Dichlorocarbene Addition to Cyclopropenes: A Computational Study
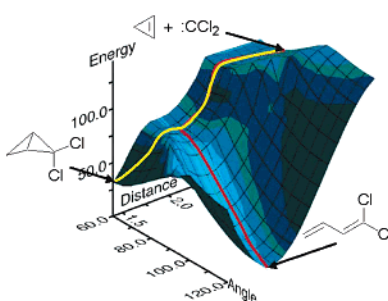
Dina C. Merrer*,† and Paul R. Rablen‡

Department of Chemistry, Barnard College, 3009 Broadway, New York, New York 10027, and Department of Chemistry and Biochemistry, Swarthmore College, 500 College Avenue, Swarthmore, Pennsylvania 19081

dmerrer@barnard.edu

Received October 18, 2004

Reaction paths for addition of dichlorocarbene to 1,2-disubstituted cyclopropenes were calculated using hybrid density functional theory (B3LYP/6-31G*) in the gas phase and in the presence of a continuum solvation model corresponding to acetonitrile. In both the gas phase and acetonitrile, :CCl₂-cyclopropene addition follows an asymmetric, non-least-motion approach. Barriers to addition range from 0 to 2 kcal/mol. The reactions proceed in concerted fashion in both the gas phase and solution to yield 1,3-dienes or bicyclobutanes. The reaction pathway on this complex potential energy surface of this reaction appears to bifurcate, and the product distribution is believed to be controlled by reaction dynamics. At the present level of theory, there appears to be no minimum on the potential energy surface corresponding to a dipolar intermediate.

Introduction

Addition to alkenes represents one of the most common and most commonly investigated reactions of singlet carbenes[1–11] and has been widely used for the synthesis of cyclopropanes. Formation of two new σ-bonds proceeds via a concerted yet asynchronous pathway in which the carbene approaches the olefin in an asymmetric fashion.[4–11] Several studies using density functional theory and MP2 calculations support this asymmetric geometry for singlet addition.[5–11]

The concerted nature of carbene−alkene addition reactions has been debated, with several intermediates proposed.[11–16] Carbene−alkene complexes were at one

† Barnard College.
‡ Swarthmore College.
(1) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971; pp 267−362.
(2) Moss, R. A. In *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1973; Vol. 1, pp 153−304.
(3) (a) Skell, P. S.; Woodworth, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 4496. (b) Skell, P. S.; Woodworth, R. C. *J. Am. Chem. Soc.* **1959**, *81*, 3383.
(4) Moore, W. R.; Moser, W. R.; LaPrade, J. E. *J. Org. Chem.* **1963**, *28*, 2200.
(5) (a) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475. (b) Hoffmann, R.; Hayes, D. M.; Skell, P. S. *J. Phys. Chem.* **1972**, *76*, 664.
(6) Keating, A. E.; Merrigan, S. R.; Singleton, D. A.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 3933.
(7) Rondan, N. G.; Houk, K. N.; Moss, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1770.
(8) Houk, K. N.; Rondan, N. G.; Mareda, J. *J. Am. Chem. Soc.* **1984**, *106*, 4291.
(9) Blake, J. F.; Wierschke, S. G.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 1919.

(10) Keating, A. E.; Garcia-Garibay, M. A.; Houk, K. N. *J. Am. Chem. Soc.* **1997**, *119*, 10805.
(11) Bernardi, F.; Bottoni, A.; Canepa, C.; Olivucci, M.; Robb, M. A.; Tonachini, G. *J. Org. Chem.* **1997**, *62*, 2018.
(12) (a) Liu, M. T. H.; Soundararajan, N.; Paike, N.; Subramanian, R. *J. Org. Chem.* **1987**, *52*, 4223. (b) Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1990**, *112*, 3915.
(13) For a review of carbene−alkene complexes, see: Merrer, D. C.; Moss, R. A. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; Elsevier: Amsterdam, 2001; Vol. 3, pp 57−71.
(14) Weber, J.; Brinker, U. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1623.
(15) Weber, J.; Xu, L.; Brinker, U. H. *Tetrahedron Lett.* **1992**, *33*, 4537.
(16) Yang, N. C.; Marolewski, T. A. *J. Am. Chem. Soc.* **1968**, *90*, 5644.

