissolved in pentane, washed twice with 15 mL of a saturated NaCl solution, dried over Na_2SO_4, and stored at −15 °C in the dark: IR (pentane) 2025 cm^{-1}; UV (pentane) 229, 293 nm.

1-Phenylcyclopentanol. A solution of phenyllithium was prepared by adding a solution of bromobenzene (10 g, 0.06 mol) in ether (16 mL) to lithium wire (0.91 g, 0.13 g-atom) in 44 mL of ether. A solution of cyclopentanone (2.0 g, 0.02 mol) in ether (4.5 mL) was added slowly with stirring to the phenyllithium solution. The mixture was stirred for 4 h after addition was complete, and excess phenyllithium was decomposed carefully with water. The aqueous layer was extracted with 150 mL of ether, and the combined organic solutions were washed with water and dried over $MgSO_4$. The ether was removed by rotary evaporation, and the residue was distilled under vacuum (bp 50 °C/0.1 mmHg; 2.0 g (51.9%)): IR (neat) 3780–3408 (OH), 3085–30–26 (CH aromatic), 2961–2872 (CH aliphatic), 1698–1447 cm^{-1} (C=C aromatic); ^1H NMR ($CDCl_3$) δ 7.53–7.48 (2H, dd), 7.39–7.22 (3H, m), 2.06–1.95 (4H, br s), 1.94–1.82 (4H, br s).

1-Phenylcyclopentene (2). A mixture of 1-phenylcyclopentanol (2.0 g, 0.01 mol) and *p*-toluenesulfonic acid monohydrate (1.6 mg) was heated under reduced pressure (0.75 mmHg) in an oil bath at 95 °C, and the product was allowed to distill from the reaction flask through a short column. The yield of colorless oil was 1.0 g (56.2%, bp 55 °C/0.75 mmHg): ^1H NMR (CDCl3) δ 7.50–7.44 (2H, dd, J = ~6.18 Hz), 7.35–7.22 (3H, m), 6.24–6.19 (1H, quintet), 2.80–2.69 (2H, m), 2.62–2.50 (2H, m), 2.13–1.97 (2H, m); MS m/e 144 (96), 129 (100), 115 (43), 91 (13), 77 (13), 66 (20), 51 (17).

1-Phenylcyclobutanol. A solution of phenyllithium was prepared by adding a solution of bromobenzene (25.5 g, 0.16 mol) in ether (40 mL) to lithium wire (2.32 g, 0.33 g-atom) in 112.5 mL of ether. A solution of cyclobutanone (5.0 g, 0.07 mol) in ether (11.25 mL) was added slowly with stirring to the phenyllithium solution. The mixture was stirred for 4 h after addition was complete, and excess phenyl lithium was decomposed carefully with water. The aqueous layer was extracted with 150 mL of ether, and the combined ether solutions were washed and dried over magnesium sulfate. The ether was removed by rotary evaporation and the residue was distilled under vacuum (bp 40–42 °C/0.05 mmHg; 5.03 g, 47.5%): IR (neat) 3358 (OH), 3085–3028 (CH aromatic), 2986–2872 cm^{-1} (CH aliphatic); ^1H NMR ($CDCl_3$) δ 7.53–7.50 (2H, dd, J = ~6.46 Hz), 7.49–7.25 (3H, m, 2.63–2.51 (2H, m), 2.44–2.30 (2H, m), 2.11–1.95 (1H, m), 1.79–1.68 (1H, m).

1-Phenylcyclobutene. A mixture of 1-phenylcyclobutanol (4.93 g, 0.03 mol) and *p*-toluenesulfonic acid monohydrate (3.9 mg) was heated under reduced pressure (0.01 mmHg) in an oil bath at 80 °C, and the product was allowed to distill (bp 37 °C/0.01 mmHg) from the reaction flask through a short column. The product obtained during this synthesis was always contaminated with a small amount of 2-phenyl-1,3-butadiene. The yield of pale yellow oil was 0.23 g (5.4%): MS sp m/e 129 (100), 115 (60), 102 (44), 91 (12), 77 (15), 63 (11), 51 (23).

Butyltriphenylphosphonium Bromide. Equimolar amounts of tetramethylene bromide (5.0 g, 0.02 mol) and triphenylphosphine (6.07 g, 0.02 mol) were heated in *p*-xylene at 130 °C for 24 h. Butyltriphenylphosphonium bromide was obtained (7.760 g, 68.6%; mp 210–211 °C): ^1H NMR (CD_3SOCD_3) δ 7.48–7.27 (15H, m), 3.33–3.21 (2H, t), 3.18–3.13 (2H, t, J = ~6.10 Hz), 1.61–1.50 (2H, quintet, J = ~6.10 Hz), 1.29–1.17 (2H, sextet).

