

# EXPLORATORY PHOTOCHEMISTRY OF ALKYL-BROMO- AND ALKYLFLUORODIAZIRINES. EXCITED-STATE HYDROGEN MIGRATION AND CARBENE FORMATION

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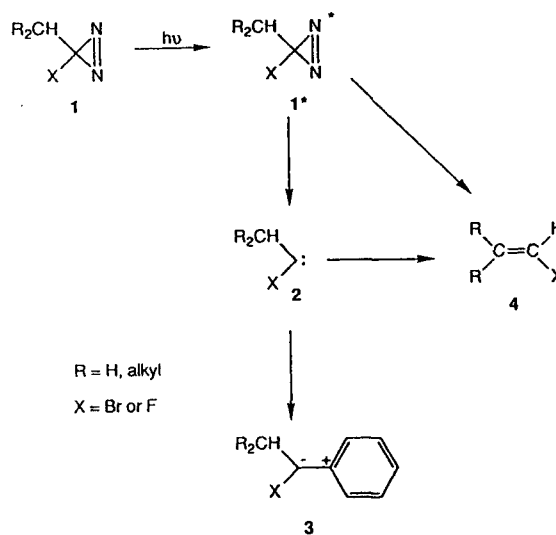
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**Laser flash photolysis of a series of alkylbromo- and alkylfluorodiazirines in pentane at ambient temperature generates alkylhalocarbenes by decomposition of the diazirine excited states. The halocarbenes can be intercepted with pyridine to form ylides. The ylides absorb intensely between 350 and 400 nm and are fairly long lived ( $\tau \gg 10 \mu\text{s}$ ), making them convenient probes of the yield and dynamics of the carbene. The yield of the ylides increases with increasing pyridine concentration up to 1.5 M. At pyridine concentrations  $>1.5 \text{ M}$  the yield of ylide is saturated, signifying that every carbene generated in a laser pulse is captured by pyridine prior to reaction with solvent or intramolecular rearrangement. The yield of trappable carbene generated from alkylbromodiazirines closely tracks the bond dissociation energy of the C—H bond adjacent to the diazirine moiety. The data indicate that the excited states of the alkylbromodiazirines suffer C—H migration (or C—C migration with cyclobutylbromodiazirine) and nitrogen extrusion in competition with carbene formation. The yield of trappable carbene derived from the alkylfluorodiazirines is independent of the bond dissociation energy of the adjacent C—H bond. This is probably a consequence of the great thermodynamic stability of  $\alpha$ -fluorocarbenes.**

## INTRODUCTION

Laser flash photolysis (LFP) is now a standard tool for the study of arylcarbenes in solution.<sup>1</sup> The aromatic chromophore facilitates UV–visible detection of the carbene intermediate. It is also possible to study non-aromatic carbenes, despite their lack of a convenient ( $\lambda > 320 \text{ nm}$ ) chromophore by trapping them with pyridine to form ylides.<sup>2</sup> Pyridine ylides absorb intensely between 350 and 420 nm and have long lifetimes ( $\tau \gg 10 \mu\text{s}$ ), properties which are ideal for monitoring the yield and dynamics of carbenes.

We have recently found that the yield of trappable alkylchlorocarbenes derived from diazirines that are produced in a laser pulse depends strongly on the nature of the alkyl group.<sup>3</sup> We concluded that acyclic alkylchlorodiazirine excited states partition between hydrogen migration which proceeds in concert with nitrogen extrusion, and carbene formation (Scheme 1). The greater the strength of the C—H bond adjacent to the diazirine moiety, the greater is the yield of trappable carbene.



R = H, alkyl

X = Br or F

Scheme 1

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In this work, these studies were extended to alkylbromo- and alkylfluorodiazirines. The results demonstrate that whereas the efficiency of carbene formation tracks the adjacent C—H bond strength of the alkylbromodiazirines, it is largely independent of this property in the case of alkylfluorodiazirines. We agree with Moss and Ho<sup>4</sup> that the well known ability of fluorine to stabilize carbene centers<sup>5</sup> dramatically improves the efficiency of carbene formation in the excited states of alkylfluorodiazirines.

