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Experimental and Computational Study of the Intramolecular Reactivity of Free *tert*-Butylphenylmethylene. Modification of the Chemistry of *tert*-Butylmethylene by the Introduction of a Phenyl Group

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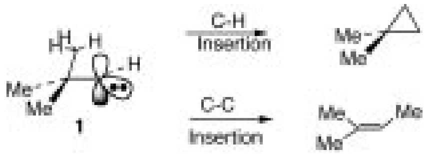
The chemistry of *tert*-butylphenylmethylene, **2**, has been investigated experimentally and computationally. Free carbene **2** was generated by the thermal rearrangement of *p-tert*-butylphenylmethylene and observed to rearrange by C−H insertion to give 1,1-dimethyl-2-phenylcyclopropane, **3**, and by C−C insertion to yield 2-methyl-3-phenyl-2-butene, **4**. An examination of the **3**:**4** ratio led to the conclusion that C−H insertion is favored over C−C insertion by 1.6 ± 0.1 kcal/mol in good agreement with a calculated (PMP2/6-31G(d)//MP2/6-31G(d)+ZPC/6-31(d)) value of 2.0 kcal/mol. The S−T gap in **2** is estimated to be 5−6 kcal/mol.

Carbenes are among the most energetic of reactive intermediates. However, they are often surprisingly selective in their intramolecular reactivities, and there is evidence that this selectivity is often imposed by the geometry of the carbene. Common routes from carbenes to kinetically stable products include insertion into bonds α to the carbene center to give alkenes and insertion into more remote bonds generating cyclic products.[1] Although carbenes with α hydrogens generally rearrange by a C−H insertion, carbene geometries can force other pathways. Examples include cyclopropylmethylene[2] and cyclobutylidene,[3] which rearrange predominately by α C−C insertion as a result of geometries in which orbital interactions favor C−C insertion.[1] In 2-norbornylidene a favorable overlap between a *β* C−H bond and the carbene p orbital leads to a *β* C−H insertion.[3d,4]



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In some cases it appears that the high energy of carbenes requires particular geometries for stabilization and that these geometries lead, in turn, to preferred reactivities. An example is *tert*-butylmethylene, **1**, in which intramolecular insertion into a *β* C−H bond is strongly preferred over insertion into an α C−C bond.[5] Calculations indicate that the $\Delta H^{\ddagger}_{\mathrm{C-C}} - \Delta H^{\ddagger}_{\mathrm{C-H}}$ of 3.7 kcal/mol is such that C−C insertion is only possible at elevated temperatures. Our own experimental results[5] and those of Glick, Likhotvorik, and Jones[6] confirm these predictions. In this case, calculations reveal an unusual geometry for the carbene in which an adjacent C−C bond is strongly bent toward the empty p orbital. Geometry optimization of **1** at the MP2/6-31G(d) level gives a bond angle of 79.8°. A comparison of the geometry of the carbene with that of the transition state for intramolecular C−H insertion reveals that they are quite similar. This fact appears to be responsible for an extremely low barrier to C−H insertion, strongly favoring it over C−C insertion. In this case, it appears that the factors that stabilize the carbene are similar to those that stabilize the corresponding carbocation.

We have now extended these investigations from *tert*-butylmethylene to *tert*-butylphenylmethylene, **2**. It is clear that going from an alkyl to a dialkyl or phenylalkyl carbene will increase carbene lifetimes and consequently the barrier to intramolecular reactions. For example, the calculated barrier to H migration in methylcarbene is ∼1 kcal/mol,[7] while it is ∼5 kcal/mol in dimethylcarbene[7a,8,9] and in phenylmethylcarbene.[10] However in the present study, we are asking what the effect of the addition of a phenyl group will have on two competing intramolecular pathways. On going from **1** to **2**, a change in carbene geometry may alter the ratio of 1,3 C−H to 1,2 C−C insertion. In this case, it seems reasonable that the

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Table 1. Relative Energies (kcal/mol) of Species on the Phenylcarbene and *tert*-Butylphenylcarbene Potential Energy Surface

