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A Nonspectroscopic Method To Determine the Photolytic Decomposition Pathways of 3-Chloro-3-alkyldiazirine: Carbene, Diazo and Rearrangement in Excited State

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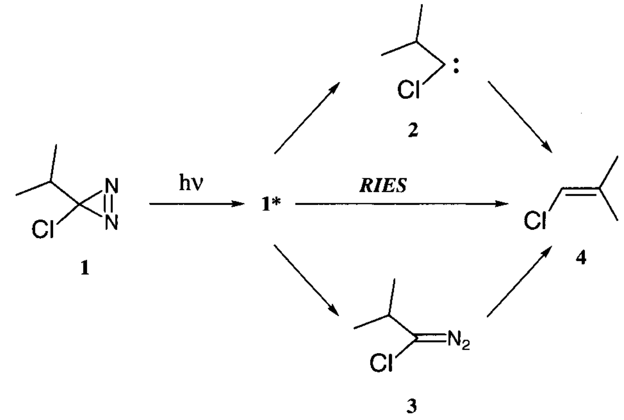
Abstract: C_{60} acts as a mechanistic probe for the formation of carbene, diazo compound, and for the rearranged product via the excited state in the photolysis of 3-chloro-3-isopropyldiazirine and 3-chloro-3-chloromethyldiazirine. The carbene adds to C_{60} to form methanofullerene, whereas the diazo compound adds to C_{60} to form fulleroid. The olefin product arises as a result of the rearrangement in the excited state.

Introduction

Carbenes have been frequently generated by the photochemical decomposition of diazirines.[1] Since their introduction in 1988, pyridinium ylides[2] have become popular as probes to study the dynamics of carbene species which lack convenient UV−vis chromophores for direct detection. In 1992, Platz and co-workers[3] discovered considerable variation in the yield of pyridinium ylide upon laser flash photolysis of solutions of alkylchlorodiazirines with equal optical densities. For example, the signal obtained from cyclopropylchlorodiazirine exceeds by more than 10-fold that obtained from isopropylchlorodiazirine. The yield of carbene is large with cyclopropylchlorodiazirine because the α-C−H bond is very strong. The α-C−H bond in isopropylchlorodiazirine is weaker, so that the yield of carbene is consistent with the fact that diazirine excited states suffer 1,2-hydrogen migration and nitrogen extrusion, in competition with carbene formation.

In 1996, Bonneau and Liu[4] studied the 1,2-hydrogen migration in isopropyl-chlorocarbene, **2**, produced by laser flash photolysis of 3-chloro-3-isopropyldiazirine, **1**. The lifetime of carbene **2**, estimated from the kinetics of growth of the pyridinium ylide absorption, is less than 20 ns at −90 °C. This experiment was not a complete success because of the low yield in the production of carbene upon the photolysis of **1** and also because the carbene lifetime is close to the response time of the detection system. In the same year, Bonneau and Liu[5] also determined the quantum yield of formation of the diazo compound, **3**, $\phi_{\text{diazo}} \approx 10-15\%$, in the photolysis of **1**. They concluded that the low quantum yield for **3** cannot alone explain the low yield for the formation of carbene **2**. Although these results are in agreement with Platz's hypothesis of an efficient rearrangement in the excited-state (RIES) process in the case of diazirine **1**, they still await confirmation. Bonneau and Liu[4] also reported the simplest interpretation of all of the existing data. The explanation is that three pathways exist for the formation of **4**, as described in Scheme 1.

Scheme 1



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Arenas and co-workers[6] made a theoretical study on the photoexcited 3H-diazirine and came to the following conclusion. By means of dynamical calculations, they demonstrated that carbene formation does not take place in the excited state and it is formed on the ground-state surface after decaying through a conical intersection.

Recently, we reported the use of C_{60} as a probe to distinguish carbene/diazo partition in the photolysis of adamantanediazirine.[7] C_{60} reacts with diazomethane to yield fulleroid. By adding onto C_{60}, carbene affords methanofullerene. We now wish to report the photolysis of two diazirines in the presence of C_{60} with the object of determining the contribution of various pathways in the decomposition of alkylchlorodiazirine.