Benzylidenecyclobutane (1). To a suspension of 0.67 g of NaH (60% suspension in mineral oil) in 1,2-dimethoxyethane (40 mL) was added 4.0 g of cyclobutyltriphenylphosphonium bromide at room temperature under argon. Several drops of ethanol were then added, and the mixture was stirred at 70 °C for 6 h. Then, benzaldehyde (1.0 g, 10 mmol) was added, and the mixture was poured into ice–water and extracted with hexane. The hexane extract was dried and concentrated to obtain a colorless oil (0.72 g, 60%): ^1H NMR ($CDCl_3$) δ 7.35–7.14 (5H, m), 6.12–6.09 (1H, quintet), 3.12–3.03 (2H, t, J = ~6.05 Hz), 2.95–2.87 (2H, t, J = ~6.05 Hz), 2.18–2.07 (2H, quintet, J = ~6.05 Hz); MS m/e 144 (37), 129 (100), 115 (67), 104 (7), 89 (13), 63 (16), 51 (14).

Propyltriphenylphosphonium Bromide. Equimolar amounts of trimethylene bromide (5.0 g, 0.02 mol) and triphenylphosphine (6.49, 0.02 mol) were heated in *p*-xylene at 130 °C for 24 hrs. Propyltriphenylphosphonium bromide was obtained (4.18 g, 36.4%; mp 228–229 °C, lit. mp 228–230 °C): ^1H NMR (CD_3SOCD_3) δ 7.48–7.28 (15H, m), 3.35–3.29 (2H, t), 3.26–3.20 (2H, t, J = ~6.10 Hz), 1.68–1.56 (2H, sextet).

Cyclobutylphenylcarbinol. In a 50-mL flask fitted with a stirrer and reflux condenser were placed 0.51 g (0.01 mol) of $NaBH_4$ and 15 mL of THF. Cyclobutyl phenyl ketone (1.95 g, 0.01 mol) was added to the milky suspension of $NaBH_4$ and the mixture refluxed overnight. Excess of $NaBH_4$ was quenched with water, and the mixture was washed with 10% HCl and the alcohol extracted with ether. The ether extracts were dried over $MgSO_4$ and concentrated to obtain a pale yellow oil (1.85 g, 93.4%): ^1H NMR δ 7.35–7.29 (5H, m), 5.56–4.52 (1H, d, J = ~6.18 Hz), 2.68–2.52 (1H, m), 2.26 (1H, br s, exchangeable), 2.18–2.00 (2H, m), 1.89–1.70 (4H, m).

Cyclobutylphenylmethyl Methyl Ether (4). To DMSO (30.82 mL) was added powdered KOH (3.46 g, 61.64 mmol). After the mixture was stirred for 5 min, cyclobutylphenylcarbinol (2.5 g, 15.41 mmol) was added followed immediately by addition of iodomethane (4.37 g, 30.82 mol). Stirring was continued for 30 min, after which the mixture was poured into water (100 mL) and extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed with water (2 × 50 mL) and dried over $MgSO_4$. Solvent was removed by rotary evaporation to yield a yellow oil (0.9 g, 33.1%): ^1H NMR ($CDCl_3$) δ 7.38–7.23 (5H, m), 4.02–3.98 (1H, d, J = ~6.18 Hz), 3.20 (3H, s), 2.58–2.51 (1H, m), 2.10–1.94 (2H, m), 1.89–1.66 (4H, m); MS m/e 176 (11), 147 (2), 121 (100), 115 (7), 91 (16), 77 (14), 51 (5).

Cyclopropylphenylcarbinol. In a 100-mL flask fitted with a stirrer and reflux condenser were placed 1.42 g (0.038 mol) of $NaBH_4$ in 40 mL of THF. Cyclopropyl phenyl ketone (5 g, 0.034 mol) was added to the milky suspension and the mixture refluxed overnight. The reaction was quenched with water, the mixture was washed with 10% HCl, and the alcohol was extracted with ether. The ether extracts were dried over $MgSO_4$ and concentrated to obtain a pale yellow oil (3.5 g, 69.0%): ^1H NMR ($CDCl_3$) δ 7.42–7.21 (5H, m), 3.97–393 (1H, d, J = ~6.18 Hz), 2.61 (1H, br s, exchangeable), 1.27–1.09 (1H, m), 0.65–0.56 (4H, m).

Cyclopropylphenylmethyl Methyl Ether. To DMSO (31 mL) was added powdered KOH (3.78 g, 67.47 mmol). After the mixture was stirred for 5 min, cyclopropylphenylcarbinol (2.5 g, 16.87 mmol) was added followed immediately by the addition of iodomethane (4.79 g, 33.74 mmol). Stirring was continued for 30 min, after which the mixture was poured into water (100 mL) and extracted with dichloromethane (3 × 100 mL). The combined organic extracts were washed with water (2 × 50 mL) and dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation to yield a yellow oil (0.8 g, 29.2%): ^1H NMR ($CDCl_3$) δ 7.37–7.31 (5H, m), 3.56–3.52 (1H, d, J = ~6.18 Hz), 3.25 (3H, s), 0.94–0.84 (2H, m), 0.72–0.61 (1H, m), 0.51–0.41 (2H, m), 0.39–0.22 (1H, m); MS m/e 162 (1), 134 (100), 121 (31), 104 (29), 91 (46), 65 (6), 51 (12).

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