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Rearrangement Pathways of 2-Hydroxy-2-methylpropylidene: An Experimental and Computational Study

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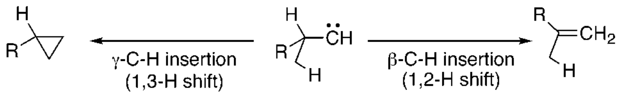
Photolysis of *exo*-2-(1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthren-1-yl)propan-2-ol in benzene-d_6 afforded phenanthrene and the β-hydroxycarbene intermediate 2-hydroxy-2-methylpropylidene. The carbene showed an overwhelming preference for 1,2-methyl migration as evident from the formation of 2-butanone as the major product via the enol 2-hydroxy-2-butene. Also produced, albeit in smaller amounts, were 1-methylcyclopropanol and 2,2-dimethyloxirane from intramolecular insertion into the C−H and O−H bonds, respectively. These results stand in sharp contrast to the intramolecular reactions of simple alkylcarbenes which usually prefer insertion into C−H bonds over 1,2-alkyl migrations. Calculations at the B3LYP/6-311+G**//B3LYP/6-31G* level of theory give a lower activation barrier for 1,2-methyl migration leading to the eventual formation of 2-butanone than for the other two pathways. The lower activation energy for methyl migration, relative to C−H and O−H insertions, strongly supports the observed experimental product distribution of the carbene. The parent carbene exists in three distinct conformations, each with stabilizing interactions between the adjacent bonds and the empty p orbital and the filled sp^2 orbital of the carbene center. The most stable conformer is perfectly poised for a 1,2-methyl migration as the C−CH_3 group is involved in a hyperconjugative interaction with the empty p orbital and the O−H bond is simultaneously interacting with the sp^2 lone pair of the carbene.

I. Introduction

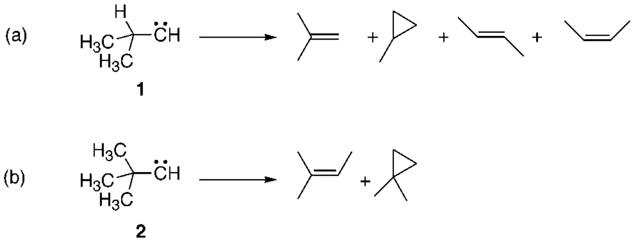
Insertions into β-C−H bonds to form olefins and, where possible, into γ-C−H bonds to form cyclopropanes are among the most common intramolecular reactions of many singlet alkylcarbenes (Scheme 1).[1] Notably, however, alkyl migrations to the divalent carbon are much less common in simple, acyclic alkylcarbenes, and do not appear to compete effectively against hydrogen migrations.

For instance, isopropylcarbene (**1**) may undergo a 1,2-H migration to produce isobutylene, 1,3-C−H insertion to produce 1-methylcyclopropane, or 1,2-methyl migration to give *cis*- and *trans*-2-butenes (Scheme 2a). Experimentally, however, the thermal and photochemical decomposition of a number of different precursors to isopropylcarbene leads to 1-methylcyclopropane and isobutylene as the dominant products with very little, if any, of the 2-butene isomers produced.[2]

Scheme 1



Scheme 2



Replacing the β-H of isopropylcarbene with a methyl group gives *tert*-butylcarbene (**2**), whose intramolecular chemistry is even more limited (Scheme 2b). *tert*-Butylcarbene can only undergo a 1,2-methyl migration to give 2-methyl-2-butene and a 1,3-C−H insertion to give 1,1-dimethylcyclopropane. However, the experimental results are most interesting. Thermal decomposition of a variety of precursors under several different conditions has

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(1) For an overview see: (a) Kirmse, W. *Carbene Chemistry*; Academic: New York, 1971. (b) *Carbenes*; Jones, M., Jr., Moss, R., Eds.; Wiley: New York, 1973; Vol. 1. (c) Moss, R. A. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Stamford, CT, 1994; Vol. 1, p 59. (d) Bonneau, R.; Liu, M. T. H. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Stamford, CT, 1998; Vol. 2, p 1. (e) Platz, M. S. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Stamford, CT, 1998; Vol. 2, p 133.

(2) (a) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1959**, *81*, 5512. (b) Kirmse, W.; Doering, W. von E. *Tetrahedron* **1960**, *11*, 266. (c) Friedman, L.; Berger, J. G. *J. Am. Chem. Soc.* **1961**, *82*, 492. (d) Friedman, L.; Berger, J. G. *J. Am. Chem. Soc.* **1961**, *82*, 500. (e) Franzen, V.; Schmidt, H. J.; Merz, C. *Chem. Ber.* **1961**, *94*, 2942. (f) Kirmse, W.; von Bülow, B. *Chem. Ber.* **1963**, *96*, 3323. (g) Neuman, R. C., Jr. *Tetrahedron Lett.* **1964**, 2541. (h) Taeger, E.; Fielder, C. *Justus Liebigs Ann. Chem.* **1966**, *696*, 42. (i) Mansoor, A. M.; Stevens, I. D. R. *Tetrahedron Lett.* **1966**, 1733. (j) Kirmse, W.; von Scholtz, H. D.; Arold, H. *Justus Liebigs Ann. Chem.* **1968**, *711*, 22.

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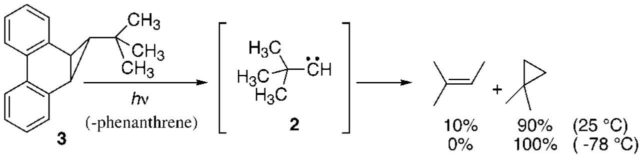
Scheme 3

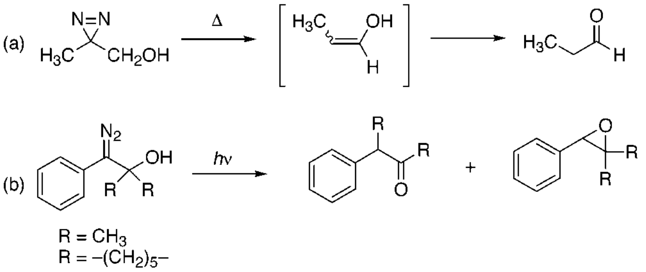


established a general preference for the formation of the cyclopropane derivative (90%) over the olefin (10%).[2d,3] Photolysis of *tert*-butyldiazomethane or *tert*-butyldiazirine, on the other hand, gives the two products in a significantly different ratio of 50:50.[3e] The latter results are clearly anomalous and are thought to be contaminated by the chemistry of the excited states of the nitrogenous precursors.[1d,e,3h] Considerable evidence has been accumulated over the years to show that the excited states of diazirines and diazo compounds can also give rise to products that were originally thought to arise from bona fide carbenes.[1d,e,4] Indeed, a more recent study of *tert*-butylcarbene, photochemically generated from a reliable non-nitrogenous source (**3**), showed the same overwhelming preference for 1,3-C−H insertion over 1,2-methyl migration (Scheme 3) as observed in the thermally generated carbene reactions.[3h] There is also a noteworthy temperature effect wherein the cyclopropane derivative is the sole product observed at −78 °C.[3g,h]

