

## An Unusually Strict Product Partition of an Excited Diazirine–Carbene System

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Photolysis of 3-*tert*-butyl-3-chlorodiazirine produces 2-chloro-3-methyl-but-2-ene and 2,2-dimethyl-1-chlorocyclopropane; the former stems from 1,2-methyl migration and nitrogen loss in the excited state diazirine, whilst the latter is a product of 1,3-CH insertion in the *tert*-butylchlorocarbene derived from the diazirine.

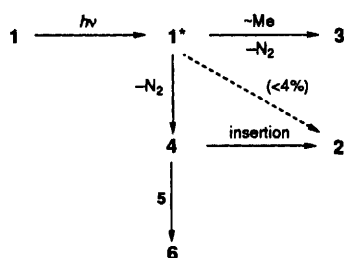
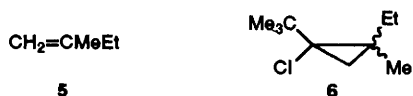
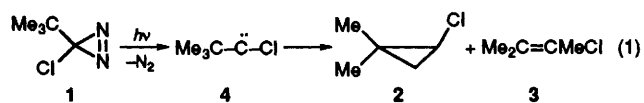
It has become increasingly clear that carbenic reactions initiated by photolysis of alkylhalodiazirines are often accompanied by the simultaneous rearrangement of a second transient. This analysis initially derived from kinetic studies that required two intermediates to account for the observed inverse relation between the product ratio (intramolecular rearrangement):(intermolecular trapping), and the concentration of an added trapping reagent.<sup>1,2</sup>

The second intermediate was first identified as a carbene–alkene complex (where the trapping reagent was an alkene<sup>1</sup>), but, more recently, the fluorescence studies of Platz and coworkers have strongly implied that the additional transient is, in fact, the photoexcited diazirine that is the immediate carbene precursor.<sup>3</sup> In the currently normative mechanism, the electronically excited diazirine undergoes nitrogen loss/rearrangement, directly affording *e.g.* a 1,2-hydride shift product, in competition with simple nitrogen loss to the carbene. The latter can either rearrange to the same intramolecular product, or be captured by an external trap.<sup>2,4</sup> Fluorescence studies demonstrate that the excited diazirine does not live long enough to react with the external trap.<sup>3</sup>

Our own studies have shown that the competitive intermolecular trapping and 1,2-hydrogen (or carbon) rearrangements of neopentylchlorocarbene<sup>5</sup> and cyclobutylchlorocarbene,<sup>6</sup> generated by photolysis of the appropriate diazirines, also fit this paradigm, with the intramolecular reaction occurring in both the carbenes and their excited state diazirine precursors. Here, we describe the unprecedented outcome of the photolysis of *tert*-butylchlorodiazirine **1**, where the excited diazirine is solely responsible for a 1,2-Me rearrangement that is eschewed by its daughter carbene in favour of a 1,3-CH insertion reaction. Moreover, there appears to be minimal overlap in this unusually strict product partition.

We previously reported that, at low concentrations of diazirine,† photolysis of **1** afforded 2,2-dimethyl-1-chlorocyclopropane **2** and 2-chloro-3-methyl-2-butene **3**.<sup>7,8</sup> A clas-

† At concentrations of **1** such that its absorbance at 362 nm in octane is less than 0.2, azine formation is suppressed.<sup>8</sup> When  $A > 0.2$ , azine formation (from **1** + **4**) is significant and complicates the mechanistic analysis.



Scheme 1

sical interpretation of these results, eqn. (1), ascribes products 2 and 3 to competitive 1,3-CH insertion and 1,2-Me migration reactions, respectively, of carbene 4, for which laser flash photolysis experiments provide absolute rate constants.<sup>8</sup> The current reinvestigation, however, reveals eqn. (1) to be an oversimplification.

Thus, generation of 4 by the photolysis of 1<sup>7,9</sup> in 2-methylbut-1-ene 5 affords (in addition to 2 and 3) the isomeric cyclopropane adducts 6, which were characterized by NMR spectroscopy and elemental analysis.

The product distribution of this reaction was followed as a function of [5] in pentane at 25 °C, using calibrated, flame ionization, capillary GC analysis. The data (Table 1, Fig. 1) show that the ratio of intermolecular addition to intramolecular insertion (6:2) is strictly linear with alkene concentration (slope, 0.965; intercept, 0.013; corr. coeff., 0.999). In contrast, the yield of 1,2-Me shift product 3 is effectively independent of the alkene concentration.

The simplest interpretation of these results is that 1,3-insertion product 2 very largely comes from carbene 4, whereas 1,2-Me shift product 3 comes only from the excited state (1\*) of diazirine 1; adducts 6, of course, arise only from the addition of 4 to alkene 5. An inverse plot (not shown) of (2:6) vs. 1:[5] is also strictly linear (slope, 0.96; intercept, 0.042 ± 0.018; corr. coeff., 0.999). If [5] were infinite, 1:[5] would be zero, so that the intercept of this correlation, 0.042 ± 0.018, represents the product ratio 2:6 where the formation of 2 is not quenched by alkene. Thus, no more than ~4% (±2%) of cyclopropane 2 can come from 1\*; at least 96% of this product descends from carbene 4. These relationships are presented in Scheme 1.