Experimental Section

Gel permeation chromatographic separation was performed on a recycling preparative HPLC with a series of Jaigel 1H and 2H columns (Japan Analytical Industry Co., Ltd.) using toluene as an eluent. The isolation of isomers was performed by using a preparative HPLC system with a Buckyprep column (Nacalai Tesque: 20 mm $\phi \times 250$ mm) with toluene as an eluent. The ratio of isomers was determined by HPLC analysis using an analytical Buckyprep column (Nacalai Tesque: 4.6 mm $\phi \times 250$ mm) with toluene as an eluent. The yields of 1-chloro-2-methyl-1-propene, 1,2-dichloroethylene, and $C_{60}CClCH_2Cl$ were determined by ^1H NMR measurement of the reaction mixture. Bibenzyl was used as an internal standard. The yield of $C_{60}CCl$(*i*-Pr) was determined by HPLC analysis. Isopropylchlorodiazirine and chloromethylchlorodiazirine were synthesized by a previously reported procedure.[8]

Photochemical Reaction of 3-Chloro-3-isopropyldiazirine with C_{60}. We photoirradiated a toluene/*o*-dichlorobenzene (1:3) solution of isopropylchlorodiazirine **1** (8.0 mg, 3.4×10^{-2} M) and C_{60} (48 mg, 3.4×10^{-2} M) with a high-pressure mercury-arc lamp for 30 min at −40 °C in a sealed Pyrex NMR tube. The reaction mixture was allowed to stand for 3 h in the dark at room temperature to complete N_2 elimination. ^1H NMR measurement of the reaction mixture showed the yield of 1-chloro-2-methyl-1-propene to be 82%. The HPLC analysis, using a Buckyprep column, demonstrated that adduct **5** was obtained in 18% yield, respectively. The HPLC analysis also showed the ratio of **5a** and **5b** as 28/72. We also carried out a preparative-scale experiment using diazirine **1** (137 mg, 3.8×10^{-2} M) and C_{60} (72 mg, 3.3×10^{-3} M) to obtain an authentic sample of the isomeric $C_{60}CCl$(*i*-Pr) adduct (**5**). We isolated adduct **5** (21 mg) by first-stage HPLC separation with a GPC column and isomers **5a** (6 mg) and **5b** (15 mg) by second-stage HPLC separation with a Buckyprep column. Compound **5a**, ^1H NMR (300 MHz, $CS_2/CDCl_3$): δ 3.36 (sept, 1H, $J = 6.6$ Hz), 1.66 (d, 6H, $J = 6.6$ Hz). ^{13}C NMR (75 MHz, $CS_2/CDCl_3$): δ 145.98 (s), 145.05 (s), 145.02 (s), 144.99 (s), 144.95 (s), 144.87 (s), 144.82 (s), 144.64 (s), 144.45 (s), 144.41 (s), 144.31 (s), 144.27 (s), 144.17 (s), 144.16 (s), 143.50 (s), 143.43 (s), 143.09 (s), 142.91 (s), 142.90 (s), 142.84 (s), 142.78 (s), 142.72 (s), 142.68 (s), 142.21 (s), 142.03 (s), 141.94 (s), 141.56 (s), 141.02 (s), 140.76 (s), 138.73 (s), 131.42 (s), 80.24 (s), 64.30 (s), 31.08 (d), 18.62 (q). UV−vis (λ_{max}, toluene): 331, 430 nm. FABMS (toluene/NBA): *m*/*z* 810 (M), 720 (C_{60}). Compound **5b**, major isomer, ^1H NMR ($CS_2/CDCl_3$, 500 MHz): δ 5.02 (sept, 1H, $J = 6.4$ Hz), 1.51 (d, 6H, $J = 6.4$ Hz). ^{13}C NMR ($CS_2/CDCl_3$, 125 MHz): δ 147.24 (s), 147.75 (s), 144.53 (s), 143.77 (s), 143.72 (s), 143.71 (s), 143.59 (s), 143.51 (s), 143.38 (s), 143.20 (s), 143.04 (s), 143.02 (s), 142.99 (s), 142.77 (s), 142.70 (s), 142.46 (s), 142.29 (s), 142.24 (s), 141.79 (s), 141.69 (s), 141.37 (s), 141.28 (s), 141.06 (s), 140.04 (s), 138.99 (s), 138.50 (s), 138.09 (s), 137.27 (s), 136.24 (s), 134.67 (s), 134.52 (s), 75.90 (s), 67.56 (s), 39.35 (d), 17.76 (q). UV−vis (λ_{max}, toluene): 339 nm. FABMS (toluene/NBA): *m*/*z* 810 (M), 720 (C_{60}). Minor isomer, ^1H NMR (500 MHz, $CS_2/CDCl_3$): δ 2.20 (sept, 1H, $J = 6.4$ Hz), 1.12 (d, 6H, $J = 6.4$ Hz). ^{13}C NMR ($CS_2/CDCl_3 = 3/1$, 125 MHz): δ 146.98 (s), 144.89 (s), 144.35 (s), 144.32 (s), 144.00 (s), 143.65 (s), 143.59 (s), 143.48 (s), 143.16 (s), 143.01 (s), 142.93 (s), 142.41 (s), 142.22 (s), 142.09 (s), 141.71 (s), 141.12 (s), 141.51 (s), 140.16 (s), 139.07 (s), 138.25 (s), 137.32 (s), 136.58 (s), 136.29 (s), 135.01 (s), 84.59 (s), 59.28 (s), 32.54 (d), 17.51 (q) (seven peaks of minor isomer might be overlapped by some of the major isomer's peaks). UV−vis (λ_{max}, toluene): 339 nm. FABMS (toluene/NBA): *m*/*z* 810 (M), 720 (C_{60}).