SCHEME 1. Pathways of :CCl$_2$ Addition to 1,2-Disubstituted Cyclopropenes

a, R = H; **b**, R = CH$_3$; **c**, R = CH=CH$_2$; **d**, R = Ph; **e**, R = (*p*-OCH$_3$)C$_6$H$_4$; **f**, R = (*p*-CF$_3$)C$_6$H$_4$
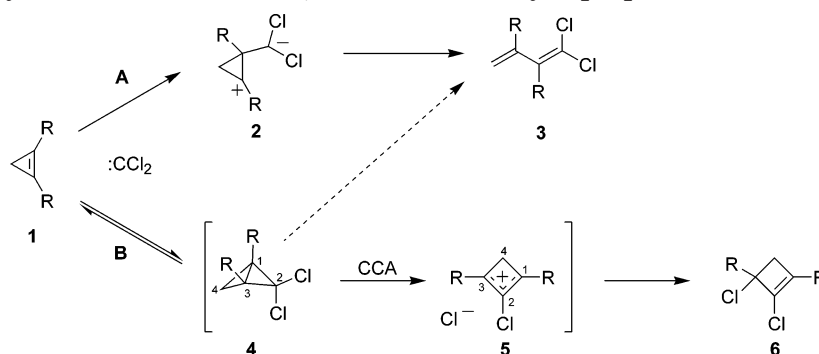
time invoked to explain cycloaddition kinetics;[12,13] however, theoretical[6,9–11] and experimental[17] studies have since indicated that carbene–alkene complexes are not free energy minima and exist neither in the gas phase nor in solution. CAS-MCSCF/6-31G* and MR-MP2/6-31G* calculations by Bernardi et al.[11] show the reaction of singlet :CF$_2$ with isobutene to involve a diradical intermediate, but that other singlet carbene additions to ethylene proceed via a concerted pathway. Intrinsic reaction coordinate (IRC) calculations at B3LYP/6-31G* and experimental kinetic isotope studies of :CCl$_2$ addition to propene and 1-butene by Houk et al. depict a relatively flat potential energy surface (PES) at carbene–alkene distances of >2.6 Å; the reaction then proceeds in concerted fashion to cycloaddition products.[6,10] However, all previous theoretical studies of singlet carbene addition to alkenes have involved unstrained, unhindered alkenes.[18] Here, we investigate theoretically the mechanism of dichlorocarbene addition to strained 1,2-disubstituted cyclopropenes.

Few experimental studies exist of carbene reactions with small-ring olefins.[19] Dichloro- and dibromocarbene react with cyclopropene and cyclobutene to give the respective 2,3-dihalocyclobutene and cyclopentene products, from cationic cyclopropyl allyl (CCA) rearrangements of the likely bicyclobutane and bicyclopentane intermediates (eqs 1 and 2).[15] A similar intermediate adduct was invoked in :CX$_2$ (X = Cl, Br) addition to benzocyclopropene to produce the respective dihalobenzocyclobutene products (eq 3).[20] However, in none of these cases were the bicyclic intermediates isolated or observed spectroscopically.
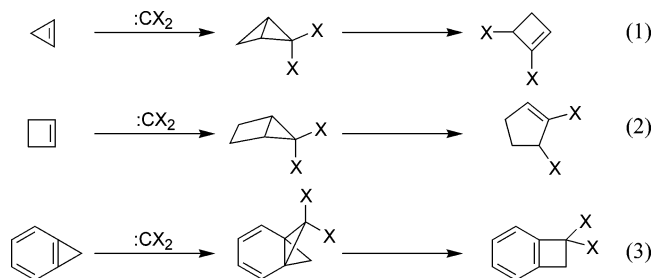
Brinker et al.'s additions of dihalocarbenes to 1,2-diarylcyclopropenes (**1d**–**f**) are notable because they not

only yielded the vicinal dihalocyclobutene products (from cyclopropyl cationic allyl (CCA) rearrangement of a bicyclobutane intermediate), but also 1,3-geminal dihalodienes (Scheme 1).[14,15] Previously,[16] the intermediacy of a zwitterion, **2**, was invoked on the pathway to these diene products. Experimental evidence for the charge-separated dipolar intermediate was obtained from product studies of asymmetrically substituted cyclopropenes, which exhibited regiochemical preferences consistent with a zwitterionic intermediate, or else a polar transition state.