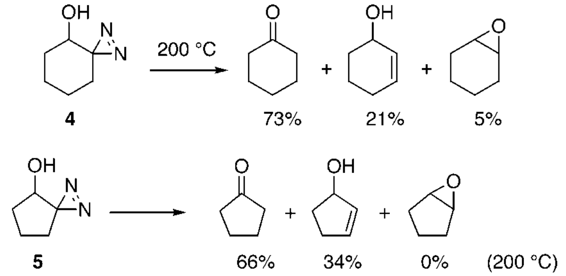
Thus, for simple acyclic carbenes, insertions into 1,2- and 1,3-C−H bonds are clearly preferred to alkyl migrations.[5] However, substituents can have a profound influence on the reactivity of carbenes.[6] In particular, electron-donating groups at the β-position are believed to accelerate 1,2-migrations of hydrogen and a phenyl ring by stabilizing the electron-deficient β-carbon in the transition state.[7] In this context, it is interesting that the introduction of a weakly electron-donating methyl group in place of hydrogen, as in going from isopropylcarbene to *tert*-butylcarbene, does not increase the preference for a 1,2-methyl migration. We, therefore, set out to examine the effect of a stronger π-electron-donating functionality, such as the OH group at the β-position, on the preference for alkyl migration vs O−H and 1,3-C−H insertion reactions.

Currently there is limited information available about the effect of β-heteroatoms on carbene reactivity.[1a,c,8] Specifically, only a few examples of (putative) β-hydroxycarbenes have been reported to date.[9,10] An acyclic β-hydroxycarbene, $HOCH_2{-}C{-}CH_3$, as generated thermally from a diazirine precursor, proceeds to rearrange exclusively via 1,2-H migration to generate propanal (Scheme 4a).[9a] Tomioka and Nunome reported the photochemical generation of a phenyl-substituted β-hydroxycarbene from the corresponding diazo precursor (Scheme 4b), and they observed an experimental 4:1 preference for alkyl (R) migration over O−H insertion and with no 1,3-C−H insertion.[9b]

Scheme 4

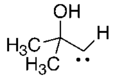


Scheme 5



Two reports[10] of β-hydroxycarbenes utilized closely related cyclic species as generated from diazirine precursors **4**[10a] and **5**[10b] (Scheme 5). In both cases, 1,2-H migrations were the dominant processes, and only small amounts of 1,3-O−H insertions were observed. Alkyl migrations, however, were conspicuously absent as evident from the lack of any ring-contracted products. However, these observations could have been due to ring-strain effects and improper orbital alignment to facilitate the alkyl migration.

In each of these previous studies,[9,10] nitrogenous precursors were utilized, and the observed product distribution may be due to species other than the desired carbene (although this is less common in thermolysis reactions). In this paper, we describe the chemistry of 2-hydroxy-2-methylpropylidene (**6**), an example of an acyclic β-hydroxycarbene, which was generated from a non-nitrogenous precursor.



6

Carbene **6** is derived by formally replacing the β-hydrogen of **1** with a hydroxyl group. As in *tert*-butylcarbene, **6** does not have the option of a 1,2-H migration.

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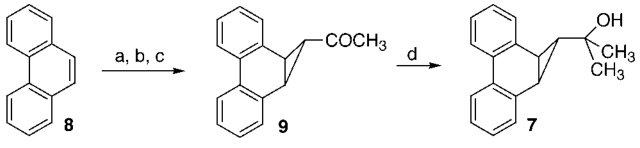
Scheme 6[a]



[a] Reagents and conditions: (a) N_2CHCO_2Et, $CuSO_4$ (cat.); (b) (1) NaOH, (2) H_3O^+; (c) (1) MeLi, (2) aqueous NH_4Cl; (d) (1) MeLi, (2) aqueous NH_4Cl.

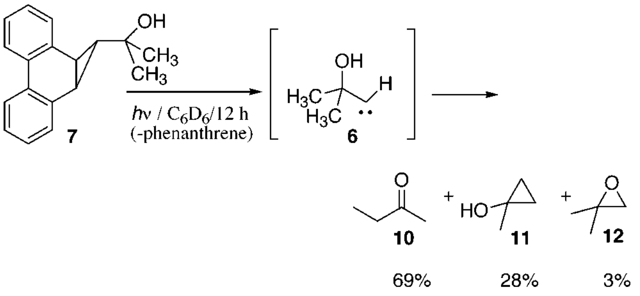
Its intramolecular reactions are limited to a possible 1,2-methyl migration as well as insertions into the γ-C−H and O−H bonds. However, in striking contrast to *tert*-butylcarbene, β-hydroxycarbene **6** shows an overwhelming preference for a methyl migration, and insertions into γ-C−H and O−H bonds are remarkably minor pathways. This interesting behavior of **6** has also been examined computationally, and the insights obtained are presented below.

II. Results and Discussion

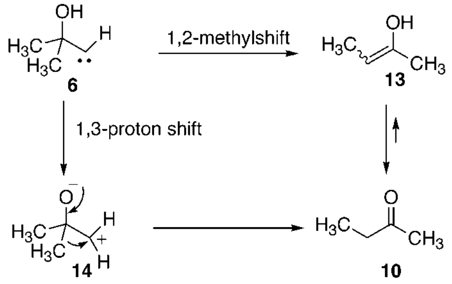
A. Synthesis of the Precursor. Cyclopropanated phenanthrene and many of its derivatives, such as **3**, have been used as reliable non-nitrogenous sources to photochemically generate several carbenes.[3h,11] Accordingly, we undertook the synthesis of *exo*-2-(1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthren-1-yl)propan-2-ol (**7**) as a precursor to the β-hydroxycarbene **6**. The synthesis of **7** was accomplished as outlined in Scheme 6. Thus, phenanthrene (**8**) was cyclopropanated with ethyl diazoacetate using $CuSO_4$ as a catalyst, and the resulting ester was hydrolyzed in situ to the corresponding carboxylic acid.[12] Treatment of the carboxylic acid with excess methyllithium followed by quenching with aqueous ammonium chloride led to the methyl ketone **9**[11h] after purification by column chromatography. The ketone was subsequently converted into the tertiary alcohol **7** by the action of methyllithium and aqueous ammonium chloride. The structure of **7** was confirmed by means of ^{1}H NMR, ^{13}C NMR, and elemental analysis. In particular, the stereochemistry of compounds **7** and **9** was established on the basis of the low *J* values of approximately 4 Hz for coupling between the two different types of protons on the cyclopropyl ring. This value is consistent with the exo substitution pattern.[13]