Photochemical Reaction of 3-Chloro-3-chloromethyldiazirine with C_{60}. We photoirradiated a toluene/*o*-dichlorobenzene (1:3) solution of 3-chloromethyl-3-chlorodiazirine (8.0 mg, 3.4×10^{-3} M) and C_{60} (24 mg, 7.0×10^{-3} M) with a high-pressure mercury-arc lamp for 3 h at −40 °C in a NMR tube. ^1H NMR measurement of the reaction mixture showed the yield of 1,2-dichloroethylene (*E*- and *Z*-) and $C_{60}C(Cl)CH_2Cl$ to be 45 and 25%, respectively. The ratio of the (*E*)- and (*Z*)-1,2-dichloroethylene was 28/72 ($E/Z = 0.38$). We also carried out a preparative-scale experiment using diazirine **7** (44.4 mg, 8.0×10^{-2} M) and C_{60} (144 mg, 2.0×10^{-2} M) to obtain an authentic sample of the isomeric $C_{60}C(Cl)CH_2Cl$ adduct (**8**). We isolated adduct **8** (7.4 mg) by HPLC separation with a Buckyprep column. Compound **8**, ^1H NMR (300 MHz, CS_2/C_6D_6): 4.68 (s, 2H). ^{13}C NMR (125 MHz, CS_2/C_6D_6): 145.19 (s), 145.15 (s), 145.11 (s), 145.06 (s), 145.00 (s), 144.79 (s), 144.75 (s), 144.70 (s), 143.54 (s), 144.47 (s), 144.36 (s), 144.29 (s), 144.05 (s), 143.58 (s), 143.28 (s), 143.10 (s), 143.00 (s), 142.87 (s), 142.78 (s), 142.19 (s), 142.11 (s), 142.03 (s), 141.68 (s), 141.24 (s), 140.96 (s), 139.14 (s), 137.12 (s), 78.27 (s), 56.69 (s), 46.80 (t). UV−vis (λ_{max}, toluene): 328, 429, 485 nm. FABMS (toluene/NBA): *m*/*z* 816 (M), 720 (C_{60}).

