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Effect of Substituents on the Thermal Decomposition of Diazirines: Experimental and Computational Studies

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The thermal decomposition of phenylchlorodiazirine (**1**), phenyl-*n*-butyldiazirine (**2**), and 2-adamantane-2,3′-[3*H*]diazirine (**3**) has been studied in solution in the presence of C_{60}. The C_{60} probe technique indicates that in the decomposition diazirine **1** yielded exclusively phenylchlorocarbene, diazirine **2** yielded mainly a diazo intermediate, and diazirine **3** yielded a mixture of carbene and diazo compound. In the case of diazirine **2**, 13% of (*E*)-1-phenyl-1-pentene resulted from the direct thermal rearrangement of diazirine without the participation of a carbene. As well, the thermal decomposition of these diazirines has been studied theoretically with ab initio and density functional methods. The experimental results are broadly in agreement with the theoretical predictions. The calculations further indicate that the rebound reaction between carbene and molecular nitrogen leading to the formation of a diazo intermediate is an important reaction in the gas-phase decomposition of diazirine.

Introduction

Since the preparation of the first diazirine compound in 1960,[1] preliminary work demonstrated that methylene and nitrogen are indeed formed by the photolytic decomposition of diazirine.[2] The publication of this result stimulated numerous investigations of diazirines as carbene precursors.[3] Presently, at least three elementary processes are known in the photolysis of diazirine.[4] They are the production of carbene, the production of a diazoalkane, and the rearrangement in the excited state of diazirine. The C_{60} probe technique[5] has determined the quantitative partitioning of these three pathways in the photolysis of isopropylchlorodiazirine. This study demonstrates that the same intermediates occur in the thermal decomposition of diazirines just as they do in photolysis.

The thermolysis of diazirines has been widely studied in the gas phase and in solution.[3c] The decompositions obey first-order kinetics even up to 90% conversion and yield either carbene or diazoalkane or a mixture of both, depending on the substituents on the diazirine ring. In 1990, Stevens and Liu, while examining the thermal decomposition of 20 diazirines,[6] found that the entropy of activation for decomposition indicates a relatively tight transition state with no additional free rotations. More importantly, these *A*-factors show a remarkable constancy for all types of substituents, despite the large change in rate of over 5 orders of magnitude. These authors proposed an encounter complex, because it permits the formation of a single rate-determining step with subsequent partitioning by two competitive product-forming processes. For differing substituents, R_1 and R_2, on the diazirines, this mechanism offers results that depend on the interplay of rate coefficients and the compound stabilities. It is difficult to determine the formation ratio of carbene and diazo compound in the thermolysis of diazirine, because of the difficulty of direct spectroscopic detection of active species. Recently, we

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have used C_{60} as a chemical probe to distinguish carbene from diazo formation during the photolysis of diazirine by determining the isomeric ratio of the formed methanofullerene and fulleroid.[5] It should be possible, therefore, to use the same methodology in the case of thermolysis.

Herein we report the results of the thermal decomposition of three diazirines in the presence of C_{60}. They are phenylchlorodiazirine (**1**), phenyl-*n*-butyldiazirine (**2**), and 2-adamantane-2,3′-[3*H*]diazirine (**3**). We also performed calculations on the energetics of the thermolytic decomposition pathways of these compounds. The thermal decomposition of diazirines **1** and **2** has been thoroughly studied[7] and will be used to validate the C_{60} methodology in the case of thermolysis. The agreement between the experimental results and the theoretical predictions offer a new insight into the mechanism of the thermolysis of diazirines.

Experimental Section

We performed gel permeation chromatographic separation on a recycling preparative HPLC using toluene as an eluent. We accomplished the isolation of isomers using a preparative HPLC system with a Buckyprep column (20 mm $\phi \times$ 250 mm), with toluene used as an eluent. We determined the ratio of isomers by HPLC analysis, using an analytical Buckyprep column (4.6 mm $\phi \times$ 250 mm) with toluene as an eluent. We determined the yields of $C_{60}CPhCl$ and $C_{60}Ad$ by HPLC analysis and the yields of $C_{60}CPh(n\text{-}Bu)$ and (*E*)-1-pheny-1-pentene by ^1H NMR measurement of the reaction mixture. We synthesized phenylchlorodiazirine, phenyl-*n*-butyldiazirine, and 2-adamantane-2,3′-[3*H*]diazirine by a previously reported procedure.[8]

Thermolysis of Phenylchlorodiazirine with C_{60}. We heated a toluene solution of phenylchlorodiazirine **1** (1.0 mg, 2.5×10^{-4} M) and C_{60} (36 mg, 2.5×10^{-3} M) at 100 °C for 18 h under darkness in a Pyrex tube. The use of a Buckyprep column in the HPLC analysis demonstrates that the adduct **4** is obtained in 99% yield. The NMR of **4** has been reported; see ref 5.