## RESULTS

### LFP studies of alkylbromodiazirines

LFP (XeF, 351 nm, 55 mJ) of methyl-, perdeuteromethyl-, ethyl-, isopropyl-, *tert*-butyl-, cyclopropyl- or cyclobutylbromodiazirine in pentane at 25 °C fails to produce detectable ( $\lambda = 300\text{--}700\text{ nm}$ ) transient intermediates. However, LFP of these diazirines in the presence of pyridine produces intensely absorbing transients (Figure 1). These transients are attributed to pyridine ylides (e.g. 3, R = alkyl, X = Br, Scheme 1) because of their similarity to the transient ylide spectra produced by reaction of dialkylcarbenes and alkylchlorocarbenes with pyridine.<sup>2</sup> The ylide

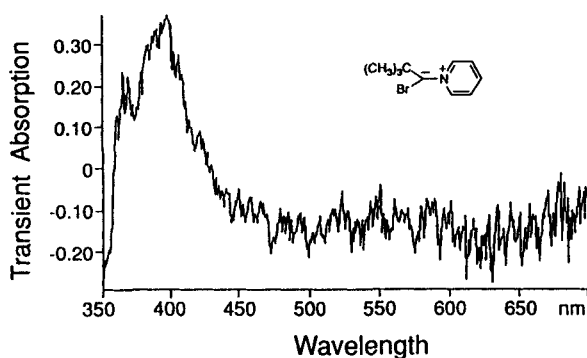


Figure 1. Transient absorption spectrum of the ylide formed by reaction of *tert*-butylbromocarbene with pyridine

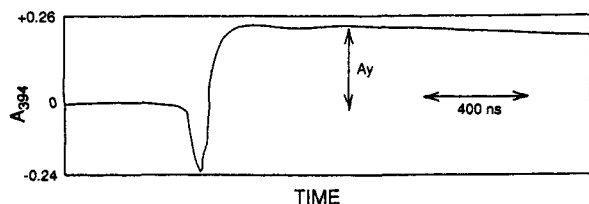


Figure 2. Rate of formation of the pyridine ylide derived from LFP of *tert*-butylbromodiazirine in the presence of pyridine ([pyridine] = 1.0 M) in pentane at 25 °C

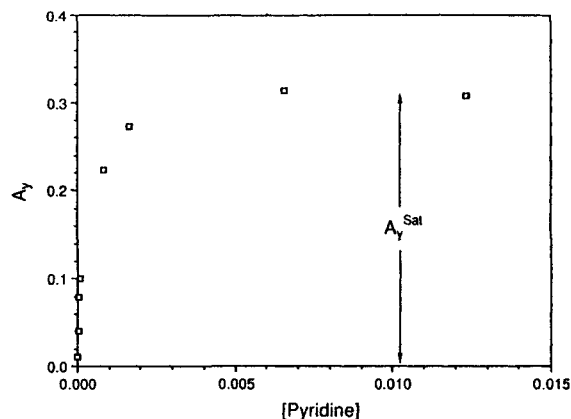


Figure 3. Optical yield ( $A_y$ ) of pyridine ylide produced by LFP of *tert*-butylbromodiazirine in pentane at 25 °C as a function of pyridine concentration, (M)

absorption increases exponentially following the laser pulse before reaching a maximum value ( $A_y$ , Figure 2) about  $0.1\text{--}1.0\ \mu\text{s}$  after the laser pulse, depending on the nature of the alkyl group.

The optical yield ( $A_y$ ) of ylide formed, in a single laser pulse measured at the absorption maximum of the ylide, is shown in Figure 3 as a function of pyridine concentration.  $A_y$  increases with increasing concentration of pyridine until a critical pyridine concentration is present, after which  $A_y$  is saturated ( $A_y^{\text{sat}}$ ). When [pyridine] > 0.01 M in the case of *tert*-butylbromocarbene, every alkylbromocarbene produced in a laser pulse is captured by pyridine to form an ylide. The critical pyridine concentration needed to achieve saturation ( $A_y^{\text{sat}}$ ) varies with the nature of the alkyl group.

Similar experiments were performed with the alkylfluorodiazirines. LFP of methyl-, ethyl-, isopropyl- and *tert*-butylfluorodiazirines in pentane fails to produce observable transient intermediates. However, LFP of the alkylfluorodiazirines in the presence of pyridine produces intensely absorbing ylides (Figure 4). It is interesting that  $\lambda_{\text{max}}$  of the alkylfluoro- (353–370 nm), alkylchloro- (365–380 nm) and alkylbromo- (372–400 nm) carbene–pyridine ylides are all different. Values of  $A_y$  and  $A_y^{\text{sat}}$  were determined for the alkylfluorocarbene–pyridine ylides as for the alkylbromo analogs.