	HF/6-31G(d)// HF/6-31G(d)	B3LYP/6-31G(d) //MP2/6-31G(d)	+ZPE/6-31G(d)[a]	PMP2/6-31G(d)// MP2/6-31G(d)	+ZPC/6-31G(d)[a]	C_p[b]	entropy[c]
phenylcarbene singlet	0.0	0.0	0.0	0.0	0.0	3.81	73.20
phenylcarbene triplet	−34.1	−5.7	−7.5	−6.0	−7.8	3.98	76.22
singlet **2** (**2a**)	0.0	0.0	0.0	0.0	0.0	6.67	100.85
triplet **2** (**2d**)	−38.7	−9.2	−10.7	−6.5	−8.0	7.32	102.95
$\mathbf{TS_{2-3}}$	18.4	6.7	5.5	3.0	1.8	6.06	95.99
$\mathbf{TS_{2-4}}$	19.4	8.0	7.4	4.4	3.8	6.34	98.44
2b	0.2	1.9	1.9	1.8	1.8	6.17	96.02
2c	2.8	4.0	3.3	3.7	3.0	5.75	92.47

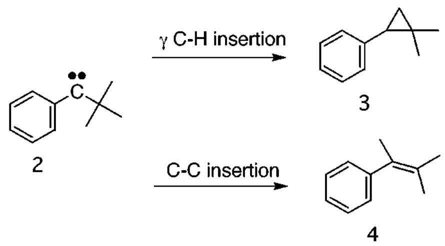
[a] Zero-point corrections (scaled by 0.90 factor) are included in relative energies. [b] Integrated heat capacities (kcal/mol) to 298 K from unscaled HF/6-31G(d) vibrational frequencies. [c] Entropies in units of cal/(mol·K) calculated using unscaled HF/6-31G(d) vibrational frequencies.

Table 2. Thermodynamic Properties and Free Energy Differencies (kcal/mol)

	PMP2/6-31G(d)// MP2//6-31G(d) +ZPC/6-31G(d)	C_p[a]	entropy[b]	ΔG(298 K)	ΔG(500 K)[c]
Ph−C−tBu singlet (C_1)	0.0	6.67	100.85	0.0	0.0
$\mathbf{TS_{2-3}}$	1.8	6.34	98.44	2.2	2.7
$\mathbf{TS_{2-4}}$	3.8	6.06	95.99	4.6	5.6
2b	1.8	6.17	96.02	2.7	3.7
2c	3.0	5.75	92.47	4.6	6.3

[a] Integrated heat capacities (kcal/mol) from HF/6-31G(d) vibrational frequencies. [b] Entropies in units of cal/(mol·K) calculated using HF/6-31G(d) vibrational frequencies. [c] Free energy differences (kcal/mol) estimated from $\Delta G(500) \approx \Delta H(298\ \text{K}) - 500\Delta S(298\ \text{K})$.

presence of the phenyl group, with its strong propensity for stabilization of an adjacent empty p orbital, may reduce the need for stabilization by adjacent σ bonds and consequently raise the barrier to intramolecular C−H relative to C−C insertion. We now report an experimental and computational investigation of **2** which provides evidence to support this hypothesis.



Results and Discussion

Computational Investigations of the Energy and Reactivity of 2. We have carried out a computational study of the geometries and energies of singlet and triplet **2** and have investigated the rearrangement of **2** by C−H insertion to give 1,1-dimethyl-2-phenylcyclopropane, **3**, and by C−C insertion to yield 2-methyl-3-phenyl-2-butene, **4**. Geometries were optimized at the HF/6-31G(d) and MP2/6-31G(d) levels. Total energies relative to **2**, obtained at various computational levels, are listed in Table 1.[11] Table 2 lists thermodynamic properties and free energies of relevant species. Single-point B3LYP/6-31G(d) calculations on the MP2 geometries gave results quite similar to those of the MP2 calculations (Table 1). The geometries and energies calculated for a number of species on this energy surface are shown in Figures 1−3. Unless otherwise noted, the energies in the following paragraphs are those calculated at the MP2/6-31G(d)//MP2/6-31G(d)+ZPC level.