Results and Discussion

The establishment of the role of the excited state in the chemistry of diazirine has been studied by fluorescence spectroscopy, as demonstrated by Platz and co-workers.[9] Alkylchlorodiazirines, which fluoresce weakly or not at all, have a low fluorescence quantum yield which makes the study of excited-state chemistry difficult. Another method entails the analysis of the products obtained under photolysis and thermolysis in the presence of various amounts of a reactive olefin at various temperatures, as performed for chloromethylchlorodiazirine and *n*-propylchlorodiazirine.[10] This method is tedious and time-consuming. Yet a different method to study the excited state of diazirine is the time-resolved photoacoustic calorimetry, which monitors the amplitude and time evolution of heat depositions following photoexcitation.[10,11]

Investigators now recognize that, when diazirines are used as the source of carbenes, several processes contribute to the formation of the final product including the rearrangement of the excited state of the diazirine. As well, the formation of the metastable diazo intermediate competes with the production of carbene. The efficiency of these three ways of decomposition of the diazirine strongly depends on the structure of the diazirine being used. No rules exist to predict the relative efficiency of these different pathways. Considering all of the procedures described earlier, we found that the C_{60} trapping methodology presents a simple way to determine the efficiencies of these

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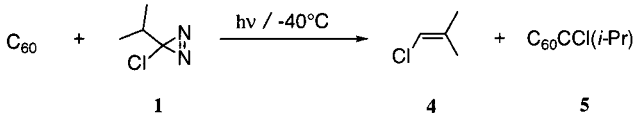
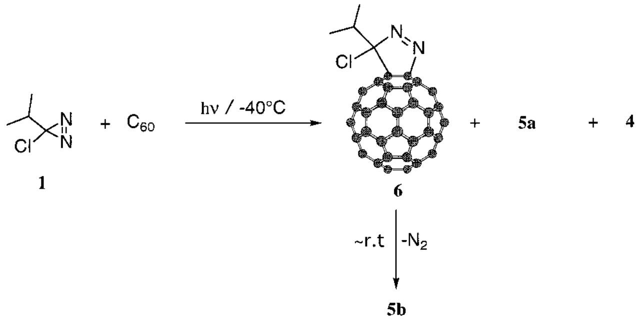
Scheme 2



Scheme 3



pathways. To test C_{60} as a chemical probe, we carried out the two experiments using isopropylchlorodiazirine (**1**) and chloromethylchlorodiazirine (**7**).

Photochemical Decomposition of Isopropylchlorodiazirine. Irradiation of a *o*-dichlorobenzene (ODCB)/toluene solution of C_{60} (3.4×10^{-2} M) and isopropylchlorodiazirine (**1**, 3.4×10^{-2} M) with a high-pressure mercury-arc lamp (cutoff < 300 nm) in a Pyrex tube at −40 °C resulted in the formation of the corresponding adduct $C_{60}CCl(i\text{-}Pr)$ (**5**) in 18% yield, which was purified by preparative HPLC with a GPC column. We also observed the formation of 1-chloro-2-methyl-1-propene (**4**) in 82% yield (Scheme 2). Adduct **5** can be readily separated into two isomers, **5a** and **5b**, by preparative HPLC with a Buckyprep column. HPLC analysis at −40 °C after reaction showed the formation of **6**, which was converted to **5b** at room temperature by N_2 elimination (Scheme 3). Compound **6** was stable at −40 °C under photoirradiation conditions. We also carried out the irradiation of **1** in the presence of C_{60} at −40 °C with a $\lambda >$ 400 nm, where C_{60} is the only light-absorbing component. In this case, we did not observe a decomposition of **1**. Thus, it is evident that $^3C_{60}{}^*$ does not play an important role in these reactions.

FAB mass spectrometry of **5a** and **5b** depicts a molecular ion peak ($C_{64}H_7Cl$ that requires *m*/*z* 810) at *m*/*z* 814−810, as well as one of C_{60} at *m*/*z* 724−720, which arises from the loss of the *i*-Pr(Cl)C group. The UV−visible absorption spectra of **5a** and **5b** are virtually identical to that of C_{60} except for a subtle difference in the 400−650 nm region. These results suggest that **5a** and **5b** retain the essential electronic and structural character of C_{60}. The UV−visible absorption spectrum of **5a** has an absorption at 430 nm, indicating a characteristic feature of a 6,6-adduct of C_{60}.[12]

The spectral data of ^1H and ^{13}C NMR and 2D NMR (HMQC and HMBC) clearly suggest that **5a** has C_s symmetry. The ^1H NMR spectrum of **5b** showed the existence of two diastereomers. The proton of the isopropyl group of the major isomer appears as a septet at 5.02 ppm, which is a typical chemical shift for a location above the five-membered ring of the fullerene subunit. The chemical shift of the same H atom of the minor isomer appears at 2.20 ppm, indicating that the isopropyl group is located on the six-membered ring. The ratio of two diastereomers is 4:1. These results cannot be explained by thermodynamical arguments.