B. Photochemical Studies. The alcohol **7** was photolyzed in benzene-d_6 at room temperature using 1,3-benzodioxole as an internal standard. The photolyzate was monitored periodically by ^{1}H NMR spectroscopy until the starting material had completely disappeared. Typically, the starting material was consumed in approximately 12 h. Analysis by ^{1}H NMR of the photolyzate revealed the presence of 2-butanone (**10**), 1-methylcyclopropanol (**11**), and 2,2-dimethyloxirane (**12**) in a relative ratio of 69:28:3 (Scheme 7) and a combined yield of 55%. The identity of the products was confirmed by comparison to authentic standards.[14] Initial attempts with GC/MS analysis were complicated by the instability of the compounds on the GC column. NMR analyses circumvented these problems completely. In separate control experiments, **10**−**12** were independently photolyzed, and it was determined that these three compounds do not interconvert under the conditions employed for the photolysis of **7**.

Scheme 7



Scheme 8



The formation of **11** and **12** may be attributed to 1,3-C−H and O−H insertions, respectively, from the carbene **6**. As there are six available C−H bonds, as opposed to only one O−H bond, insertion into the weaker C−H bond is favored over that into the stronger O−H bond by a factor of 1.6. The major product of the reaction, 2-butanone, likely arises from a 1,2-migration of the methyl group in **6** to give enol **13**, which subsequently tautomerizes to **10**. It has been pointed out, however, that β-hydroxycarbenes could, in principle, undergo a 1,3-proton shift to afford a zwitterionic intermediate such as **14** (Scheme 8).[10b] Carbocation rearrangement in **14** could then also lead to the ketone **10**. Deuterium labeling experiments would not distinguish between these two pathways; however, a previous computational study of the carbene derived from **5** indicates that the zwitterionic intermediate is unlikely to be involved.[10b] We should also note that Kirmse and Buschhoff have experimentally investigated the alkoxy analogue of **6**, in which the proton-shift issue was eliminated. However, their studies utilized diazo or diazirine precursors, and significant differences were observed under photolytic, thermal, and Cu- or acid-catalyzed reactions.[4i]

The rearrangement of **6** is in sharp contrast to those of both **1** and **2** in that neither of the latter two carbenes

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(13) Wan, P.; Budac, D.; Earle, M.; Shukla, D. *J. Am. Chem. Soc.* **1990**, *112*, 8048.

(14) The ketone **10** and epoxide **12** were commercially available. The alcohol **11** was prepared according to a literature procedure. See: DePuy, C. H.; Klien, R. A.; Dappen, G. M. *J. Org. Chem.* **1962**, *27*, 3742.

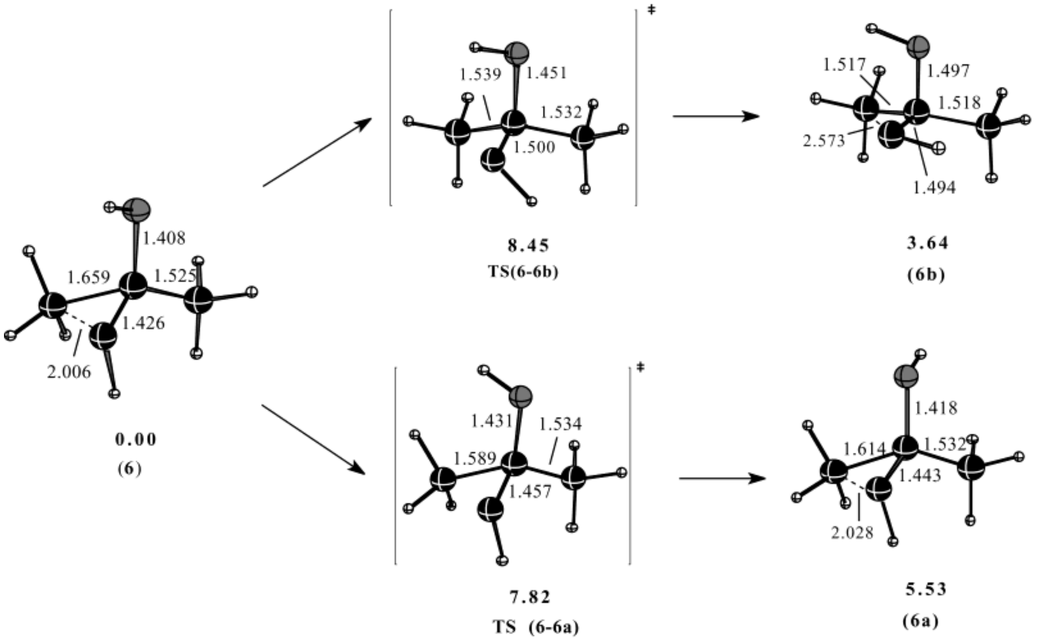

Figure 1. Interconversion pathways for **6**. The free energies at 298 K (relative to **6**) at the B3LYP/6-311+G**//B3LYP/6-31G* level are given below each structure. Key bond distances are shown in angstroms.

shows much, if any, participation of a 1,2-methyl migration. Thus, it appears that the presence of the β-hydroxy group strongly perturbs the rearrangement pathways available to **6**, thereby favoring 1,2-methyl migration. Our computational investigation into the properties and transformations of **6** is presented in the next section.

C. Computational Studies. Theoretical studies on the effect of bystander substituents on the reaction of carbenes have gained considerable attention.[7,8b,15] Such studies have often been employed to rationalize the experimentally observed product distribution. Even though the effect of substituents on the mode of rearrangement in many cyclic carbenes has been studied, analogous studies with acyclic carbenes are not widely available. It is particularly interesting to understand the factors responsible for the changes in rearrangement preferences for a β-hydroxycarbene. From the previous discussions, the experimentally observed product ratio for the rearrangement of **6** suggests that methyl migration is favored over insertions into the γ-C−H and O−H bonds. To rationalize the observed product distribution, we have also undertaken a computational investigation of the major rearrangement pathways available to **6**.