As revealed in Figure 5, the value of  $A_y^{\text{sat}}$  for the alkylbromocarbene–pyridine ylides tracks the C—H bond dissociation energies of the C—H bond adjacent to the diazine moiety (assuming that the  $\alpha$ -diazirine moiety affects the strength of a neighboring C—H bond as does a neighboring methyl group). When this C—H bond is particularly strong (cyclopropyl C—H) or absent (*tert*-butyl), the value of  $A_y^{\text{sat}}$  is high.<sup>6,7</sup> In

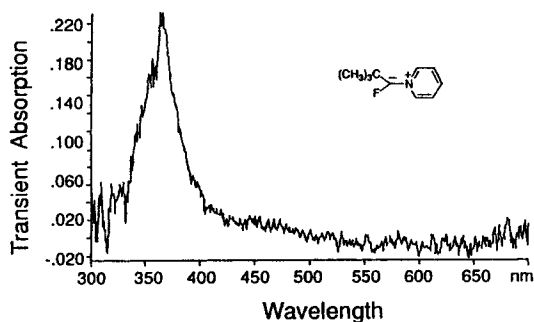


Figure 4. Transient absorption spectrum of the ylide formed by reaction of *tert*-butylfluorocarbene with pyridine

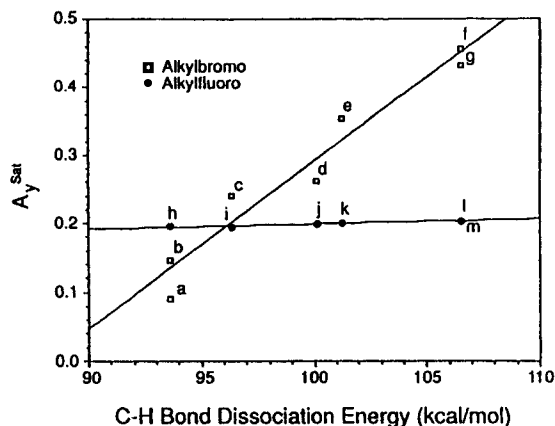


Figure 5. Yield of ylides formed at saturated pyridine concentrations ( $A_y^{\text{sat}} \pm 10\%$  error) as a function of the C—H bond dissociation energy adjacent to the diazine moiety:<sup>6,7</sup> (a) bromocyclobutyl-; (b) bromoisopropyl- (c) bromoethyl-; (d) bromomethyl-; (e) bromotrideromethyl-; (f) bromocyclopropyl-; (g) bromo-*tert*-butyl-; (h) fluoroisopropyl-; (i) ethylfluoro-; (j) fluoromethyl-; (k) fluorotrideromethyl- (l) cyclopropylfluoro-; (m) *tert*-butylfluorodiazirine.  $\square$ , Alkylbromo;  $\bullet$ , alkylfluoro.

marked contrast, the magnitude of  $A_y^{\text{sat}}$  is independent of the alkyl C—H bond strength in the alkylfluorocarbenes. *tert*-Butylbromocarbene-pyridine ylide has a larger value of  $A_y^{\text{sat}}$  than the *tert*-butylfluoro analogue. This must reflect differences in extinction coefficients between  $\alpha$ -brominated and  $\alpha$ -fluorinated pyridine ylides or differences in the quantum yield of diazine decomposition with halogen.

## DISCUSSION

The alkylbromodiazirine data are fully consistent with Scheme 1 ( $R = \text{alkyl}, X = \text{Br}$ ). Photolysis of diazirine 1 produces a singlet excited state  $^1\mathbf{1}^*$ , which can either extrude nitrogen to form the carbene or migrate a

hydrogen in concert with nitrogen extrusion (our data allow the possibility that  $\alpha$ -hydrogen migrates first to nitrogen to form a vinyl azo compound, which subsequently extrudes nitrogen). The low yield of ylide when  $R = \text{isopropyl}$  or cyclobutyl is not due to a greater speed of the intramolecular rearrangement of the carbene because sufficient pyridine has been added to saturate the yield of ylides derived from these carbenes. Thus the alkylbromodiazirine data are completely analogous to earlier studies of alkylchlorodiazirine excited-state rearrangements.<sup>3,4,8</sup>

There is no evidence for migration of an adjacent C—C bond in *tert*-butylbromodiazirine excited states. However, Moss and Ho<sup>4</sup> have presented evidence that a strained C—C ring bond of cyclobutylchlorodiazirine migrates in the excited state. Our data do not differentiate between C—H and C—C bond migration in bromocyclobutylidiazirine excited states.