To understand more fully the addition of dihalocarbenes to strained alkenes such as 1,2-disubstituted cyclopropenes, and to probe the possible existence of a zwitterionic intermediate (**2**) in these reactions, we have investigated theoretically the reaction paths shown in Scheme 1. Path A was calculated using hybrid DFT in the gas phase and also in the presence of a continuum model of acetonitrile solvation (PCM model). Additionally, attempts were made to model zwitterions **2** independently using B3LYP/6-31G* in the gas phase and in acetonitrile.

Results and Discussion

:CCl$_2$ Addition to Cyclopropenes – Path A. The addition of :CCl$_2$ to cyclopropenes **1a**–**d** follows an asymmetric, non-least-motion path, in accord with previous findings for singlet carbene–alkene reactions with unstrained olefins.[4–11] As the carbene approaches the alkene, it rotates from electrophilic attack to nucleophilic attack. Figure 1 shows the B3LYP/6-31G* optimized geometries for :CCl$_2$ addition to **1a** at *r* = 3.4, 2.8, and 2.3 Å, where *r* is the distance from the carbene carbon to the midpoint of the alkene. This process is representative for :CCl$_2$ addition to **1b**–**d** as well.

An interesting aspect of the :CCl$_2$ + cyclopropene reaction path is that it leads in concerted fashion to either of two products, butadiene **3** (as found experimentally by Brinker[14,15]), or bicyclobutane **4**, the classical carbene

(17) Nigam, M.; Platz, M. S.; Showalter, B. M.; Toscano, J. P.; Johnson, R.; Abbot, S. C.; Kirchhoff, M. M. *J. Am. Chem. Soc.* **1998**, *120*, 8055.
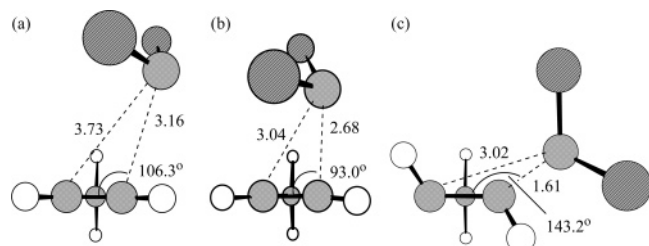
(18) Sevin, F.; McKee, M. L.; Shevlin, P. B. *J. Org. Chem.* **2004**, *69*, 382. This paper details reactions of carbenes with cyclopropane and more generally discusses reactions of carbenes with strained ring compounds to give new σ- and π-bonds simultaneously, as we observe here.

(19) (a) Trost, B. M.; Atkins, R. C. *J. Chem. Soc., Chem. Commun.* **1971**, 1254. (b) Dehmlow, E. V. *Tetrahedron Lett.* **1975**, 203. (c) Hart, H.; Nitta, M. *Tetrahedron Lett.* **1974**, 2109. (d) Mahler, W. *J. Am. Chem. Soc.* **1962**, *84*, 4600.

(20) Kagabu, S.; Saito, K. *Tetrahedron Lett.* **1988**, *29*, 675.

FIGURE 1. Dichlorocarbene addition to cyclopropene (**1a**) at different values of r: (a) $r = 3.4$ Å, (b) $r = 2.8$ Å, (c) $r = 2.3$ Å. Bond lengths are given in angstroms.
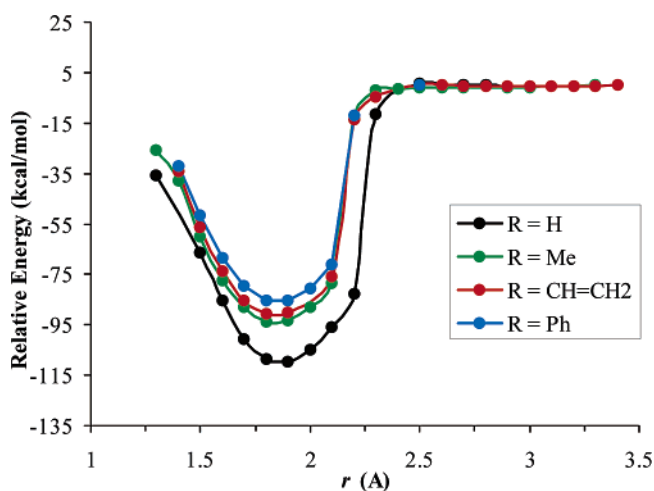

FIGURE 2. Relative electronic energies (uncorrected) of :CCl$_2$ addition to 1,2-disubstituted cyclopropenes calculated at B3LYP/6-31G* in the gas phase; r is the distance between the carbene carbon and the midpoint of the alkene.