Density functional theory methods have been successfully utilized to gain valuable insights for a number of interesting carbenes.[16] We have chosen to use the hybrid B3LYP method[17] for the present study. Full geometry optimizations of **6** in both singlet and triplet electronic states were performed using the B3LYP/6-31G* level of theory. Using the most stable conformer of each multiplicity, the singlet state is found to be the ground state, and the triplet state is higher in energy by 1.8 kcal/mol at the B3LYP/6-311+G**//B3LYP/6-31G* level. At the CBS-QB3 level of theory, the singlet state of **6** is similarly favored by 3.3 kcal/mol over the triplet state. We have focused our attention only on the singlet surface to explore the possible rearrangement pathways.

The singlet carbene has been found to exist in three major conformers (**6**, **6a**, and **6b**) with interesting structural features (Figure 1). The most stable conformer of **6** is found to have a syn $H-O-C-C_{carbene}$ arrangement. The conformer with an anti $H-O-C-C_{carbene}$ arrangement (**6a**) is found to be 5.53 kcal/mol higher in free energy (298 K) at the B3LYP/6-311+G**//B3LYP/6-31G* level. All three conformers (**6**, **6a**, and **6b**) are within 5.53 kcal/mol of each other. It can be seen from the optimized geometry of **6** (and **6a**) that one of the $C-CH_3$ bonds is elongated compared to a typical C−C single bond. This is due to a hyperconjugative interaction between the $C-CH_3$ bond and the empty p orbital on the carbene carbon. An elongated $C-CH_3$ bond is of particular relevance for methyl migration in **6**. Furthermore, there is also a significant difference in the C−O bond length of **6**, **6a**, and **6b**. These differences are derived from a hydrogen-bonding arrangement between the O−H group and the carbene's sp^2 lone pair and donation of the oxygen

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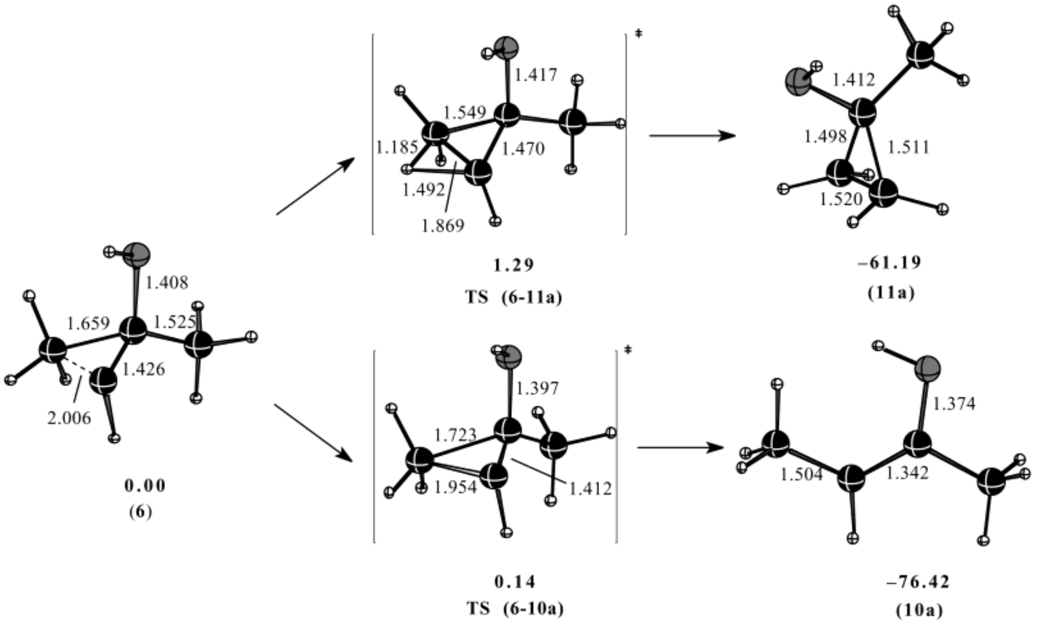

Figure 2. Rearrangement pathways for **6** (with a syn arrangement for H−O−C−C$_{carbene}$). The free energies at 298 K (relative to **6**) at the B3LYP/6-311+G**//B3LYP/6-31G* level are given below each structure. Key bond distances are shown in angstroms.

Table 1. Activation Energies (kcal/mol) Computed at the B3LYP/6-31G* Level[a]

reaction	ΔE_{BW}	ΔH_{298}	ΔG_{298}
6 → TS(6−10a) → 10a	0.06	−0.42	0.09
6 → TS(6−11a) → 11a	2.34	1.12	2.02
6a → TS(6a−10b) → 10b	0.99	0.64	0.86
6a → TS(6a−11b) → 11b	1.06	0.01	0.89
6b → TS(6b−12) → 12	6.44	4.48	5.05
6 → TS(6−6a) → 6a	9.19	8.23	8.58
6 → TS(6−6b) → 6b	8.51	7.46	7.80

[a] ΔE_{BW} represents the energies evaluated at the bottom of the well and do not include the ZPE corrections. Other parameters (ΔH_{298} and ΔG_{298}) contain scaled ZPE as well as thermal and entropic corrections as appropriate.

lone pair into the empty p orbital of the carbene center. Also, the barriers to interconversion among **6**, **6a**, and **6b** are quite large (~8 kcal/mol), and the conformation in which the carbene is born may play a key role in determining its reactions (Figure 1).

Rearrangement pathways for the carbene emanate from the different conformations via unique transition states (Figures 2−4). Calculated activation barriers at the B3LYP/6-31G* level are given in Table 1. It can be noted that the free energy of activation for the methyl migration in **6**, leading to the formation of (*Z*)-enol **10a**, is ~0.1 kcal/mol (Figure 2). A similar process from **6a** leading to **10b** is found to have a slightly higher barrier (~0.8 kcal/mol, Figure 3). *The very low free energy of activation for methyl migration is due to the congenial molecular geometry of the singlet carbene and the transition state for methyl migration. In particular, the elongated* $C-CH_3$ *bond in* **6** *(and* **6a***) is oriented in a manner to stabilize the empty p orbital on the carbenic carbon and is perfectly poised to migrate the methyl group.*[16a]

