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A verification of the photolytic decomposition pathways of 3-*tert*-butyl-3-chlorodiazirine based on the application of the C_{60} probe technique

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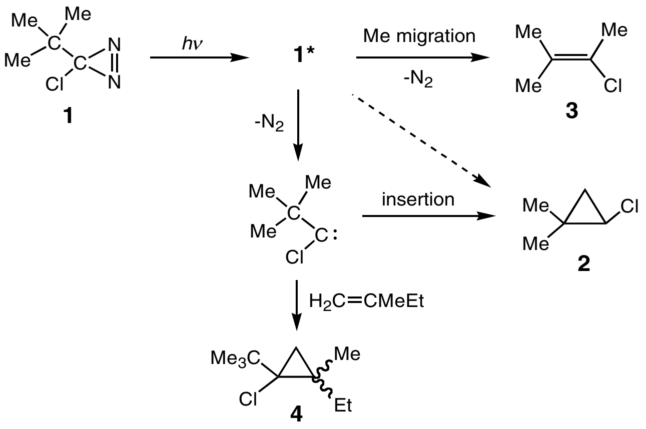
Abstract—C_{60} acts as a mechanistic probe for the formation of carbene and for the rearranged product via the excited state in the photolysis of 3-*t*-butyl-3-chlorodiazirine.

It is now clear that the generation of carbenes by photolysis of alkylchlorodiazirines is often accompanied by electronically excited diazirine, which directly affords the final rearranged product, as demonstrated by the fluorescence studies of Platz and co-workers.[1] The elegant methodology of Moss et al.[2] presented convincing evidence for excited diazirine in the photolysis of 3-*t*-butyl-3-chlorodiazirine (**1**) yielding 2,2-dimethyl-1-chlorocyclopropane (**2**, 87%) and 2-chloro-3-methyl-2-butene (**3**, 13%) as products (Scheme 1). Photolysis of diazirine **1** in 2-methyl-1-butene afforded cyclopropane adduct **4**, in addition to the products **2** and **3**. When the product distribution of this reaction was studied as a function of the concentrations of 2-methly-1-butene, the ratio of intermolecular/intramolecular product, **4**/**2**, was linear with alkene concentration. The yield of 1,2-methyl shift product **3**, was independent of the alkene concentration. This suggests that **3** was formed exclusively from the excited diazirine. These results convincingly demonstrate that the carbene partitioned directly into products **2** and **4**.



Scheme 1.

We have recently introduced the C_{60} probe technique, which is a nonspectroscopic method to determine the photolytic decomposition pathways of diazirines.[3] The carbene adds to C_{60} to form methanofullerene, whereas the diazo compound adds to C_{60} to form fulleroid.[3,4] In particular, the partitioning of carbene, diazo and rearrangement in excited state (RIES) are quantitatively obtained. For example, the photolysis of 3-chloro-3-isopropyldiazirine in the presence of C_{60} resulted in the

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Keywords: C_{60}; Diazirine; Photolytic decomposition; Carbene; RIES process.

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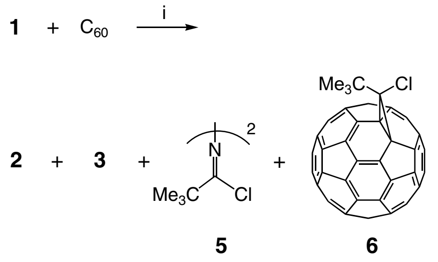

Scheme 2. Reagents and conditions: (i) *hν* (>300 nm), ODCB/C_6D_6 (9/1), −30 °C.

formation of 5% carbene, 13% diazo and 82% RIES product. The results obtained from chemical derivatization by 3-chloro-3-isopropyldiazirine agree with results obtained by laser flash photolysis[5] and fluorescence studies[1] of the same compound.

We now wish to report the photolysis of diazirine **1** in the presence of C_{60}. We prepared diazirine **1** by the oxidation of the corresponding amidine by NaOCl according to Graham's procedure.[6] We photolyzed (>300 nm) solution of diazirine **1** (0.9×10^{-2} M) in the presence of C_{60} (2.6×10^{-2} M) in ODCB/C_6D_6 (9/1) at −30 °C for 15 h to an approximately 80% conversion. We repeated this experiment three times and averaged the results.

^{1}H NMR (300 MHz, *o*-dichlorobenzene/C_6D_6 (9/1)) measurement of the reaction mixture showed the yields of 2,2-dimethyl-1-chlorocyclopropane (**2**, 3%, δ 1.13 (s), 0.87 (s)), 2-chloro-3-methyl-2-butene (**3**, 6%, δ 1.91, 1.69, 1.52 (each br s)), azine (**5**, 6%, δ 1.23 (s)) and 6,6-methanofullerene adduct (**6**, 55%, δ 1.81 (s)) (Scheme 2). The NMR data of compounds **2**, **3** and **5** are in excellent agreement with those published by Moss and Ho.[2b] We isolated the adduct **6** by HPLC separation with Buckyprep column, and characterized by means of a spectroscopic analysis.[7]

On the basis of these observations, we have concluded that the formation of yield of adduct **6** in the photoreaction of C_{60} with diazirine **1** reveal the formation of yield of carbene. Also, the yields of **2** and **3** reveal the formation of the products via the RIES processes. The rate constant for C–H insertion of *t*-BuCCl carbene is slow, $9.3\times10^5\,s^{-1}$.[2] As a result, the carbene can either be trapped by C_{60} or react to a lesser extent with diazirine **1** to form azine **5**.[8] The formation ratio of carbene/RIES in this reaction was estimated as 87/13.

Our results agree with Moss's estimate that in the photolysis of diazirine **1** yields 87% carbene, and that 4% of **2** and 9% of **3** derive from the RIES processes. The agreement between our result with that of Moss is remarkable considering that the two methodologies used completely different experimental approaches. We believe that our C_{60} probe technique presents unambiguous results in the assignment of photolytic decomposition pathways in diazirine. The application of diazirines as photoactivatable reagents is an area of intense research in biochemistry and molecular biology.[9]

Diazirines have been used as photoaffinity reagents to label receptors and also to act as reagents for investigating the organization of biological membranes. When diazirines are irradiated, the loss of nitrogen to yield carbenes is the optimum desirable reaction because the carbenes react covalently with the receptors. In view of these reactions, the understanding of the various elementary processes in the photochemistry of diazirines is of paramount importance. We are convinced that the C_{60} probe can be used to obtain quantum yields in the photolysis of diazirines.

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7. ^{1}H NMR (300 MHz, $CS_2/CDCl_3$ (3/1)): δ 1.93 (s, 9H); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ (3/1)): δ 148.24, 145.87, 145.10, 144.98, 144.94, 144.90, 144.73, 144.49, 144.31, 144.20, 144.09, 143.53, 143.51, 143.05, 142.98, 142.94, 142.85, 142.80, 142.04, 141.97, 141.57, 140.68, 140.59, 140.42, 139.83, 138.98, 78.53, 67.52, 44.46, 29.57; MS (MALDI-TOF, matrix: 1,1,4,4-tetraphenyl-1,3-butadiene) *m*/*z* 824 (M^-).
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