The minimum energy geometry calculated for singlet **2** is shown in structure **2a** in Figure 1. It is interesting that **2**, unlike phenylcarbene (PC),[12] does not adopt a conformation that allows maximum overlap between the carbene p orbital and the aromatic π orbitals. Instead, the minimum energy conformer, **2a**, has its phenyl ring twisted by 38.4° out of the plane formed by the carbene carbon and its attached atoms. Conformer **2b**, which allows maximum interaction between the carbene p orbital and the aromatic π orbitals, is calculated to lie 1.8 kcal above **2a** and has one imaginary frequency (HF/6-31G(d)). Steric interactions between the *tert*-butyl group and the ortho hydrogens appear to bring about the calculated 38.4° degree rotation about the carbon phenyl bond in **2a**. These same steric interactions increase the bond angles about the carbene carbon from 106° in PC to 119° in **2**. Similar factors appear to dictate the geometry of phenylmethylcarbene (PMC), which is calculated to have a bond angle of 116.7° and be twisted by 39.4° (BPW91/cc-pVDZ).[10,13] It is interesting that the ylid generated in the reaction of **2** with pyridine has an abnormally short wavelength $\lambda_{\max}$, which has been attributed to a large bond angle in the ylid.[14] A twisting of the phenyl group in the ylid analogous to that in the carbene could also be a factor. An alternate carbene conformation, **2c**, in which the phenyl ring is rotated to

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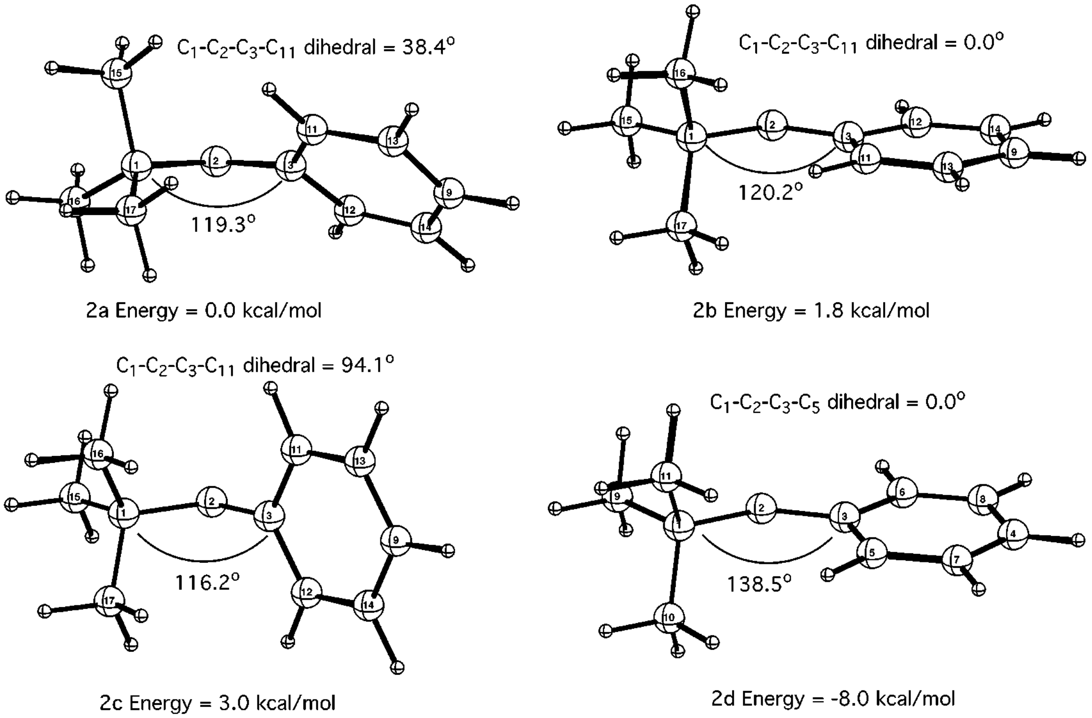