Formation of **11** by 1,3-C−H insertion is slightly higher in energy (~1.3 kcal/mol, Figure 2) compared to the methyl migration process. The free energy of activation (4.6 kcal/mol) leading to the formation of **12** from carbene **6b** is found to be the highest energy pathway among the three major routes considered in this study (Figure 4). It is also interesting to note that neither **6** nor **6a** can give rise to the O−H insertion product. Instead, only **6b** can form the O−H insertion product because the migration occurs by interaction of the oxygen lone pair with the empty p orbital of the carbene center. In the more stable **6**, the O−H hydrogen interacts with the sp^2 lone pair orbital of the carbene, and the $C-CH_3$ bond interacts with the empty p orbital of the carbene. As such, the O−H group must rotate from its preferred conformation in **6** (with a hydrogen bond between the O−H hydrogen and the carbene lone pair) to the orientation in **6b** to insert into the O−H bond. In **6b**, the O−H bond is pointed away from the carbene sp^2 lone pair, and instead, the oxygen lone pair is coordinated to the carbene's empty p orbital. Carbene **6b** is, therefore, higher in energy than **6** and **6a**. Furthermore, the free energy of activation to form oxirane **12** from **6b** (via **TS(6b−12)**) is ~4.6 kcal/mol (Figure 4), and oxirane **12** formation will not compete effectively with enol **10a** formation.

We have examined the effect of basis set on the energetics of these reactions, by single-point energy calculations with the 6-31+G** and 6-311+G** basis sets at the B3LYP level. These results are provided in Table 2. Comparison of the computed free energy of activation with the larger basis sets reveals trends similar to those of the B3LYP/6-31G* results. Explicit inclusion of electron correlation has also been considered by evaluating energies at the CCSD(T) level with the 6-31+G** and cc-pVDZ basis sets.[18] The computed energies, without the inclusion of zero-point vibrational energy and thermal corrections, are provided in Table 3. Interestingly, all of the previously noted trends, such as the preferences for 1,2-methyl migration to form the (*Z*)-enol **10a**, remain the same with each theoretical level. These results are in very good agreement with the experimental product ratio of 69:28 for **10**:**11** as given in Scheme 7.

Important geometrical details for the different processes are highlighted in Figures 1−4. The $C-CH_3$ bond length in **6** (1.659 Å) is longer than those in **6a** (1.614 Å) and **6b** (1.517 Å). Corresponding $C-CH_3$ bond lengths

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[18] Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

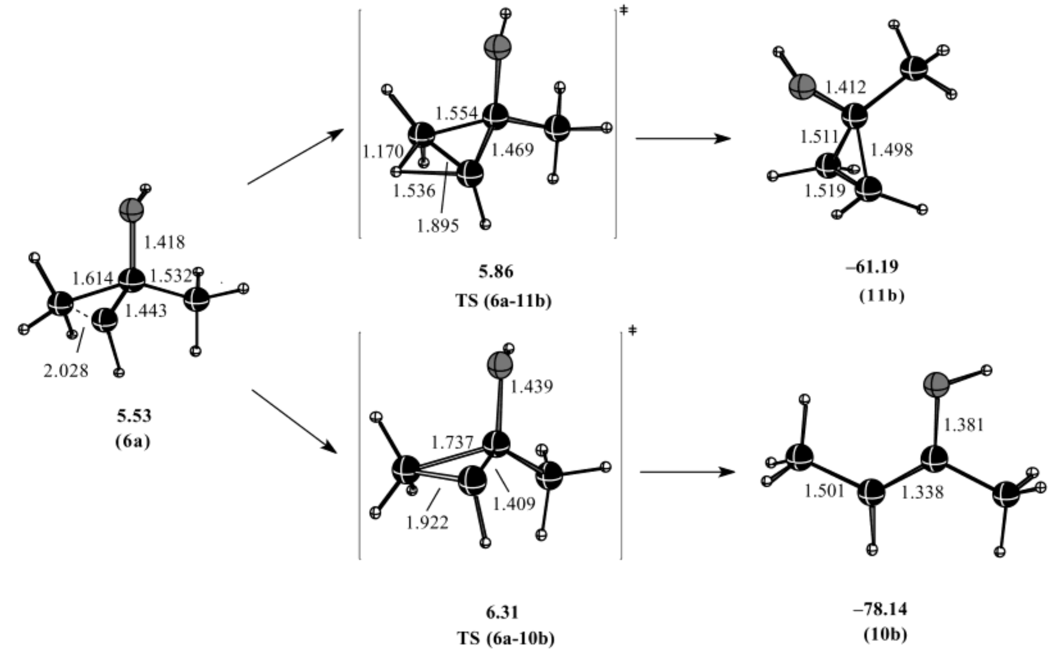

Figure 3. Rearrangement pathways for **6a** (with an anti arrangement for H−O−C−C$_{carbene}$). The free energies at 298 K (relative to **6**) at the B3LYP/6-311+G**//B3LYP/6-31G* level are given below each structure. Key bond distances are shown in angstroms.

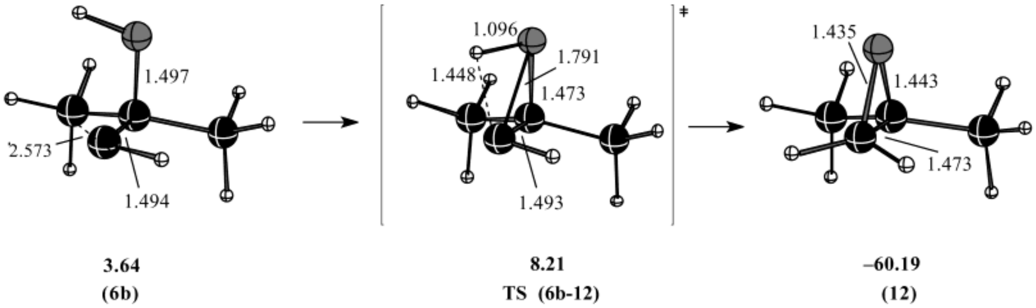

Figure 4. Rearrangement pathways for **6b** (with hydroxyl hydrogen in a pseudo-gauche arrangement with the carbene center). The free energies at 298 K (relative to **6**) at the B3LYP/6-311+G**//B3LYP/6-31G* level are given below each structure. Key bond distances are shown in angstroms.