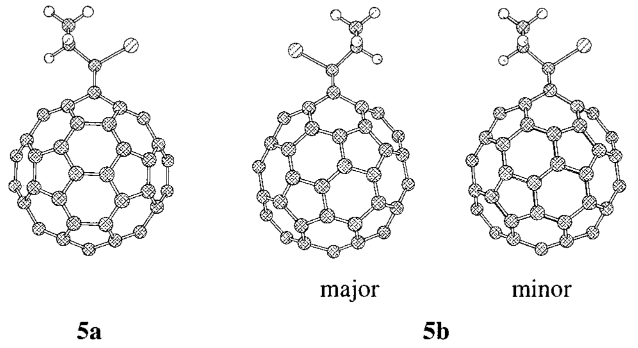
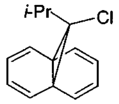
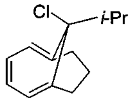
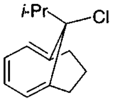


Figure 1. The optimized structure of **5a** and **5b** (major and minor) at the B3LYP/3-21G* level.

Table 1. The Density Functional Calculations for **5a**, **5b** (Major and Minor), and C_{60} at the B3LYP/3-21G Level

	 **5a**	 major **5b**	 minor	C_{60}
Relative Energy (Kcal / mol)	-3.59	-0.28	0.00	
HOMO level (eV)	-6.27	-6.39	-6.42	-6.51
LUMO level (eV)	-3.51	-3.52	-3.55	-3.57

We carried out the density functional calculations[13] at B3LYP/3-21G* level for **5a** and two diastereomers of **5b** with the Gaussian 98 program[14] (Figure 1). These three isomers have almost identical stability (Table 1). Hence, a mechanism for diastereoselective cluster opening reactions must account for the kinetically controlled process. Schick and Hirsch reported the highly diastereoselective formation of fulleroids via thermal decomposition of the corresponding pyrazolines in the reaction of C_{60} with monoalkylated diazomethanes.[15] They demonstrated that the kinetic product is the fulleroid with the bulkier substituent located above a five-membered ring. In our case, the difference of the two substituents (Cl and *i*-Pr) is small as compared with those of monoalkylated diazomethanes. Thus, the diastereoselectivity of **5b** might be decreased.

On the basis of these observations, the formation yields of **5a**, **5b**, and **4** (5, 13, and 82%) in the photoreaction of C_{60} with isopropylchlorodiazirine **1** reveal the formation yields of car-

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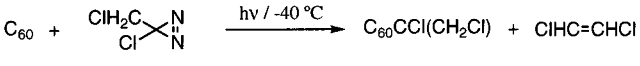
Scheme 4



7 8 9

Table 2. Redox Potentials[a] in V of C_{60},[b] **5a**, and **5b**

compound	ox E_1	red E_1	red E_2	red E_3
C_{60}	+1.21[c,d]	−1.12	−1.50	−1.95
6,6-C_{60}CCl(*i*-Pr) (**5a**)	+1.24[c]	−1.14	−1.51	−2.10
5,6-C_{60}CCl(*i*-Pr) (**5b**)	+1.11[c]	−1.14	−1.51	
6,6-C_{60}Ad[e]	+1.07[c]	−1.21	−1.58	−2.06
5,6-C_{60}Ad[e]	+1.10[c]	−1.18	−1.55	−2.02
C_{60}CClPh[e]	+1.29[c]	−1.13	−1.54	−2.02

[a] Half-cell potentials unless otherwise stated. Values are relative to ferrocene/ferrocenium couple. [b] Reference 17. [c] Irreversible. [d] Value was obtained by differential pulse voltammogram. [e] Reference 7.

bene, diazo compound, and RIES process during the reaction. Bonneau and Liu have already determined that approximately 13% goes to diazo compounds from **1** in the laser flash photolysis of **1**.[5] On the other hand, Platz claims that the quantum yield of the carbene is only 10% for *i*-PrClCN$_2$ photolysis.[3] He assumed that the RIES for this diazirine must be high, for example, 70−80%. Present results obtained from chemical derivatization of C_{60} by **1** are in agreement with these findings. We are now convinced that C_{60} can be used as a chemical probe for the photochemical reaction of diazirine.