Thermolysis of Phenyl-*n*-butyldiazirine with C_{60}. We heated an *o*-dichlorobenzene/C_6D_6 (10/1) solution of phenyl-*n*-butyldiazirine (**2**, 0.2 mg, 2.7×10^{-3} M) and C_{60} (8.5 mg, 2.7×10^{-2} M) at 80 °C in a sealed NMR tube for **7** h under darkness. ^1H NMR measurement of the reaction mixture and HPLC analysis with a Buckyprep column demonstrated the formation of fulleroid $C_{60}CPh(n\text{-}Bu)$ (**5a**) in 70% yield. We deduced the yield by the integrated values of NMR signals and the HPLC peaks. ^1H NMR also indicated the formation of (*E*)-1-phenyl-1-pentene (**7**, 13%), a small amount of the isomeric fulleroid (**5b**, 4%), and methanofullerene (**6**, 4%). Compound **5a**: ^1H NMR (300 MHz, CS_2/ $CDCl_3$ = 4/1) δ 7.90 (d, 2H, J = 7 Hz), 7.51 (t, 2H, J = 7 Hz), 7.38 (t, 1H, J = 7 Hz), 1.57 (t, 2H, J = 7 Hz), 1.11−1.01 (m, 4H), 0.78 (t, 3H, J = 7 Hz); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ = 4/1) δ 147.16 (s), 146.65 (s), 144.96 (s), 144.57 (s), 144.26 (s), 144.01 (s), 143.73 (s), 143.54 (s), 143.46 (s), 143.36 (s), 142.92 (s), 142.86 (s), 142.83 (s), 142.76 (s), 142.53 (s), 142.49 (s), 142.27 (s), 141.93 (s), 141.90 (s), 141.70 (s), 141.63 (s), 141.10 (s), 140.75 (s), 140.26 (s), 139.99 (s), 139.51 (s), 138.59 (s), 138.24 (s), 137.96 (s), 137.68 (s), 136.36 (s), 135.91 (s), 134.81 (s), 130.54 (d), 128.44 (d), 127.39 (d), 61.22 (s), 35.95 (t), 26.37 (t), 23.21 (t), 14.14 (q); UV−vis (λ_{max}, toluene) 330, 433, 499 nm; FAB MS (toluene/NBA), *m/z* 866 (M), 720 (C_{60}). Compound **5b**: ^1H NMR (500 MHz, ODCB/C_6D_6 (10/1)) δ 3.77 (t-like, 2H, J = 8 Hz), 0.82 (t, 3H, J = 7 Hz), other signals overlapped with major isomer signals. Compound **6**: ^1H NMR (300 MHz, $CS_2/CDCl_3$ = 4/1) δ 7.86 (d, 2H, J = 7 Hz), 7.46 (m, 3H), 2.83 (t-like, 2H, J = 8 Hz), 1.81 (m, 2H), 1.51 (m, 2H), 0.99 (t, 3H, J = 7 Hz); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ = 4/1) δ 148.65 (s), 147.84 (s), 145.66 (s), 144.99 (s), 144.94 (s), 144.92 (s), 144.84 (s), 144.61 (s), 144.58 (s), 144.52 (s), 144.46 (s), 144.27 (s), 144.23 (s), 143.86 (s), 143.57 (s), 142.94 (s), 142.85 (s), 142.80 (s), 142.74 (s), 142.06 (s), 141.93 (s), 140.83 (s), 140.57 (s), 137.87 (s), 137.42 (s), 136.94 (s), 131.95 (d), 128.21 (d), 127.96 (d), 79.93 (s), 52.36 (s), 34.12 (t), 29.24 (t), 23.21 (t), 14.37 (q). Compound **7**: ^1H NMR (500 MHz, ODCB/C_6D_6 (10/1)) δ 7.2 (5H, overlapped with solvent signals), 6.28 (d, 1H, J = 16 Hz), 6.10 (dt, 1H, J = 16, 7 Hz), 2.07 (q, 2H, J = 7 Hz), 1.40 (sext, 2H, J = 7 Hz), 0.80 (t, 3H, J = 7 Hz). We heated an *o*-dichlorobenzene/DMSO (1/1) solution of phenyl-*n*-butyldiazirine (**2**, 2.0×10^{-4} M) and C_{60} (2.0×10^{-3} M) at 80 °C in a sealed tube for 7 h under darkness. The HPLC analysis indicated the formation of fulleroid **5a** in 76% yield, which was a little higher than the yield under the same reaction condition, except for the absence of DMSO.

Thermolysis of 2-Adamantane-2,3′-[3*H*]diazirine with C_{60}. We heated an *o*-dichlorobenzene solution of 2-adamantane-2,3′-[3*H*]diazirine (**3**, 0.15 mg, 5.0×10^{-4} M) and C_{60} (7.2 mg, 5.0×10^{-3} M) at 150 °C for 1 h under darkness in a Pyrex tube. By using a Buckyprep column, the HPLC analysis demonstrates that adduct **8** and **9** are obtained in 95% yield. The HPLC analysis also showed the ratio of **8** and **9** as 35/65. For NMR of **8** and **9**, see ref 5.

Computational Methods. We performed geometry optimizations of all stationary points associated with thermal decomposition of three diazirine compounds with the hybrid density functional theory (DFT) using the B3LYP[9] functional with 6-31G(d) basis sets.[10] The most important paths related to product distribution of substituted diazirine compounds are those for the isomerization of diazirines to diazoalkanes, for N2 extrusion from diazirine, and for the rebound of molecular nitrogen to singlet carbene (Scheme 1). We also calculated geometries of three stationary points (diazirine and saddle points for paths I and II) by the complete active space self-consistent field (CASSCF)[11] method using the 6-31G(d) basis sets, since the transition state for the isomerization of diazirine to diazoalkane is not well described by density functional theory because of its multiconfigurational character. The molecular orbitals that constitute the active space of CASSCF calculations are shown in Figure 1. These orbitals are characterized by one σ(N−N), one π(N−N), and two σ(C−N) orbitals and their antibonding counterparts. Thus, eight electrons are distributed among eight orbitals. We use the notation CASSCF(8,8) to denote the active space of CASSCF calculations, where the first number in parentheses represents the number of active electrons, while the second is the number of the active orbital. Since CASSCF calculations do not account for dynamical correlation, energies were improved by using the second-order multireference Møller−Plesset (MRMP) method,[12] which is a multireference generalization of single reference MP2 theory. Hereafter, we will use the notation MRMP(8,8)/6-31G(d)//CASSCF(8,8)/6-31G(d), which means that the energies are calculated at the MRMP(8,8)/6-31G(d) level on the geometries optimized at the CASSCF(8,8)/6-31G(d) level.