In the absence of the external trap, about 13% of the intramolecular products 2 and 3 are formed from 1\* (~9% of 3 and ~4% of 2), whilst ~87% of the products (*i.e.* 2) comes from carbene 4. The exclusive formation of 1,2-Me shift product 3 from 1\*, together with the near-exclusive formation of 1,3-CH insertion product 2 from carbene 4, represents an unusually strict dichotomy of intramolecular product formation between an excited state diazirine and its daughter carbene.<sup>4</sup>

It is worth noting that our results provide clear evidence for 1,2-carbon migration in an excited state diazirine, a reaction for which White and Platz found 'no evidence'.<sup>3</sup> Additionally, the present identification of the two product-forming inter-

Table 1 Product distributions for photolysis of diazirine 1 in alkene 5<sup>a</sup>

[5]/mol dm <sup>-3</sup>	2 (%)	3 (%) <sup>b</sup>	6 (%)	6:2
0.00	90.7	9.3	0.0	0.00
0.25	71.7	9.8	18.6	0.26
0.35	66.1	10.1	23.8	0.36
0.50	60.2	9.3	30.6	0.51
0.70	53.5	9.3	37.2	0.70
1.00	47.4	9.9	42.6	0.90
1.50	36.2	9.3	54.6	1.51
2.00	30.1	9.4	60.5	2.01
2.50	26.5	9.3	64.2	2.42
3.00	23.6	9.2	67.2	2.85
3.50	20.7	8.6	70.7	3.41
4.00	18.7	8.8	72.5	3.88

<sup>a</sup> At 25 °C, λ > 430 nm. The absorbance of 1 was < 0.1; azine formation<sup>8</sup> was negligible. Reproducibility of GC integration, ±2%.

<sup>b</sup> Average value 9.3 ± 0.3.

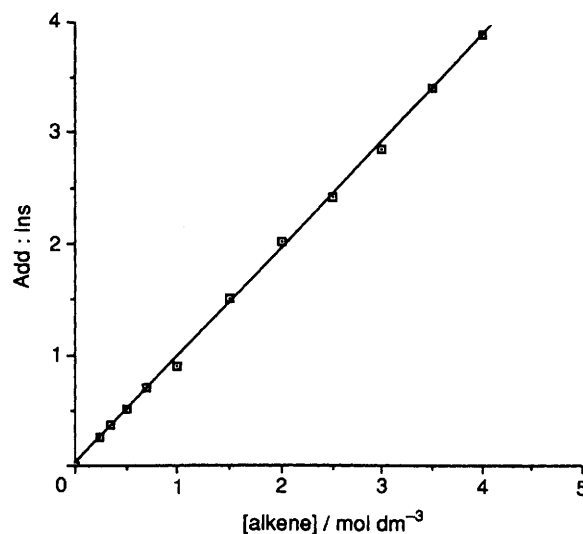


Fig. 1 The product ratio of intermolecular addition (Add) to intramolecular insertion (Ins), 6:2 vs. [5] in pentane at 25 °C

mediates as excited state diazirine and carbene is not only in general accord with the Goodman-Platz mechanism,<sup>2,4</sup> but counts against the likelihood of carbene-alkene complexes<sup>1</sup> as significant intermediates in these reactions.

Our results must not be taken to imply that carbene 4 cannot undergo 1,2-Me rearrangement under any circumstances. Indeed, thermolysis of 1 at 79 °C produces 9.6% of 3 and 90.4% of 2. Accepting that thermolysis of 1 does not populate 1\*, this result implies that, given appropriate thermal activation, a 1,2-Me shift of 4 and 3 is modestly competitive with 1,3-CH insertion to 2; *i.e.* eqn. (1) is valid in the thermal reaction.‡ As would be expected, and in contrast to the photolytic process, the yields of both 3 and 2 decrease when the thermolysis is conducted in either 9.4 mol dm<sup>-3</sup> alkene 5 (or 9.2 mol dm<sup>-3</sup> trimethylethylene), whilst the ratio 2:3 remains constant at 8.6:1 (or 8.1:1).

Finally, we need to reconsider the reported<sup>8</sup> absolute rate constant for the 1,3-CH insertion of 4 to 2. It was previously assumed that eqn. (1) held during laser flash photolytic experiments, so that the observed rate constant for the disappearance of carbene 4 (9.3 ± 1.1 × 10<sup>5</sup> s<sup>-1</sup>) was partitioned between the formation of products 2 and 3.

‡ However, Fox *et al.* have shown that even thermal reactions of nitrogenous precursors can masquerade as carbene reactions.<sup>10</sup>

Because **3** must now be attributed to **1\*** under photolytic conditions, the rate constant  $9.3 \times 10^5 \text{ s}^{-1}$  should be reassigned solely to the 1,3-CH carbene insertion. Moreover, the previously described differential activation parameters,<sup>8</sup> also predicated on a partition of carbene **4** between products **2** and **3**, are rendered invalid because the primary partitioning event is now seen to direct **1\*** to either **3** or **4**.

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