At first glance it seems curious that cyclobutyl C—C bonds migrate but that cyclopropyl C—C bonds do not. However, it is important to note the differences in the thermodynamic driving forces in these systems. The rearrangement of methylcyclopropane to cyclobutene increases strain by  $2 \text{ kcal mol}^{-1}$  ( $1 \text{ kcal} = 4.184 \text{ kJ}$ ), but the rearrangement of methylcyclobutane to cyclopentene leads to a decrease in strain of  $20 \text{ kcal mol}^{-1}$ .<sup>6,7</sup>

The trappable yield of carbene formed from alkylfluorodiazirines is independent of the nature of the alkyl group. This is in good agreement with the report of Moss and Ho.<sup>4</sup> We agree that the dramatic ability of fluorine to stabilize thermodynamically a carbene center<sup>5</sup> accelerates the decomposition of the alkylfluorodiazirine excited states to form carbenes. This acceleration renders competitive bond migrations in the diazine excited states unimportant. (Other interpretations of the data are possible. The 'non-trappable' intermediate can be an excited state of the carbene or a carbene-pyridine complex. We prefer the diazine excited state interpretation because photolysis necessarily produces this species.)

There is no *a priori* reason for a plot of  $A_y^{\text{sat}}$  versus bond dissociation energy to resemble linearity. The large yield of cyclopropyl and *tert*-butylbromopyridine ylides we observe demonstrate that relative to other alkylbromodiazirines there is little excited-state rearrangement chemistry in these systems. Our data do not exclude the possibility that *tert*-butyl- and cyclopropylbromodiazirines suffer some excited-state rearrangement chemistry. Indeed, the linear plot shown in Figure 5 implies that the quantum yield for carbene formation in these diazirines is still less than unity.

## CONCLUSIONS

The excited states of acyclic alkylbromodiazirines suffer 1,2-hydrogen migration in concert with nitrogen extrusion in competition with carbene formation. The

strength of the adjacent C—H bond determines the importance of the hydrogen migration pathway. Alkylfluorodiazirine excited states decompose cleanly to carbenes owing to the dramatic ability of fluorine to thermodynamically stabilize carbene centers.

### EXPERIMENTAL

All chemicals were obtained from Aldrich. Solvents were of spectroscopic grade. Pentane was purified by stirring repeatedly over concentrated H<sub>2</sub>SO<sub>4</sub> until no further discoloration was observed and then washed with dilute hydrogen-carbonate solution and distilled from P<sub>2</sub>O<sub>5</sub>. Pyridine was purified by distillation from KOH pellets and stored over the same.

The alkylbromodiazirines were prepared according to literature preparations<sup>9</sup> and trapped at  $-78^{\circ}\text{C}$  in pentane. The alkylfluorodiazirines were prepared from the alkylbromodiazirines by the procedure of Moss *et al.*<sup>10</sup> The alkylbromodiazirines were trapped in spectroscopic-grade DMSO at  $-78^{\circ}\text{C}$ . The DMSO solution was thawed and added to 1:1 molar equivalent of molten tetrabutylammonium fluoride, which had been previously dehydrated by heating at  $50^{\circ}\text{C}$  under vacuum for at least 24 h. This mixture was stirred for 24 hr at room temperature in a flask shielded from light. The alkylfluorodiazirine was isolated from this solution by bubbling with dry argon through a 28 cm tube containing KOH and indicating Drierite before being trapped in pentane at  $-78^{\circ}\text{C}$ .

Optical yield experiments were performed with all diazirines on the same day. The alkylfluorodiazirine experiments utilized solutions of diazirines with matching absorbance values at 351 nm ( $A_{351\text{ nm}} = 0.095 \pm 0.006$ ) and identical pyridine concentrations well beyond the concentrations required to saturate the ylide yield ( $[\text{pyridine}] = 1.45\text{ M}$ ). The alkylbromodiazirine experiments utilized solutions of the diazirines with matching absorbance values at 351 nm ( $A_{351\text{ nm}} = 0.50 \pm 0.04$ ) and identical pyridine concentrations well beyond the concentrations required to saturate the ylide yield ( $[\text{pyridine}] = 1.75\text{ M}$ ). The

laser flash photolysis apparatus has been described elsewhere.<sup>11</sup>

### ACKNOWLEDGMENT

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