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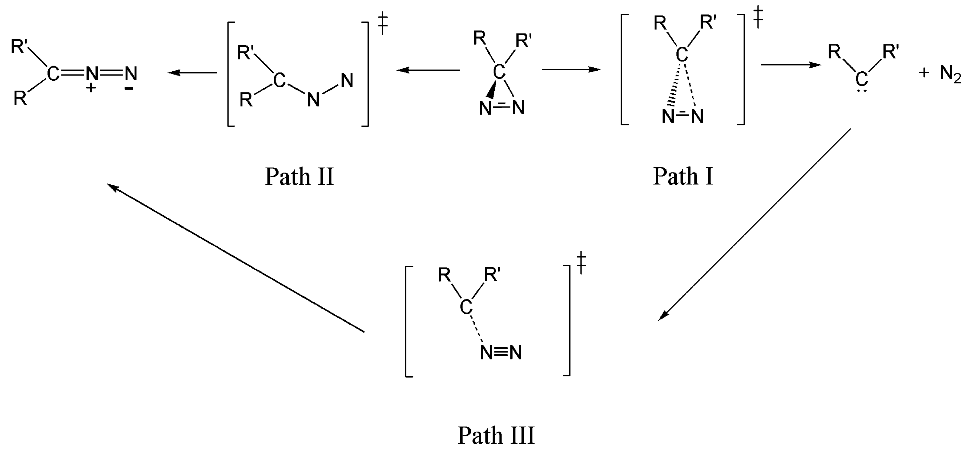
SCHEME 1



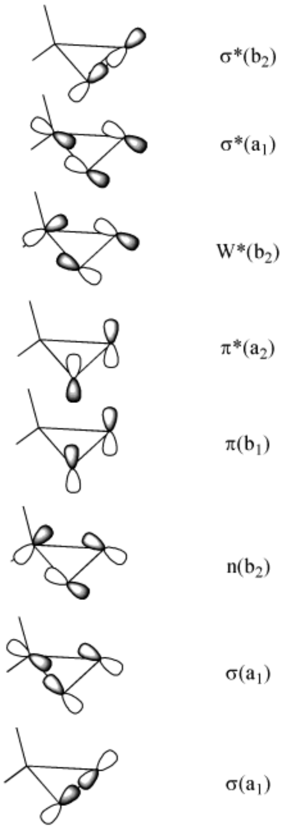
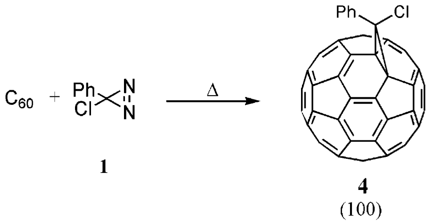


FIGURE 1. Active orbitals of diazirine considered for CASSCF-(8,8) and MRMP(8,8) calculations. Notation of orbitals are adopted from C_{2v} symmetry.

As the thermodynamic data of transition states, zero-point corrected energies ($\Delta E^{\ddagger}_{\text{zero}}$), enthalpies ($\Delta H^{\ddagger}$), entropies ($\Delta S^{\ddagger}$), and Gibbs free energies ($\Delta G^{\ddagger}$) were evaluated using harmonic vibrational frequencies and geometries calculated at the CASSCF(8,8)/6-31G(d) level and energies ($\Delta E^{\ddagger}$) calculated at the MRMP(8,8)/6-31G(d)//CASSCF(8,8)/6-31G(d) level. We performed MRMP calculations with the MR2D[13] program implemented in the GAMESS[14] code. We carried out CASSCF and B3LYP calculations with the Gaussian 98 program.[15]

SCHEME 2



Results and Discussion

Numerous chemical transformations have been developed since the isolation of C_{60} in preparatively useful quantities.[16,17] C_{60} has a unique reactivity, which differs significantly from that of classical planar aromatics. C_{60} reacts with carbenes to yield methanofullerene and with diazomethane to yield fulleroid.[18] These results obtained from chemical derivatization of C_{60} by diazirine are in agreement with all the laser flash photolysis work reported previously,[19] which means that C_{60} acts as a chemical probe for the photochemical reactions of diazirine.[5]

To test C_{60} as a chemical probe in the thermal reaction, we carried out an experiment using a diazirine in which