FIGURE 3. B3LYP/6-31G* fully optimized geometry in acetonitrile (PCM) when R = H at $r' = 1.50-2.25$ Å at the start of the calculation.

addition product. Butadiene **3** is the exclusive product when the geometry of the carbene−cyclopropene system is optimized at decreasing fixed distances of separation ($r = 1.2-3.5$ Å, in 0.1-Å increments) both in the gas phase and in an acetonitrile solvent continuum (SCRF-PCM[21]). The gas-phase results are depicted in Figure 2. In contrast, IRC calculations in the gas phase predict the formation of only **4**. With both methods, however, there are no minima on the PES of this reaction that correspond to zwitterionic intermediates. We will address the apparent conflict between the IRC and stepped-energy results below.

It was not surprising that charge-separated zwitterions (**2**) were not observed as energy minima in the gas phase. To further investigate the potential existence of **2**, we attempted to independently optimize the proposed dipolar intermediates in acetonitrile at B3LYP/6-31G*. The C−C bridgehead bond distances of fully optimized B3LYP/6-31G* bicyclobutanes **4** were partially optimized in an acetonitrile continuum at $r' = 1.5, 1.75, 2.0$, and 2.25 Å. The force constants of each of these partially optimized structures were then calculated, and the geometries were subsequently fully optimized from each value of r'. The fully optimized geometries for all R groups, as represented in Figure 3 by R = H, did not yield zwitterions: the structures instead collapsed to the bicyclobutane
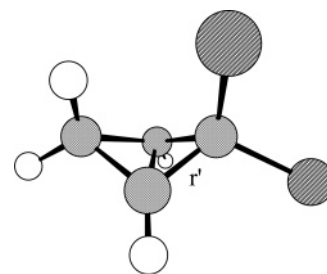
minima. Similar results were found in the gas phase for the species obtained from the reactions of :CCl$_2$ with 1-methylcyclopropene and 1-aminocyclopropene. Even the strongly electron-donating amino group could not sufficiently stabilize the positive charge on the zwitterion. Thus, in contrast with Brinker's experimental findings,[14,15] :CCl$_2$ addition to 1,2-disubstituted cyclopropenes does not appear to proceed through dipolar intermediates, as calculated at this level of theory.

That IRC calculations predicted bicyclobutane **4** as the sole product of :CCl$_2$ addition to cyclopropene, whereas point-by-point reaction coordinate calculations gave only butadiene **3** as the energy minimum, gave us pause. Due to the enormous exothermicity of this reaction (approximately -75 and -100 kcal mol^{-1} to form **4** and **3**, respectively), we suspected that a mechanistic bifurcation and nonstatistical reaction dynamics might be implicated.[22,23] We therefore calculated a PES of the :CCl$_2$-parent cyclopropene reaction at B3LYP/6-31G* and CCSD-(T)/6-31G*//B3LYP/6-31G*. We defined two seemingly relevant coordinates for the PES: the distance, r, between the carbene center and center of the cyclopropene π-bond, and the cyclopropenyl bond angle, θ. The former coordinate decreases from effective infinity to $\sim$1.8 Å or less during the formation of either product. The angle coordinate, on the other hand, remains relatively constant at $\sim$60° during formation of the bicyclobutane product, but increases from $\sim$60° to $\sim$120° during formation of the butadiene product. For these PES calculations, $r = 1.4-3.0$ Å in 0.1-Å increments and $\theta = 60-120°$, in 5° increments. Similar results were obtained at both levels of theory; the CCSD(T)/6-31G*//B3LYP/6-31G* surface is shown in Figure 4.