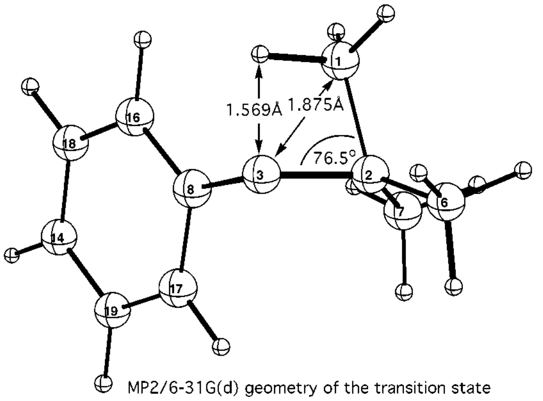
2a Energy = 0.0 kcal/mol

2b Energy = 1.8 kcal/mol

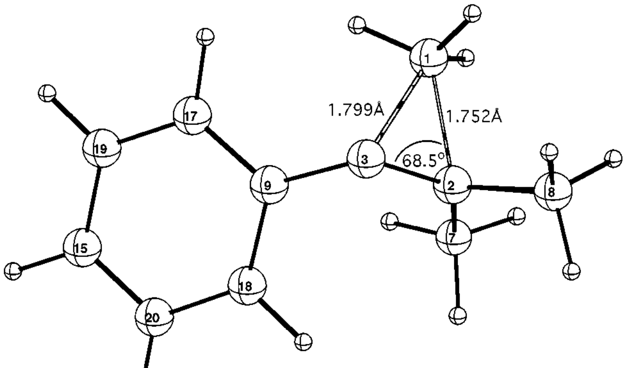
2c Energy = 3.0 kcal/mol

2d Energy = -8.0 kcal/mol

Figure 1. Energies and geometries calculated (MP2/6-31G(d)//MP2/6-31G(d)+ZPG/6-31(d)) for various conformations and electronic states of carbene **2**.

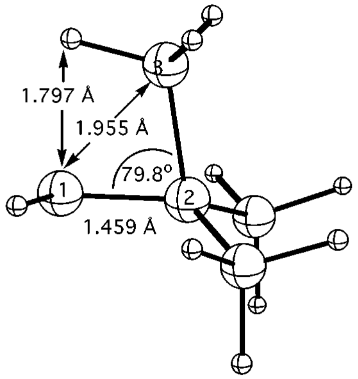


MP2/6-31G(d) geometry of the transition state for C-H insertion by 2 ($TS_{2\text{-}3}$).

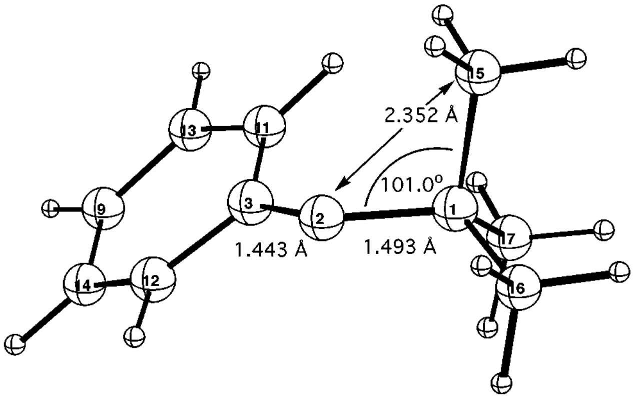


MP2/6-31G(d) geometry of the transition state for C-C insertion by 2 ($TS_{2\text{-}4}$).

Figure 2. MP2/6-31G(d) geometries of the transition states for C−H and C−C insertion by **2**.



MP2/6-31G(d) geometry of singlet 1.



MP2/6-31G(d) geometry of singlet 2.

Figure 3. Comparison of the MP2/6-31G(d) geometries of singlet **1** and **2**.

allow an overlap between the aromatic π orbitals and the filled carbene sp^2 orbital, is 3.0 kcal/mol higher in energy than **2a** and has two imaginary frequencies. Since the carbene p orbital in conformation **2c** is not stabilized by conjugation with the phenyl, one might expect stabilization by the adjacent $C-CH_3$ σ bond, as we observe in **1**. However, this interaction, with its abnormally small

C−C−CH_3 angle, would raise steric interactions between ortho hydrogens and the methyl groups and is not observed.