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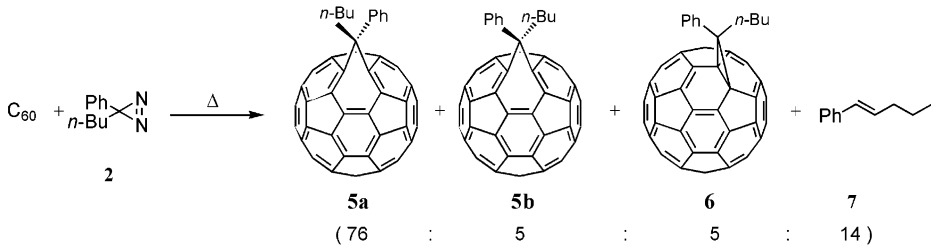
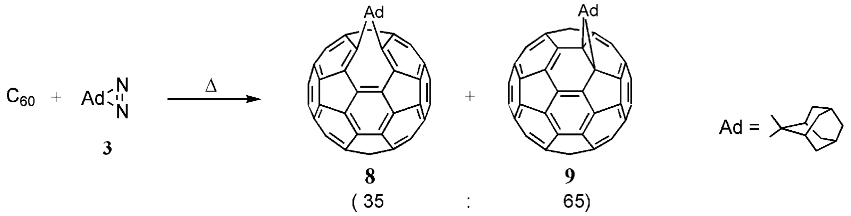
SCHEME 3



SCHEME 4



a thermal decomposition pathway had been already characterized.[7b,20] We carried out the thermal decomposition of phenylchlorodiazirine (**1**) in the presence of C_{60}, because this diazirine produces phenylchlorocarbene as the sole product. The reaction of **1** with C_{60} at 100 °C in toluene in darkness affords the corresponding adduct C_{60}-CPhCl (**4**) in 99% yield (Scheme 2). The HPLC analysis and NMR spectroscopic investigation verify that **4** is a methanofullerene of C_{60}. This agrees with the intermediacy of the carbene as the sole product of thermolysis, because the isomeric diazo compound would presumably give rise to both fulleroid and methanofullerene. On the basis of these observations, we propose using C_{60} to measure carbene/diazo compound partitioning, which operates not only in the photolysis of diazirine but also in the thermolysis of diazirine.

To investigate the thermal rearrangement of diazirine to diazo compound, we carried out the thermolysis of phenyl-*n*-butyldiazirine (**2**) in *o*-dichlorobenzene/C_6D_6 in the presence of C_{60}. The HPLC analysis using a Buckyprep column showed the formation of fulleroid C_{60}CPh-(*n*-Bu) (**5a**) in 70% yield (Scheme 3). The stereostructure of fulleroid **5a** with the *n*-butyl group located above the five-membered ring was confirmed by ^{1}H NMR.[21] The yield of fulleroid **5a** was 76% when DMSO was used as solvent. In addition, we detected 4% of methanofullerene **6**, 4% of the minor fulleroid **5b**, and 13% of (*E*)-1-phenyl-1-pentene (**7**). These results indicate that the major decomposition pathway for diazirine **2** is the formation of diazomethane, in agreement with the thermal decomposition of the compound.[7b] The rate constant for 1,2-H migration is not known for *n*-Bu-C-Ph, but it should be similar to the lifetime for *n*-propyl-C-Ph in pentane, which has been reported to be $\tau = 114$ ns at 25 °C.[22] With such a long lifetime, the carbene produced by thermolysis of diazirine **2** should be quantitatively trapped by C_{60} to give methanofullerene. We concluded, therefore, that the formation of (*E*)-1-phenyl-1-pentene results from the direct thermal rearrangement of diazirine without the participation of a carbene. In addition, if the rate constant for 1,2-H migration for *n*-Bu-C-Ph is taken to be 8.8×10^6 s^{-1} based on ref 22 and log $A = 11.0$,[4c] this leads to a value of 5.5 kcal/mol for the activation energy for the 1,2-H migration. This is in agreement with the value of 6.6 kcal/mol derived from our calculation; see Figure 2.

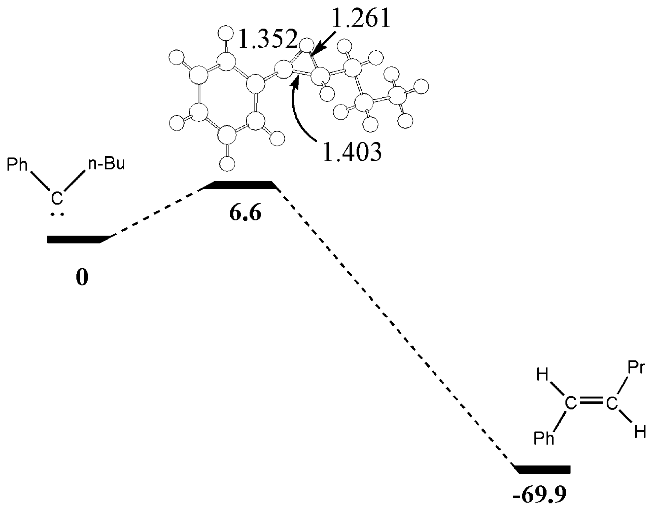


FIGURE 2. Energy profile (kcal/mol) for 1,2-H migration in *n*-Bu-C-Ph. Calculations were performed at the B3LYP/6-31G(d) level.

The reaction of a 1,2-dichlorobenzene solution of 2-adamantane-2,3′-[3*H*]-diazirine (**3**, 5.0×10^{-4} M) and C_{60} (5.0×10^{-3} M) at 150 °C in a Pyrex tube in darkness resulted in the formation of the corresponding adduct C_{60}Ad in 95% yield, which we purified by a preparative HPLC with a GPC column. Adduct C_{60}Ad can be readily separated into two isomers, **8** and **9**, by preparative HPLC with a Buckyprep column (Scheme 4). The HPLC analysis also showed that the ratio of **8** and **9** is 35/65.