Photochemical Decomposition of Chloromethylchlorodiazirine. We irradiated a *o*-dichlorobenzene (ODCB)/toluene solution of C_{60} (3.4×10^{-2} M) and chloromethylchlorodiazirine (**7**, 3.4×10^{-2} M) under the same conditions as diazirine **1** to afford the corresponding adduct $C_{60}CCl(CH_2Cl)$ (**8**), which was purified by preparative HPLC with a Buckyprep column. We also observed the formation of 1,2-dichloroethylene (**9**) (Scheme 4). The **8**/**9** ratio is 36/64. Hence, the RIES process for diazirine **7** is 64%. The *E*/*Z* ratio of **9** is 28/72. The HPLC analysis and spectroscopic investigation by means of NMR measurements verify that **8** is a 6,6-adduct of C_{60}.

Bonneau and co-workers reported the determination of the carbene formation (α) and the RIES efficiency (1 − α) of **7** by time-resolved photoacoustic calorimetry ($\alpha = 0.49$) as well as by the thermolysis and photolysis of **7** in the presence of olefins ($\alpha = 0.54 - 0.42$).[10] They also reported that the rearrangement of free carbene ClCH$_2$CCl gives ∼6% of **9-*E*** and ∼94% of **9-*Z*** from a thermolysis experiment. Photolysis of the same diazirine gives ∼15% of **9-*E*** and ∼85% of **9-*Z***. This was explained by the RIES process which produced **9** with a much larger *E*/*Z* ratio than that of the free carbene. If the efficiency of RIES is ∼52%, then the RIES process gives ∼25% of **9-*E*** and ∼75% of **9-*Z***. Present results obtained from chemical derivatization of C_{60} by **7** are in agreement with these findings, especially that the *E*/*Z* ratio (28/72) of **9** is very close to Bonneau's results (25/75) indicating that all **9** is formed via RIES process in our reaction. This experiment reiterates that our C_{60} trapping methodology acts as a probe for the partitioning of carbene, diazo and excited-state chemistry in the photolysis of diazirines.

Electrochemical Properties of Fullerene Derivatives. In view of the electron-acceptor character of C_{60}, there is a great interest in the electrochemical behavior of C_{60} derivatives bearing an organic addend.[16] We studied the redox potentials of the prepared compounds by cyclic voltammetry at room temperature. The data are collected in Table 2, together with C_{60}, C_{60}CClPh, and C_{60}Ad as reference compounds. Adduct **5a** exhibits three one-electron reversible reduction waves and one irreversible oxidation, such as that observed for the parent C_{60}. However, we observed two reversible reduction waves and one irreversible oxidation for **5b**. The salient feature is that the 5,6-adduct **5b** has a low oxidation potential (+1.11 V) as compared to that of the 6,6-adduct **5a** (+1.24 V). Interestingly, the 6,6-adduct of C_{60}Ad has a low oxidation potential (+1.16 V) as compared to that of the 5,6-adduct of C_{60}Ad (+1.45 V). Meanwhile, the first reduction potentials related to C_{60} are cathodically shifted, which indicates that the introduction of a *i*-Pr(Cl)C group results in decreasing the electron-accepting properties. This finding agrees with that previously observed for other dihydrofullerenes. It may be explained by the raising of the LUMO energy of the adducts.

Conclusion

Our proposal uses C_{60} to measure carbene/diazo partitioning functions not only in the carbene/diazo case but also in the measurement of RIES, which is neither a carbenic nor a diazo process. This method complements Platz's fluorescence experiment and Bonneau and Liu's relative rate and time-resolved photoacoustic studies. We believe that this paper presents the first set of unambiguous results in the assignment of decomposition pathways in diazirine.

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