Table 2. Activation Energies (kcal/mol) Computed Using the B3LYP/6-31G* Geometries[a]

	B3LYP/6-31+G**			B3LYP/6-311+G**		
reaction	ΔE_{BW}	ΔH_{298}	ΔG_{298}	ΔE_{BW}	ΔH_{298}	ΔG_{298}
6 → **TS(6−10a)** → **10a**	0.17	−0.31	0.19	0.11	−0.37	0.14
6 → **TS(6−11a)** → **11a**	1.47	0.25	1.15	1.61	0.39	1.29
6a → **TS(6a−10b)** → **10b**	1.11	0.74	0.97	0.93	0.53	0.79
6a → **TS(6a−11b)** → **11b**	0.51	−0.54	0.21	0.63	−0.44	0.33
6b → **TS(6b−12)** → **12**	8.43	3.65	4.06	9.60	4.17	4.57
6 → **TS(6−6a)** → **6a**	8.62	7.66	8.01	8.43	7.47	7.82
6 → **TS(6−6b)** → **6b**	8.82	7.77	8.11	9.16	8.11	8.45

[a] ΔE_{BW} represents the energies evaluated at the bottom of the well and do not include ZPE corrections. Other parameters (ΔH_{298} and ΔG_{298}) include scaled ZPE as well as thermal and entropic corrections as appropriate.

at the transition states **TS(6−6a)** and **TS(6−6b)** are shorter than that in **6** (Figure 1) due to the reduced hyperconjugation between the empty p orbital on the carbenic carbon and the C−CH$_3$ bond. An important consequence of the geometrical features of the carbenes **6** and **6a** is that the activation barrier for formation of the (*Z*)-enol from **6** is slightly lower than that from **6a**. In the transition state, the C−CH$_3$ bond has to undergo further elongation compared to that in the parent carbene so as to effect the methyl migration.

The distance between the carbenic carbon and the carbon bearing the hydroxyl group shows an expected variation on going from reactant to product. At the early transition state **TS(6−10a)**, this bond is shortened and eventually converts to a double bond in the product. The 1,3-C−H insertion transition states **TS(6−11a)** and **TS(6a−11b)**, which form **11**, possess a bridged hydrogen as revealed by the structural features. Formation of the cyclopropane ring takes place concomitantly as the migration of the H atom from the methyl to the carbenic carbon. A similar situation occurs in the transition state for the O−H insertion, as evident from the structural details of **TS(6b−12)**. Migration of the H is accompanied by the formation of the oxirane ring, resulting in **12**.

Involvement of a zwitterionic structure by a 1,3-proton shift (Scheme 8) is addressed by a separate series of calculations. All attempts to locate an optimized geometry for the proposed zwitterionic intermediate **14** led to spontaneous methyl migration to the carbocation center to generate **10** or C−O bond formation to generate **12**. The preference for each process depended strongly on the starting C$_{carbene}$−C−O bond angle, but no intermediates could be found, despite exhaustive attempts. The zwitterionic structure **14** would also be favored by polar

Table 3. Activation Energies (kcal/mol) Computed at the B3LYP and CCSD(T) Levels Using Various Basis Sets[a]

	B3LYP			CCSD(T)	
reaction	6-31G*	6-31+G**	6-311+G**	6-31+G**	cc-pVDZ
6 → **TS(6−10a)** → **10a**	0.06	0.17	0.11	0.66	0.55
6 → **TS(6−11a)** → **11a**	2.34	1.47	1.61	1.37	0.82
6a → **TS(6a−10b)** → **10b**	0.99	1.11	0.93	2.32	2.34
6a → **TS(6a−11b)** → **11b**	1.06	0.51	0.63	0.89	0.28
6b → **TS(6b−12)** → **12**	6.44	8.43	9.60	6.68	5.30
6 → **TS(6−6a)** → **6a**	9.19	8.62	8.43	7.54	7.58
6 → **TS(6−6b)** → **6b**	8.51	8.82	9.16	6.58	7.02

[a] The values are evaluated without ZPE and thermal corrections using the B3LYP/6-31G* optimized geometries in all cases.

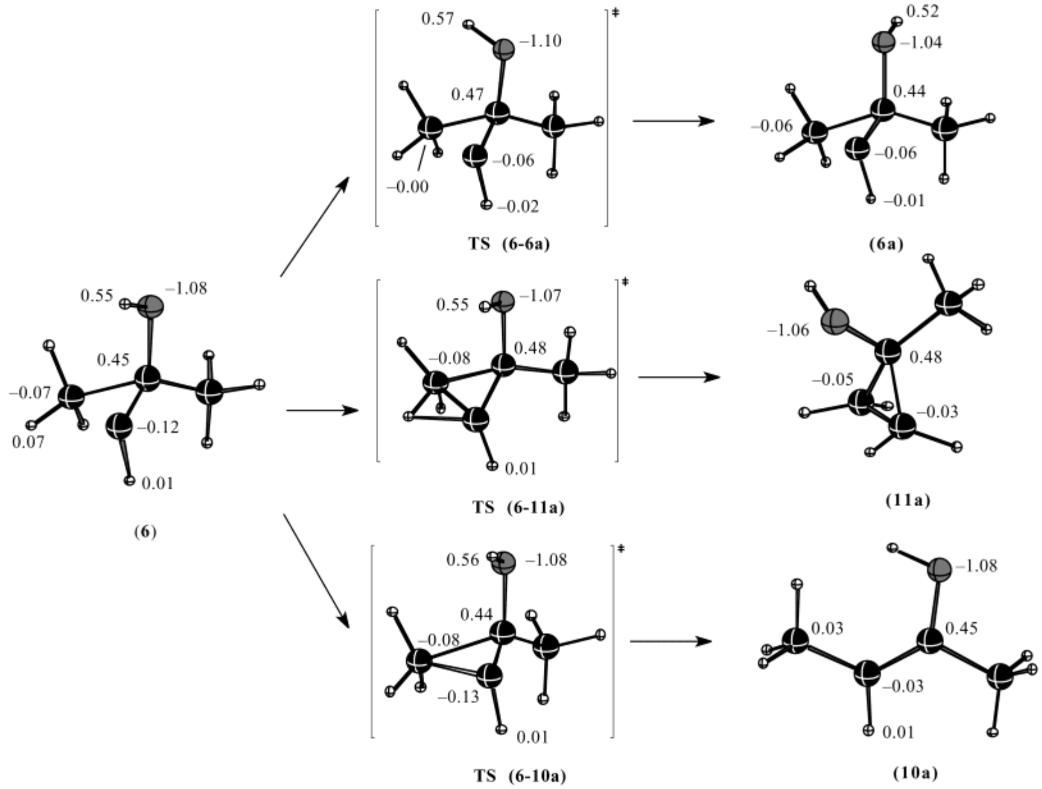

Figure 5. Atomic charges at the AIM level (in electrons) for the rearrangement pathways for **6** using the B3LYP/6-311+G**//B3LYP/6-31G* wave functions.

solvents, and such effects are not considered in these gas-phase calculations. (We should also note that the current experiments were performed in benzene.) Thus, any involvement of a 1,3-proton shift in **6** will essentially be accompanied by instantaneous formation of **10** or **12**. It was also conceivable that a transition state would exist in which proton transfer and methyl migration occurred simultaneously. Attempts to locate such a transition state ultimately led to the same transition state (**TS(6−10a)**) for 1,2-methyl migration from **6** to **10a**, in which the O−H bond participates to stabilize the sp^2 lone pair in the transition state.