Inasmuch as fulleroid easily rearranges to methanofullerenes, we carried out thermolysis of pure **8** and **9** by themselves. We observed no interconversion occurring between **8** and **9** under thermal conditions.

The thermal decomposition of the diazoadamantane to adamantylidene is negligible under the present experi-

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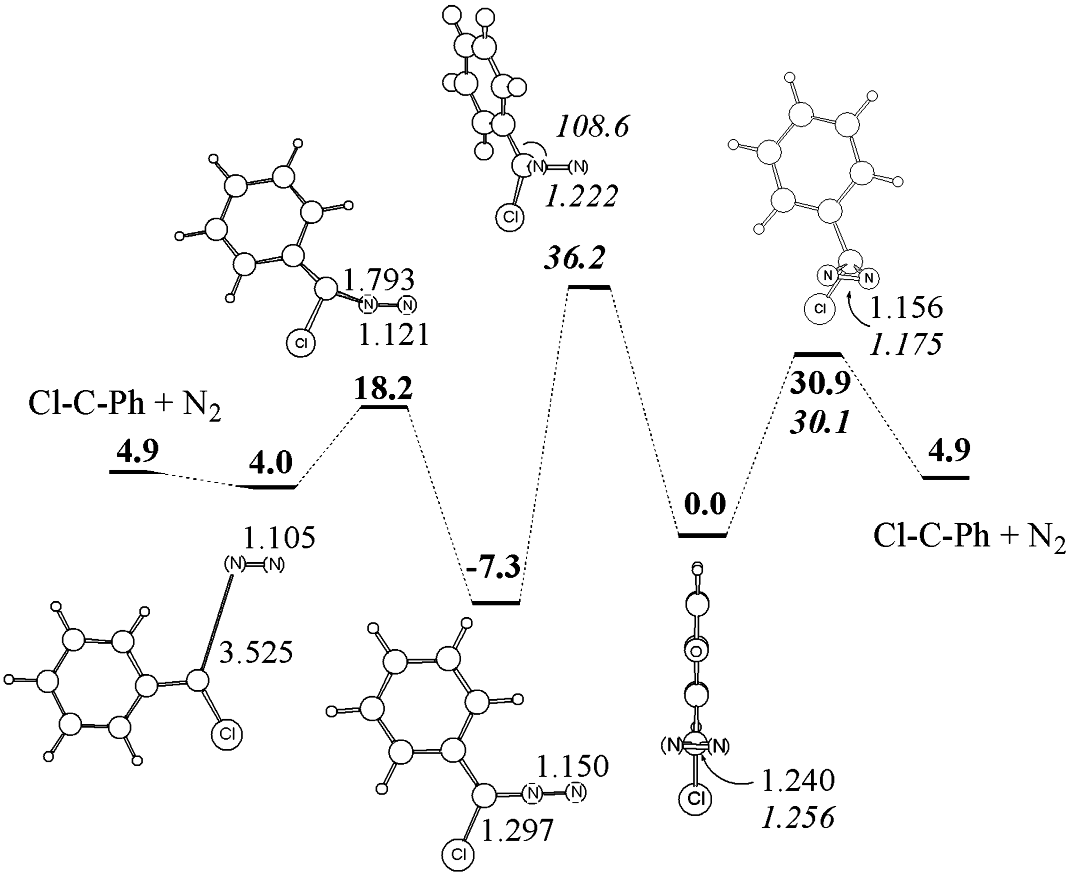

FIGURE 3. Energy profile (kcal/mol) of thermal decomposition of **1** calculated at the B3LYP/6-31G(d) level. Italic values are at the MRMP(8,8)/6-31G(d)//CASSCF(8,8)/6-31G(d) level.

mental conditions, because diazoadamantane is rapidly trapped by C_{60} to give fulleroid **8**. This is supported by the fact that we do not detect azine among the products, whereas in the absence of C_{60}, diazoadamantane forms azine by a slow second-order reaction.[19] On the basis of these observations, the isomeric ratio of **8** and **9** (35:65) in the thermal reaction of C_{60} with diazirine **3** reveals the formation ratio of diazo compound and carbene during the reaction. In view of these results, 2-adamantane-2,3′-[3*H*]diazirine gives carbene in preference to the diazo compound upon thermal activation.

We calculated the thermal decomposition of phenylchlorodiazirine (**1**), phenyl-*n*-butyldiazirine (**2**), and 2-adamantane-2,3′-[3*H*]diazirine (**3**) with density functional theory (DFT) and ab initio methods.

The energy profile of the thermal decomposition of **1** is illustrated in Figure 3. The barrier height for path II was computed to be 36.2 kcal/mol, which is 6.1 kcal/mol higher than that of 30.1 kcal/mol for path I at the MRMP(8,8)/6-31G(d)//CASSCF(8,8)/6-31G(d) level. The weak complex of carbene and molecular nitrogen can be transformed into diazoalkane. The barrier for the recombination of carbene and nitrogen in path III was computed to be 14.3 kcal/mol. These calculations suggest that the main product of thermal decomposition of phenylchlorodiazirine is carbene, which is directly formed by the extrusion of nitrogen from diazirine.