As expected, **2** has a triplet ground state with a singlet−triplet (S−T) splitting of 8.0 kcal/mol calculated at the PMP2/6-31G(d)//MP2/6-31G(d)+ZPC/6-31(d) level. To assess the singlet−triplet splitting accurately, we have calculated the S−T in PC at this level and compared it to our value for **2**. Recent computational studies place the S−T splitting in PC at 4−6 kcal/mol,[12] in good agreement with experiment.[15] Our PMP2/6-31G(d)//MP2/6-31G(d)+ZPC/6-31(d) value for S−T in PC is 7.8 kcal/mol, indicating that our calculated singlet−triplet gap in **2** is too high by ∼3 kcal/mol, leading to an actual value of 5−6 kcal/mol. A comparison of this S−T gap to that we have reported in **1** of 1−2 kcal/mol demonstrates that the presence of the phenyl group increases the S−T gap by 4−5 kcal/mol. In contrast to singlet **2**, the triplet adopts a geometry, **2d**, that allows maximum overlap between the carbene p orbital and the π orbitals of the ring. In this case, the phenyl ring lies in the plane formed by the carbene carbon and its attached atoms. It is probable that the ability of the triplet to accommodate a larger angle about the carbene carbon than the singlet (138.5° vs 119.3°) brings about lowered steric interactions between the *tert*-butyl group and the ring, allowing maximum overlap between the carbene p orbital and the aromatic π orbitals in the planar carbene conformer. These considerations may be responsible for an abnormally large S−T gap in **2**. In the absence of steric interactions, the addition of alkyl groups to carbene centers lowers the S−T gap.[16] Thus, we may have expected a smaller S−T gap in **2** relative to PC. However, geometry constraints placed on singlet **2** by its electronic structure increase steric interactions, raise the energy of the singlet, and increase the S−T gap.

An inspection of the minimized geometry calculated for singlet **2a** in Figure 3 reveals a Me−C_α−$C_{carbene}$ angle of 101.0°, in marked contrast to the angle of 79.8° calculated for carbene **1**.[5] While the smaller than normal Me−C_α−$C_{carbene}$ angle in **2** indicates some stabilization by the adjacent C−C σ bond, the effect is far less dramatic than in **1**. In the present case, it appears that, although the stabilization of the carbene p orbital by the phenyl is not optimal, it is sufficient to avoid the necessity of appreciable bridging by neighboring σ bonds.

This lack of stabilization by bridging in **2** leads to a ground-state geometry in **2a** which is quite different from the geometry calculated for the transition state for intramolecular C−H insertion to give **3** (**TS**$_{\mathbf{2-3}}$ in Figure 2). Thus, unlike carbene **1**, which is calculated to undergo intramolecular C−H insertion with little or no barrier, there is a higher barrier (1.8 kcal/mol) in **2**. The geometries of **1** and **2** are compared in Figure 3. A comparison of the geometries of the transition states in Figure 2 with that of **2a** reveals that geometric factors lower the differences in energies required for intramolecular C−H and C−C insertion in **2** relative to **1**. Not only do **TS**$_{\mathbf{2-3}}$ and **TS**$_{\mathbf{2-4}}$ have substantially smaller Me−C_a−$C_{carbene}$ angles than **2a** (76.4° and 68.5°, respectively) but the phenyl groups have rotated completely out of the plane formed by the carbene carbon and its attached atoms. In the present case, the energy required to reach the transition state for C−C insertion (**TS**$_{\mathbf{2-4}}$ in Figure 2) of 3.8 kcal/mol is only 2.0 kcal/mol higher than that required for C−H insertion. This is an energy difference that can be evaluated experimentally. In the following paragraphs we report our efforts to make this evaluation.