The potential energy surface for these carbene rearrangements is quite flat, and our calculated activation barrier for the transformation of **6** → **TS(6−10a)** → **10a** is less than 1 kcal/mol. Indeed, computational methods have a certain uncertainty with regard to their "accuracy", and the B3LYP method can underestimate the energies of carbenes.[16m] Furthermore, with such a flat potential energy surface, dynamical and energetic effects of the carbene and the carbene precursor may become important as has been elegantly discussed in the literature in other systems.[19] However, the calculations presented here do reproduce the experimental observations quite nicely.

The effect of the *β*-hydroxyl group on various migration processes of the carbene can be further understood with the help of charge density analyses for both the reactant **6** and the transition states. We have evaluated the atomic charges on all of the systems using Bader's theory of atoms in molecules (AIM)[20] and the natural population analysis (NPA) method of Reed and Weinhold[21] at the B3LYP/6-311+G**//B3LYP/6-31G* level (the NPA results are provided in the Supporting Information). Trends from the AIM and NPA analyses were found to be in fairly good agreement.

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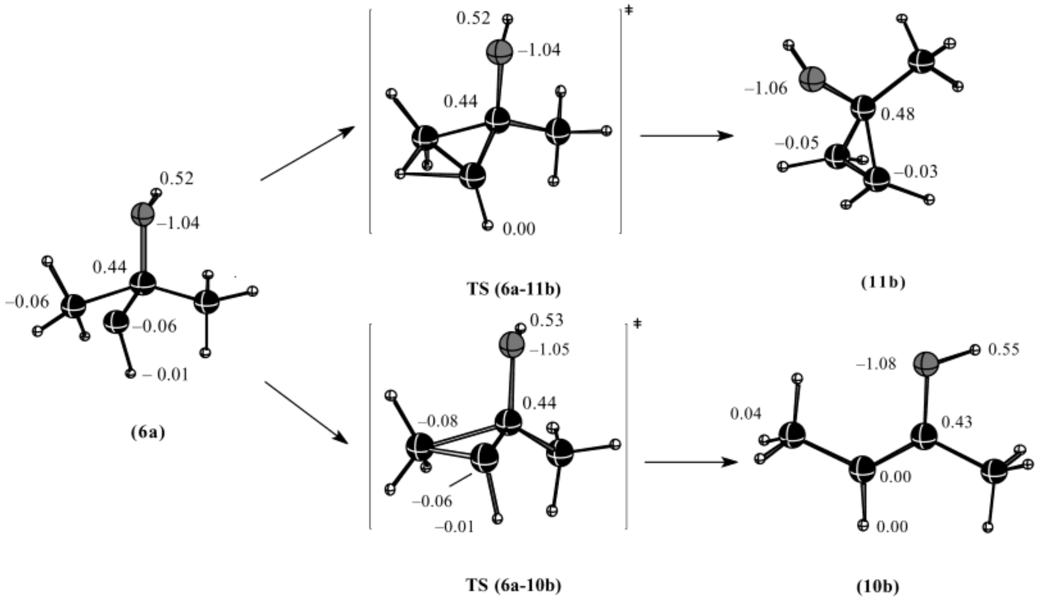

Figure 6. Atomic charges at the AIM level (in electrons) shown for the rearrangement pathways for **6a** using the B3LYP/6-311+G**//B3LYP/6-31G* wave functions.

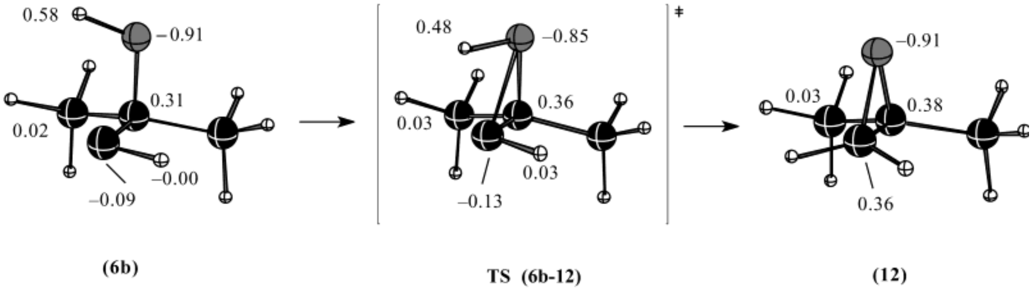

Figure 7. Atomic charges at the AIM level (in electrons) shown for the rearrangement pathways for **6b** using the B3LYP/6-311+G**//B3LYP/6-31G* wave functions.

At the AIM level, the carbenic carbon in **6** is found to have slightly more negative charge than those in the **6a** and **6b** conformers. As shown in Figures 5−7, there are only minor differences in the charge distributions among the various conformers of the reactant and the transition states. (Due to numerical instabilities associated with the numerical integration, charges on some of the ring atoms could not be determined at the AIM level.) The OH group polarizes the attached carbon atom to have a net positive charge (+0.45 e in **6**). The carbenic carbon becomes slightly more negatively charged in the transition state as compared to the reactant, and the adjacent positive charge of the carbon bearing the OH group would help to electrostatically stabilize the carbenic carbon. This electrostatic effect would, therefore, lower the activation barriers for methyl migration, as is observed.

On the basis of the free energies of activation as well as the charge density distribution, it can be easily understood that the major rearrangement pathway is the methyl migration as compared to the C−H and O−H insertion pathways. This prediction is in very good agreement with the observed product distribution, where the primary product happens to be the enol (which is then converted to the tautomeric ketone).

III. Conclusions

The experimental and computational results for **6** are in excellent agreement, and demonstrate a preference for 1,2-methyl migration to form 2-butanone as the final product. The most stable conformer of **6** is perfectly poised for a 1,2-methyl migration as the C−CH_3 group is involved in a hyperconjugative interaction with the empty p orbital at the carbene center, and the O−H bond is simultaneously interacting with the sp^2 lone pair of the carbene. The β-hydroxy substituent polarizes the attached carbon to be positively charged, thereby favoring the transition state for methyl migration by electrostatic stabilization of the negative charge that is generated at the carbene center in the migration transition state.