The case of **2** is quite different. As Figure 4 shows, the barrier for path II is 32.8 kcal/mol. This value is only 0.7 kcal/mol lower than that of 33.5 kcal/mol for path I. The dipole moment of the transition state (TS) for path II is 2.96 D, whereas that for N_2 extrusion is 1.83 D.[23] This difference in dipole moment implies that the barrier for path II with such a highly polar TS should be lowered relative to path I when the reaction occurs in a polar solvent, such as DMSO. We computed the barrier height for path III to be 5.6 kcal/mol. Owing to such a small barrier, it is to be expected that the diazoalkane can also be formed from the rebound of molecular nitrogen to carbene. These results suggest that the thermal decomposition of **2** can produce either carbene or diazoalkane, depending on the reaction condition. When **2** is treated in a polar solvent, routes for diazoalkane formation can be direct isomerization from the diazirine and the rebound of molecular nitrogen to carbene.

For **3**, the barrier height for path II is 44.1 kcal/mol, whereas the barrier for path I is 34.4 kcal/mol (Figure 5). This result indicates that diazoalkane may not be directly formed from the isomerization reaction of **3**. The barrier for path III is 2.1 kcal/mol, which is significantly lower than those for other diazirines (**1** and **2**). These results suggest that a main route for diazoalkane formation should be through path III, not through path II. It is expected that in the absence of trapping reagent, diazoalkane is easily formed from path III.

Table 1 summarizes the computed thermodynamic data on paths I and II for three diazirines. The trends of $\Delta E^{\ddagger}_{\mathrm{zero}}$, $\Delta H^{\ddagger}$, and $\Delta G^{\ddagger}$ are not significantly different from

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[23] Evaluated at the CASSCF(8,8)/6-31G(d) level.

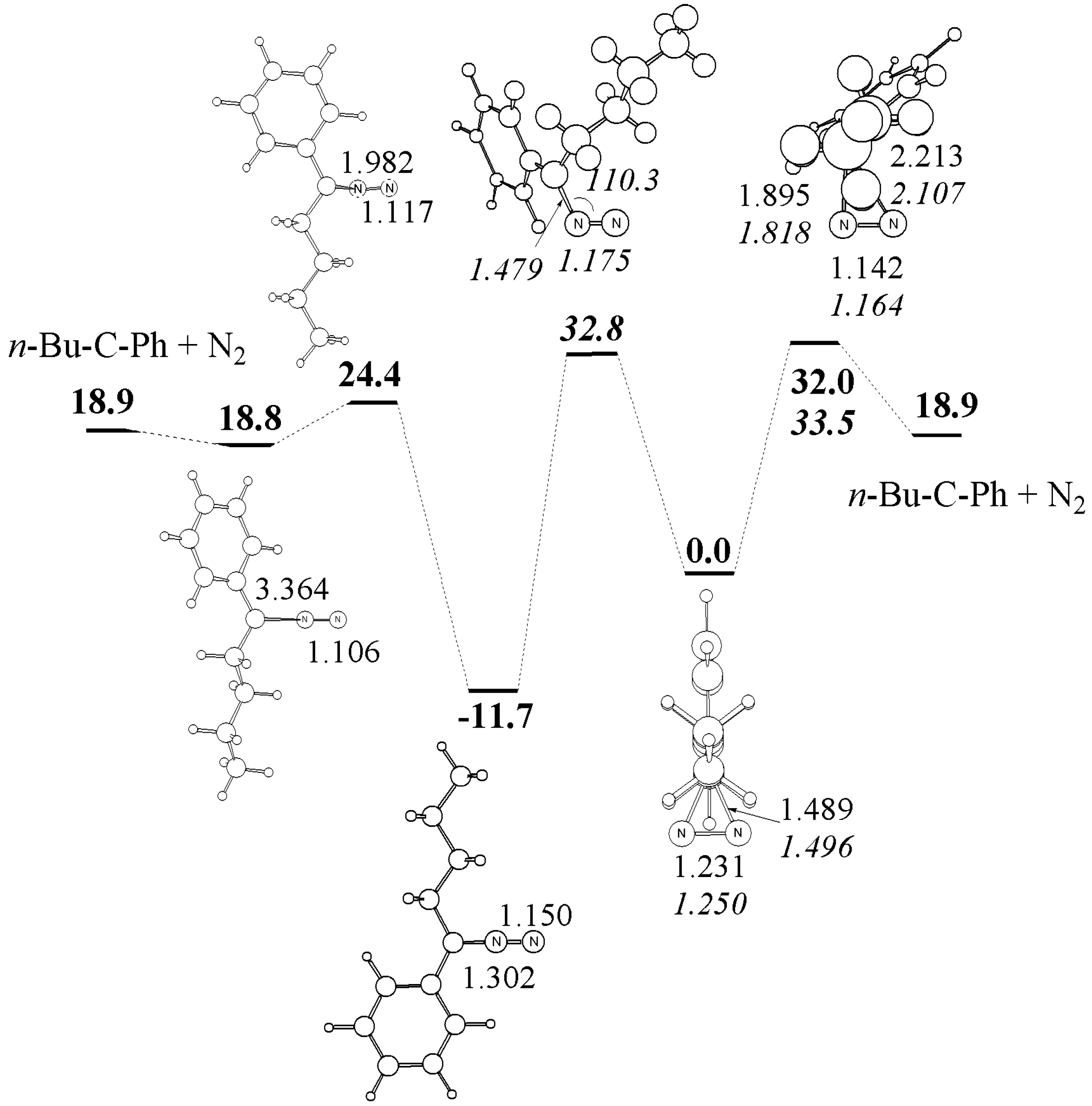

FIGURE 4. Energy profile (kcal/mol) of the thermal decomposition of **2** at the B3LYP level. Italic values are at the MRMP(8,8)/6-31G(d)//CASSCF(8,8)/6-31G(d) level.