The PES calculated here reveals a relatively flat region at the start of the reaction, represented by $r = 3.0$ Å and $\theta \approx 60°$, followed by a rapid decline to two minima: one at $r = 1.4$ Å and $\theta = 60°$, corresponding to bicyclobutane **4a**; the other at $r = 1.8$ Å and $\theta = 120°$, corresponding to butadiene **3a**. At most, a very small barrier intervenes between the isolated starting materials and the initial descent. This common route then diverges at $r = 1.9$ Å

(21) (a) Miertus, S.; Tomasi, J. *Chem. Phys.* **1982**, *65*, 239. (b) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117.

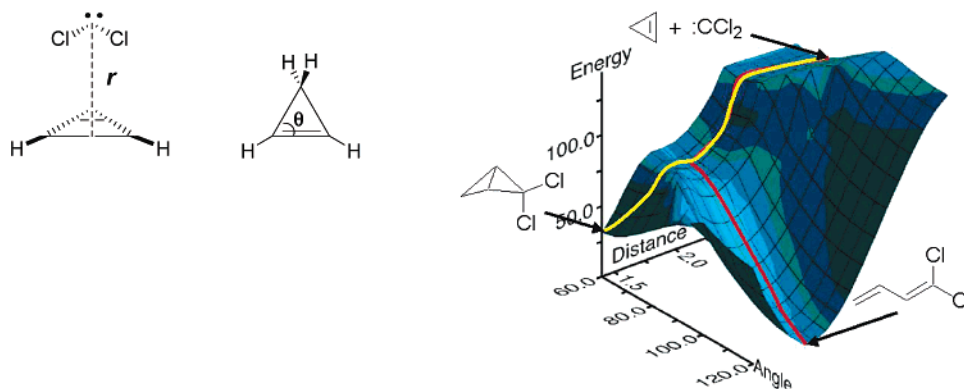(22) (a) Carpenter, B. K. In *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Jones, M., Jr., Eds.; Wiley: Hoboken, NJ, 2004; pp 925−960. (b) Carpenter, B. K. *Angew. Chem., Int. Ed.* **1998**, *37*, 3340.

(23) Mechanistic bifurcations have been implicated in ene reactions of singlet oxygen (Singleton, D. A.; Hang, C.; Szymanski, M. J.; Meyer, M. P.; Leach, A. G.; Kuwata, K. T.; Chen, J. S.; Greer, A.; Foote, C. S.; Houk, K. N. *J. Am. Chem. Soc.* **2003**, *125*, 1319), bond shifting of cyclooctatetraene (Castaño, O.; Palmeiro, R.; Frutos, L. M.; Luisandrés, J. *J. Comput. Chem.* **2002**, *23*, 732), and the formation of a semibullvalene (Zhou, C.; Birney, D. M. *Org. Lett.* **2002**, *4*, 3279).

FIGURE 4. PES of :CCl$_2$ + cyclopropene at varying carbene−alkene distances, *r*, and cyclopropenyl bond angles, θ (CCSD(T)/6-31G*//B3LYP/6-31G*).

and $\theta = 68°$ to butadiene (**3a**) and bicyclobutane (**4a**) products. From this bifurcation point, one reaction trajectory (red) continues to proceed downhill via a more steeply descending path to butadiene, while the other trajectory (yellow) must cross a small barrier (∼2 kcal/mol) from the branch point to reach bicyclobutane product.

From this PES, butadiene **3a** would seem to be the favored (i.e., major) product in all cases; however, cyclobutene **6a**, formed from rearrangement of **4a**, is obtained in greater amount experimentally.[14] Thus, at first glance, our computational results appear to contradict the experimental findings. However, the extreme exothermicity of this reaction makes it an excellent candidate for control by nonstatistical reaction dynamics.[22] Although butadiene is the global minimum of this system, its formation is possible only by a very abrupt change in momentum as the molecules traverse the PES. In contrast, bicyclobutane is formed via a straight, more direct reaction trajectory. Thus, the enormous amount of kinetic energy and momentum gained during the initial descent from starting materials is not entirely dissipated by collisions and supplies enough energy to carry the molecules over the 2 kcal/mol barrier to bicyclobutane via a straight trajectory, thereby bypassing the sharp directional turn required to traverse the minimum-energy path to butadiene.