IV. Experimental and Computational Methods

General Procedures. Reactions requiring anhydrous conditions were carried out under an argon atmosphere with oven-dried equipment. Tetrahydrofuran was dried by passage through two columns (2 ft × 4 in.) of activated alumina. All other solvents and reagents were used as obtained from commercial sources. Column chromatography was performed on silica gel (70−230 mesh) or neutral alumina (80−100 mesh) using the indicated solvent system. For preparative thin-layer chromatography, 20 × 20 cm glass plates, coated with a tapered layer of silica gel, were used. NMR spectra were recorded at 400 MHz for ^{1}H and 100 MHz for ^{13}C.

***exo*-1-(1a,9b-Dihydro-1*H*-cyclopropa[*l*]phenanthren-1-yl)ethanone (9).** As described in a previously published procedure,[12] phenanthrene (25.6 g, 143 mmol) and copper sulfate (0.510 g, 3.18 mmol) were steadily heated to melting whereupon ethyl diazoacetate (16 mL, 152 mmol) was added dropwise to the mixture. Heating was discontinued upon completion of addition, and the contents of the flask were solidified within 1 h. Then, sodium hydroxide (10% in EtOH, 100 mL) was added, and the reaction mixture was heated to reflux for 12 h. Ethanol was removed under reduced pressure, water (250 mL) was added, and the reaction mixture was gently boiled for 15 min. The reaction mixture was then filtered and the filtrate cooled and acidified to a pH of 5.5. A tan, creamy precipitate was obtained that was recrystallized from glacial acetic acid to afford white crystals of the carboxylic acid in typical low yield (19% yield, 6.23 g). The carboxylic acid (1.05 g, 4.45 mmol) was dissolved in THF (30 mL) and the solution cooled to 0 °C. To this solution was added CH_3Li (1.60 M in diethyl ether, 5.85 mL, 9.35 mmol) in a dropwise fashion, and the resulting solution was stirred for 25 h. Aqueous NH_4Cl (25 mL) was then added, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL). The combined organics were washed with water (50 mL) and brine (50 mL), dried over Na_2SO_4, and filtered, and the solvent was removed under reduced pressure to give the crude ketone. This material was recrystallized from EtOH (447 mg, 46% yield): mp 182−184 °C (lit.[11h] mp 185−186 °C); IR (KBr pellet) 1677 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.05 (m, 2 H), 7.48 (m, 2 H), 7.34 (m, 4 H), 3.29 (d, $J = 3.7$ Hz, 2 H), 2.31 (s, 3 H), 1.40 (t, $J = 3.7$ Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 208.5, 133.7, 130.1, 130.0, 128.4, 127.5, 123.7, 34.6, 33.3, 31.9. Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 86.77; H, 6.08.

***exo*-2-(1a,9b-Dihydro-1*H*-cyclopropa[*l*]phenanthren-1-yl)propan-2-ol (7).** The ketone **9** (720 mg, 3.10 mmol) was dissolved in THF (15 mL) and the solution cooled to 0 °C. A solution of CH_3Li (1.6 M in diethyl ether, 2.5 mL, 4.00 mmol) was added dropwise, and the resulting solution was stirred for 1 h. Aqueous NH_4Cl (40 mL) was added, and the layers were separated. The aqueous layer was extracted with ether (50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated at reduced pressure. The residue was purified by flash chromatography on alumina (9:1 hexanes/ethyl acetate) followed by preparative thin-layer chromatography using hexanes/ethyl acetate (95:5), to give the tertiary alcohol product (85.4% yield, 662 mg): mp 120−122 °C (lit.[22] mp 100−116 °C); IR (KBr pellet) 3545, 3475, 1238, 1186 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.03 (m, 2 H), 7.41 (m, 2 H), 7.23 (m, 4 H), 4.45 (br s, 1 H), 2.58 (d, $J = 4.5$ Hz, 2 H), 0.17 (t, $J = 4.5$ Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 135.9, 129.7, 128.9, 127.9, 126.1, 123.3, 69.3, 35.9, 29.5, 22.9. Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.21; H, 7.28.

General Procedure for Photolysis. In a typical experiment, a solution of the tertiary alcohol **7** (16.3 mg, 0.065 mmol) in C_6D_6 containing a precisely weighed amount of 1,3-benzodioxole (6.8 mg, 0.056 mmol) as an internal standard was taken in an NMR tube and deoxygenated. This solution was then photolyzed at room temperature in a Rayonet photochemical reactor to generate the carbene **6**. The photolysis reaction was monitored periodically by ^1H NMR and continued until the starting material was consumed. The products of photolysis were compared to authentic samples of 2-butanone and 2,2-dimethyloxirane, which were purchased, and 1-methylcyclopropanol, which was synthesized according to a literature procedure.[14]

Computational Methods. Full geometry optimizations of minima as well as transition states have been performed using the B3LYP[17] hybrid Hartree−Fock density functional theory method,[23] using the 6-31G* basis set. All calculations were performed with Gaussian 98.[24]

Each stationary point was characterized as either a true minimum or a transition state by the corresponding Hessian index of 0 and 1, respectively. Each transition state (**TS(R−P)**) was then carefully confirmed (opt=calcfc) to connect to the respective reactant (**R**) and product (**P**), after displacement (by ∼10%) along the normal mode for the imaginary vibrational frequency.

The effect of electron correlation was evaluated by refining the energies using single-point energy calculations at the coupled cluster[25] and B3LYP[17] methods using basis sets of increased flexibility. Single-point energy calculations on the B3LYP/6-31G* optimized geometries were performed at the CCSD(T)/6-31+G**, CCSD(T)/cc-pVDZ, B3LYP/6-31+G**, and B3LYP/6-311+G** levels. All of these basis sets included six Cartesian d functions.[26] Single-point energy calculations were performed using the “scf=tight” option. Zero-point vibrational energies (at the B3LYP/6-31G* level) have been scaled by 0.9806[27] and are included in the reported energies, except for the CCSD(T) relative energies. The standard CBS-QB3 method[28] was utilized as implemented in Gaussian98.

Atomic charges were evaluated at the AIM[20] and NPA[21] levels using the wave functions from the B3LYP/6-311+G**//B3LYP/6-31G* calculations. The AIM charges were generated with AIMALL.[29]

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Supporting Information Available: Spectral data (^1H NMR, ^{13}C NMR, and IR) for **7** and computational results, including absolute energies at all levels of theory, Cartesian coordinates and vibrational frequencies for all stationary points, and figures for the NPA atomic charges. This material is available free of charge via the Internet at http://pubs.acs.org.

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