that of $\Delta E^{\ddagger}$. The order of barrier height of **2** is slightly changed when thermodynamical properties are taken into account. The free energy barriers ($\Delta G^{\ddagger}$) for paths I and II of **2** are 30.6 and 31.6 kcal/mol at the experimental temperatures, respectively. Apparently, this small energy difference of 0.9 kcal/mol also suggests that the product distribution of **2** depends on the polarity of solvents. It has been observed for the thermal decomposition of many diazirines that the values of log *A* are in the range 13.06–14.76.[3b] Because of this remarkable similarity in *A*-factors, a common encounter complex has been postulated to explain the product distribution of the thermal decompositions of diazirines. However, calculations of *A*-factors show that log *A* is 14.38 for path I of **1**, 14.53 for path II of **2**, and 15.76 and 15.89 for paths I and II of **3**, respectively, revealing the constancy of *A*-factors. In addition, the calculated values agree reasonably well with the experimental values observed in gas and solution phases. Obviously, these results suggest that it is unnecessary to postulate an encounter complex.

Conclusion

Generally, experimental results broadly agree with theoretical predictions. The major features of the thermal decomposition of diazirines are clear. They can give predominantly carbene, a diazo intermediate, or a mixture of both, depending on the substituents on the ring. The percentage of these two competitive pathways is based solely on their energies of activation and less likely on their entropies of activation, because all thermal decomposition of diazirines have similar *A*-factors. In view of the similarity in the *A*-factors, Stevens and Liu proposed a single path leading to the formation of a carbene–nitrogen encounter complex prior to the formation of carbene or diazo compound. Our calculations do not show a local minimum in the transformation from diazirine to carbene or the diazo compound, and it is, therefore, unlikely for a complex to be formed. Our calculations indicate that the dipole moments of the transition state for isomerization and that of the N_2 extrusion are not much different, so that these two

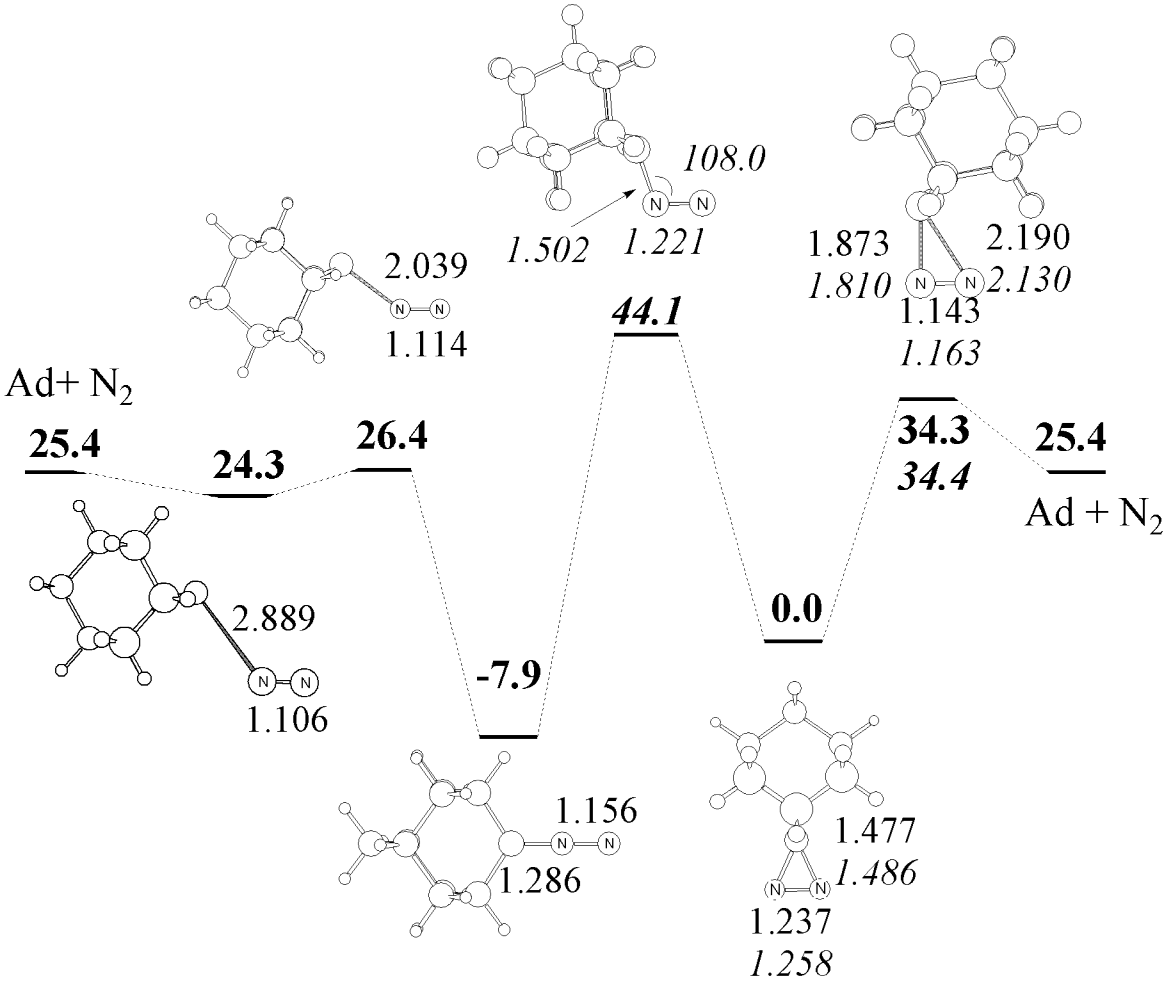

FIGURE 5. Energy profile (kcal/mol) of thermal decomposition of **3** at the B3LYP level. Italic values are at MRMP(8,8)/6-31G-(d)//CASSCF(8,8)/6-31G(d) level.