The concepts of direct trajectories[22b,24a] and the conservation of angular momentum across complex PES's have been implicated previously to explain product formation in other dynamically controlled reactions.[24−27] A particularly relevant example is the ring closure of trimethylene in cyclopropane stereomutation:[26] trimethylenes formed by disrotation re-closed not by conrotation (as predicted by transition state theory) but by disrotation, despite having to cross a higher barrier for this process.[26a] Closely related to this is Carpenter's hypothesis of "dynamic matching",[22b,24b,25,27] in which a specific pathway is favored based on the best correlation between

(24) (a) Carpenter, B. K. *J. Am. Chem. Soc.* **1996**, *118*, 10329. (b) Carpenter, B. K. *J. Am. Chem. Soc.* **1995**, *117*, 6336.
(25) Suhrada, C. P.; Houk, K. N. *J. Am. Chem. Soc.* **2002**, *124*, 8796.
(26) (a) Doubleday, C., Jr.; Bolton, K.; Hase, W. L. *J. Am. Chem. Soc.* **1997**, *119*, 5251. (b) Hrovat, D. A.; Fang, S.; Borden, W. T.; Carpenter, B. K. *J. Am. Chem. Soc.* **1997**, *119*, 5253.
(27) Reyes, M. B.; Carpenter, B. K. *J. Am. Chem. Soc.* **2000**, *122*, 10163.
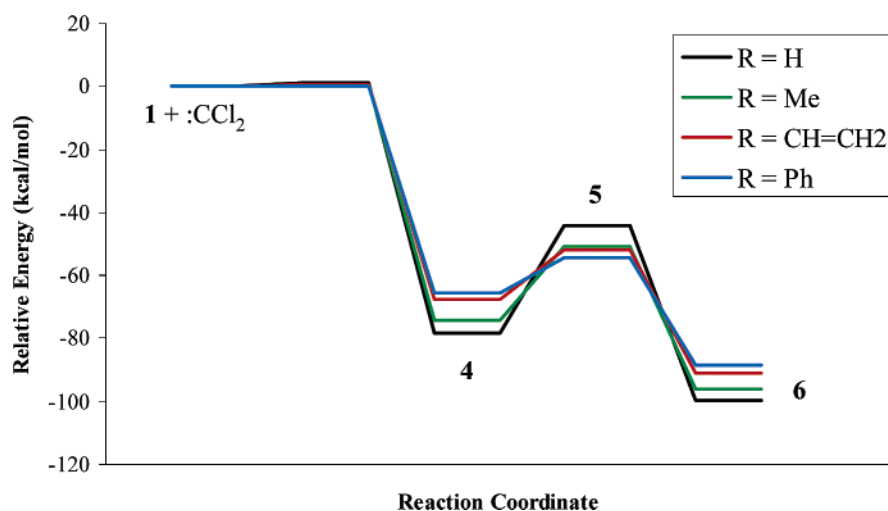
a molecule's entrance and exit channel from an intermediate. While we have not found :CCl$_2$-cyclopropene addition to involve a strictly defined intermediate, we believe the divergence of reaction paths at the bifurcation point of the PES, and the experimental preference for formation of bicyclobutane product, to be a consequence of these types of dynamical effects. We therefore support the idea that this system is governed by nonstatistical dynamics, thereby accounting for Brinker et al.'s experimental findings.

Thus, the :CCl$_2$-cyclopropene reaction is more complex than originally anticipated. Based on the results reported here, it is clear that this system can only be properly treated by dynamics calculations. These calculations are currently underway and will be reported separately. It is expected that the dynamics results will not only help resolve the complexity of this system, but also provide insight into similar carbene−alkene and carbene−alkyne addition reactions.