Experimental Investigations of the Energy and Reactivity of 2. A persistent problem in examining carbene reactivity is the fact that one must take care to ensure that it is the reactions of the free carbene rather than those of a precursor that are being studied.[14,17] This seems to be a particular problem in the case of nitrogenous carbene precursors (diazo compounds and diazirines) in which the precursor, either in its ground or excited state, also yields carbene type products. This problem has been circumvented in two general ways. The first is simply to avoid the use of nitrogenous precursors and employ alternatives such as the deoxygenation of carbonyl compounds by atomic carbon[5,18,19] and cheleotropic extrusion of carbenes from cyclopropanes.[6,19] The second approach is to use a nitrogenous precursor followed by rearrangement to a new carbene that is distinctively separated from its precursor on the reactive energy surface. This method has been used successfully by generating a carbene that undergoes the phenylcarbene rearrangement[20,21] to a new carbene that is now capable of intramolecular rearrangement to stable products.[18,22] In the present investigation, we have used the second of these approaches to study **2**.

Generation of 2 by the Phenylcarbene Rearrangement. In an attempt to avoid complications associated with the chemistry of nitrogenous carbene precursors, we have followed the lead of Chambers and Jones[22] and generated **2** by the phenylcarbene rearrangement of *p*-*tert*-butylphenylcarbene, **5**. The starting point for the formation of **2** was *p*-*tert*-butylbenzaldehyde tosylhydrazone lithium salt, **6**. When **6** is mildly heated, *p*-*tert*-butylphenyldiazomethane, **7**, is evolved and may then be passed into a tube furnace and pyrolyzed to yield **5**. The phenylcarbene rearrangement then converts **5** to the *m*- and *o*-*tert*-butylphenylcarbenes, **8** and **9**, and then to **2**. When Chambers and Jones[22] studied this reaction, they found that some **9** was intramolecularly trapped as dimethylindane while the remainder rearranged to **2**, which had been previously shown[23] to yield both **3** and **4**

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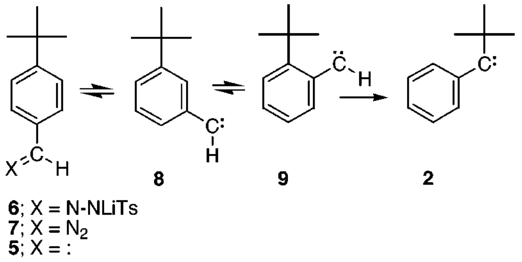

in an 85:15 ratio. Since similar products are formed in the present study, we have focused our attention on measuring the ratio of **3** to **4** as a function of temperature in order to obtain an experimental evaluation of the differences in enthalpy and entropy between the intramolecular C–C and C–H insertions.

When **2** is produced by the phenylcarbene rearrangement of **5**, the ratio of **3** to **4** decreases from 4.03 to 3.13 as the temperature is raised from 350 to 500 °C. Figure 4, which shows plot of ln(**3**:**4**) vs $1/T$ leads to a $\Delta\Delta H^{\ddagger}$ ($\Delta H^{\ddagger}_{C-C} - \Delta H^{\ddagger}_{C-H}$) of 1.6 ± 0.1 kcal/mol and a $\Delta\Delta S^{\ddagger}$ ($\Delta S^{\ddagger}_{C-C} - \Delta S^{\ddagger}_{C-H}$) of −0.2 ± 0.2 eu. Hence, C–H insertion by **2** is more favorable than C–C insertion by 1.6 ± 0.1 kcal/mol. These values are in good agreement with the calculated $\Delta\Delta H^{\ddagger}$ of 2.0 kcal/mol and in reasonable agreement with a calculated $\Delta\Delta S^{\ddagger}$ of 2.45 eu and confirm the prediction that C–C and C–H insertion are competitive in **2**.

Summary and Conclusions. The results of these investigations indicate that the introduction of a phenyl group on going from **1** to **2** lowers the difference in barriers between intramolecular C–H and C–C insertion from 3.6 to 2 kcal/mol. While part of this effect may result from the added phenyl group stabilizing the carbene and raising the barriers to intramolecular insertions, we feel that it is the dramatic differences in geometries between **1** and **2** that increase the barrier to C–H insertion relative to C–C insertion in **2**. The geometry of **2** no longer resembles that of the transition state for 1,3 C–H insertion, and the 1–2 C–C insertion now becomes competitive. Quite good agreement between experimental and computational evaluations of the difference in barrier heights for the two intramolecular reactions of singlet **2** is observed with a modest expenditure of computational resources. These investigations demonstrate that the intramolecular reactivity of free singlet **2**, like that of several other carbenes, may be rationalized by an examination of its geometry.