TABLE 1. Calculated Thermodynamic Data on the Thermal Decomposition of Diazirines at Room Temperature[a]

diazirine	product	$\Delta E^{\ddagger}$	$\Delta E_{\text{zero}}{}^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$
PhClCN$_2$ (**1**)	diazo compd	36.2	34.0	34.9 (35.1)	9.0 (9.6)	32.3 (31.3)
	carbene	30.1	27.7	28.6 (28.9)	8.4 (9.2)	26.1 (25.2)
Ph(*n*-Bu)CN$_2$ (**2**)	diazo compd	32.8	31.1	31.1 (31.4)	−1.0 (−1.1)	31.4 (31.5)
	carbene	33.5	30.9	31.2 (31.3)	1.7 (1.9)	30.7 (30.6)
AdN$_2$ (**3**)[b]	diazo compd	44.1	42.1	42.3 (42.3)	4.5 (4.4)	41.0 (40.3)
	carbene	34.4	32.1	32.4 (32.5)	3.6 (3.8)	31.4 (30.8)

[a] Given in parentheses are values calculated at the experimental temperature; **1**, 100 °C; **2**, 80 °C; **3**, 150 °C. All values are in kcal/mol, except for $\Delta S^{\ddagger}$ in cal/mol K.

pathways cannot be distinguished by examining their entropies of activation alone. Frey and Steven[24] showed that in the gas-phase photolysis of alkyldiazirines, two paths to the product are essential in order to account for the energy distribution of the products. Figuera has confirmed this conclusion by more extensive analyses.[25] Our present result on the thermal decomposition of diazirine **3** also required there be two paths to account for the product formation.

Our calculations have also shown that the activation energy of the rebound reaction of carbene and nitrogen (2.2−14.3 kcal/mol) in the gas phase depends solely on the substituent on the ring. Amrich and Bell[26] photolyzed 3-H diazirine in the gas-phase under nitrogen using monochromatic light of 320 nm. By monitoring the UV spectrum they detected the formation of diazomethane. They claim that most of the excited diazirine decomposed to methylene and nitrogen, while some isomerized to the excited diazomethane. The latter could either decompose to methylene and nitrogen or be stabilized by collision. From the quantum yield of products they concluded that about 20% of the primary decomposition of diazirine proceeds by isomerization to diazomethane. These results are at variance with those of Moore and Pimentel,[27] who

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(24) Frey, H. M.; Stevens, D. R. *J. Chem. Soc.* **1963**, 3514; **1964**, 4700; **1965**, 1700 and 3101.

(25) Figuera, J. M.; Perez, J. M.; Tobar, A. *AnQuim.* **1976**, *72*, 737; *J. Chem. Soc., Faraday Trans 1* **1978**, *74*, 809.

(26) Amrich, M. J.; Bell, J. A. *J. Am. Chem. Soc.* **1964**, *86*, 292.

carried out the photolysis of diazirine in a solid nitrogen matrix. They detected diazomethane but concluded from results using a ^{15}N matrix that it derived from the reaction of methylene and nitrogen. In 1968, Shilov and co-workers[28] photolyzed diazirine in ^{15}N-labeled nitrogen and deduced an E_a of 8 kcal/mol for the reaction of singlet CH_2 with N_2, but Laufer and Okabe later revised this figure to 3.1 kcal/mol for the same reaction.[29] The thermal decomposition of diazirine may give carbene, a diazo intermediate, or a combination of both, depending on the substituents on the ring. On rare occasion, thermally excited diazirine rearranges directly to product without forming the carbene as an intermediate.

In the photolysis of dimethyldiazirine, Modarelli et al.[30] proposed that the diazirine is excited to a S_1 singlet state, which can be thought of as a biradical. The biradical would probably have a lifetime of several picoseconds and may not appear as a minimum in the calculation.[31] This biradical can isomerize to dimethyldiazomethane, extrude nitrogen to form dimethylcarbene, or rearrange directly to propene in concert with the loss of nitrogen. Our thermolysis results are in agreement with the model of Modarelli et al. Apart from the extra energy involved, the considerable similarity in overall results between photolysis and thermolysis strongly suggests that the intermediates involved are indeed the same. It is noteworthy that it is the change in the ratio of these paths that gives rise to the change in product composition between photolysis and thermolysis. The importance of this occurrence lies in the fact that our experimental results support their model, which only explains the course of various elementary processes in the photolysis of diazirines. Our studies have demonstrated that this hypothesis can be extended to the investigation of thermolysis as well.

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Supporting Information Available: Spectroscopic data of **5a** and **6** and tables of total energies and atomic coordinates of the compounds in Figures 2−5. This material is available free of charge via the Internet at http://pubs.acs.org.

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