PES of Bicyclobutane Intermediate CCA Rearrangement to Cyclobutenes − Path B. The PES of the formation of [1.1.0]bicyclobutane intermediate **5** and its rearrangement, via a cyclopropyl allyl cation−chloride ion pair (**5**), was calculated at B3LYP/6-31G* in the gas phase. Figure 5 and Table 1 show the ZPE-corrected energies for this reaction path. The barriers to formation of the bicyclobutane intermediates were 1−3 kcal/mol. Rearrangement to cyclobutenyl products **7** followed a CCA rearrangement mechanism, the barriers to which ranged from 11 to 34 kcal/mol. It is interesting to note that the CCA ion pair, **5**, represents the transition state for this step rather than a discrete intermediate. The geometries of **5** (Table 2) vary according to R: the dissociated chloride ions in **5a** (R = H) and **5b** (R = CH$_3$) are located more equidistant from the origin and destination carbons, C-2 and C-3, respectively, whereas Cl$^-$ is positioned closer to C-2 than C-3 in **5c** (R = CH=CH$_2$) and **5d** (R = Ph). This trend is not surprising, as C-3 (and C-1) in **5c** and **5d** can better stabilize the positive charge density of the CCA cation by resonance via the vinyl and phenyl R groups.

The possible rearrangement of **4** to 1,3-butadiene **3** was also investigated. These paths were kinetically unfavorable at this level of theory: $\Delta E^{\ddagger} = 46−51$ kcal/mol (Figure 6).[28] These results are in agreement with Brinker et al.'s experimental findings,[14,15] that the cyclobutenyl products

FIGURE 5. Calculated energies (ZPE-corrected) for the CCA rearrangement of **4** to **6**.

TABLE 1. Relative[a] (ΔE) Energies of the Stationary Points of Path B Calculated at B3LYP/6-31G*[b]

R	H	CH$_3$	CH=CH$_2$	Ph
1 + :CCl$_2$	0.0	0.0	0.0	0.0
tr. state	0.9	0.7	0.6	c
4	−78.3	−74.2	−67.6	−65.7
5	−43.9	−50.7	−51.8	−54.4
6	−99.8	−96.2	−90.9	−88.4

[a] In kcal/mol, with ZPE correction. [b] In the gas phase. [c] The reaction **1** + :CCl$_2$ → **4** was barrierless.

TABLE 2. Geometries of the Transition States, 5, for CCA Rearrangement of 4 to 6 Calculated at B3LYP/6-31G*[a]
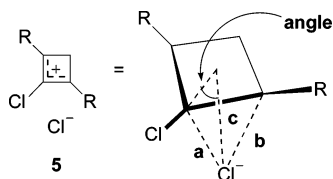
	R = H	R = CH$_3$	R = CH=CH$_2$	R = Ph
a (Å)	2.56	2.57	2.52	2.48
b (Å)	2.74	2.88	3.17	3.06
c (Å)	2.96	2.98	2.69	2.70
angle (deg)	58.4	58.2	69.0	66.3
ring dihedral (deg)	−27.2	−25.6	−18.6	−19.6

[a] In the gas phase.

are a result of CCA rearrangement of the [1.1.0]bicyclobutane intermediates and that the bicyclobutanes do not rearrange to 1,3-butadiene products.

Conclusions

Density functional theory and in some cases CCSD(T) were used to calculate the gas-phase reaction paths of dichlorocarbene addition to 1,2-disubstituted cyclopropenes **1a**−**d**. These reactions were also investigated in acetonitrile using the PCM model. The barriers to addition ranged from 0 to 2 kcal/mol. At these levels of theory, dipolar intermediates are not minima on the reaction coordinate for carbene addition to these strained olefins, in contrast to conclusions drawn from previous experi-
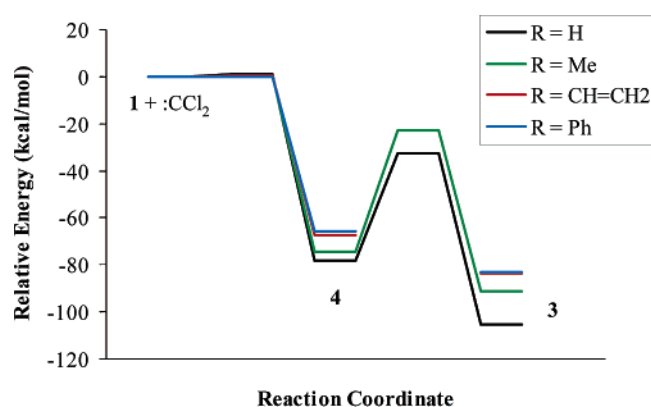