Experimental Section.

General Information. All ^{1}H and ^{13}C NMR were recorded on Bruker AM 250 or Bruker AM 400 spectrometers. Infrared spectra were obtained with an IR-44 IBM FT-IR. The GC/MS were recorded on a Fisons Trio 2000 quadrupole spectrometer interfaced with a Hewlett-Packard Series II 5890 gas chromatograph equipped with 30 m × 0.25 mm o.d. DB-5 column. *p-tert*-Butylbenzaldehyde was used as received from Aldrich. 1,1-Dimethyl-2-phenylcyclopropane, **3**,[24] 2-methyl-3-phenyl-2-butene, **4**,[25]1,1-dimethylindane,[26] and *p-tert*-butylbenzaldehyde tosylhydrazone[23] were prepared by literature methods.

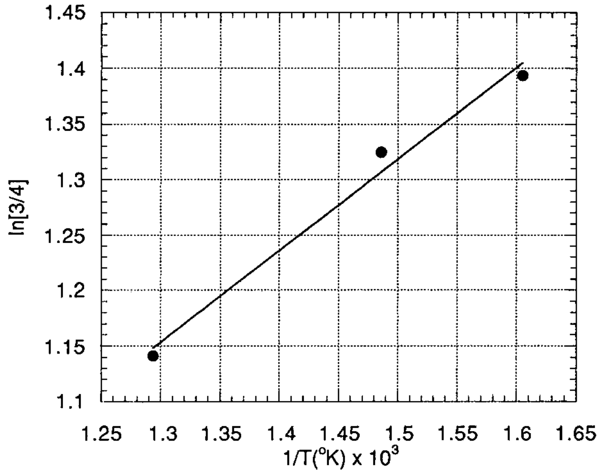

Figure 4. ln(**3**:**4**) as a function of $1/T$ in the pyrolysis of *p-tert*-butylphenyldiazomethane, **7**.

Pyrolysis of *p-tert*-Butylbenzaldehyde Tosylhydrazone Lithium Salt, 6. All surfaces of the reaction vessel, including the quartz chips packed into the pyrolysis tube, were cleaned with a solution of ethanol and potassium hydroxide (base bath), rinsed with tap water, and oven-dried prior to initial use. The pyrolysis tube and packing were not cleaned between uses, and the system was left under vacuum between uses. *p-tert*-Butylbenzaldehyde tosylhydrazone lithium salt, **6** (0.5 mmol), was placed in a reservoir which could be heated by means of an oil bath. This reservoir was connected directly to the pyrolysis tube which extended into a tube furnace. The reservoir containing the salt was heated to 125 °C over 1 h. While the reservoir was heating, the pressure slowly increased from 5 to 55 mTorr at 105 °C and then decreased from that point. The diazo compound, **7**, generated by heating the lithium salt was pyrolyzed at 623, 673, and 773 K. Three products, 1,1-dimethylindane, 1,1-dimethyl-2-phenylcyclopropane, **3**, and 2-methyl-3-phenyl-2-butene, **4**, were generated. Products were identified by a comparison of their ^{1}H and ^{13}C NMR and GC/MS with those of authentic samples. The following ratios of **3**:**4** were determined by GC and are the result of 4–7 experiments at each temperature: 4.03 ± 0.11 (623 K); 3.67 ± 0.07 (673 K); 3.13 ± 0.15 (773 K).

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Supporting Information Available: Total energies (hartrees) at the HF/6-31G(d)//HF/6-31G(d), PMP2/6-31G(d)//MP2/6-31G(d), and B3LYP/6-31G(d)//MP2/6-31G(d) levels and zero-point energies (kcal/mol) at the HF/6-31G(d) level are given in Table S1 for various species. Cartesian coordinates of structures optimized at the MP2/6-31G(d) level are also included (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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