FIGURE 6. Calculated energies (ZPE-corrected) for the kinetically unfavorable rearrangement of **4** to **3**.

mental results. The products for these reactions are either 1,3-butadienes or classical [1.1.0]bicyclobutanes. Calculation of a two-dimensional PES for the addition of dichlorocarbene to cyclopropene revealed a surface that can be used qualitatively to rationalize the experimental observations in terms of a dynamically bifurcated pathway. Pathways to both bicyclobutane and butadiene begin in the same fashion, with little or no initial barrier for approach of the carbene to the alkene. As the reacting species draw closer, and the energy drops rapidly, a highly curved path with no barrier leads to the butadiene product. On the other hand, an almost perfectly straight pathway with a very small barrier leads to the bicyclobutane product. Under these circumstances, it is not difficult to see how a mixture of products can be obtained, and how dynamic effects might even favor the butadiene product, despite the presence of a small secondary barrier that is apparently absent along the alternative pathway. [1.1.0]Bicyclobutane intermediates resulting from :CCl$_2$-cyclopropene addition are 65−78 kcal/mol more stable

(28) The values for the transition states reported herein were determined via the quadratic synchronous transit method. Additionally, a similar structure was found for the **4a** → **3a** rearrangement, using an appropriate structure selected off the PES (Figure 4) as a starting point for the transition state calculations; this transition state was approximately 2.5 kcal/mol higher in energy than the one reported in the text.
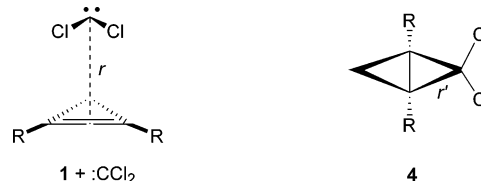
than the separated species. These bicyclic intermediates react solely by CCA rearrangement to cyclobutene products.

Computational Methods

All calculations were carried out with Gaussian 98[29] or Gaussian 03[30] using B3LYP/6-31G*,[31,32] unless otherwise noted. All stationary points were confirmed by frequency calculations, except those noted below; the calculated frequencies were scaled by 0.9806.[33]

The reaction coordinate for the addition of :CCl$_2$ to cyclopropene was defined as the distance, r, from the carbenic center to the midpoint of the alkene, as per Keating et al.'s method for CCl$_2$ additions to simple alkenes.[6,10] The geometries and energies of Path A were calculated at distances of r ranging from 1.4 to 3.5 Å. For this set of calculations, all energies are reported as uncorrected electronic energies, and only the stationary points for maximum separation of the carbene and **1** (i.e., $r \geq 3.0$ Å), the transition state, and the energy minima were confirmed by frequency calculations. In addition, IRC calculations[34] were also conducted for the Path A addition reaction. The PES for the reaction of :CCl$_2$ + **1a** was computed at B3LYP/6-31G* and at CCSD(T)/6-31G*// B3LYP/6-31G*.[35]

1 + :CCl$_2$ **4**

Charge-separated zwitterions **2** were modeled in an acetonitrile solvent continuum using the PCM model[21] via the following method. The C–C bridgehead bond distances of fully geometry-optimized [1.1.0]bicyclobutanes **4** were subsequently optimized at $r' = 1.50$, 1.75, 2.00, and 2.25 Å. The frequencies of each of these partially optimized structures were then calculated; using the calculated force constants, the geometries were subsequently fully optimized at each value of r'.

The geometries and energies of the cycloaddition/CCA-rearrangement pathway (Path B) and the kinetically unfavorable **4** → **3** rearrangement were computed in the gas phase. The electronic energies reported for these pathways include zero-point energy corrections.

Supporting Information Available: Cartesian coordinates and imaginary frequencies (where applicable) of all stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

JO048161Z

(29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennussi, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. C.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11; Gaussian, Inc.: Pittsburgh, PA, 2001.

(30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

(31) (a) Lee, C.; Wang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(32) Young, D. C. *Computational Chemistry*; Wiley: New York, 2001; pp 19−31.

(33) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(34) (a) Gonzalez, C.; Schlegel, B. *J. Phys. Chem.* **1990**, *94*, 5523. (b) Gonzalez, C.; Schlegel, B. *J. Chem. Phys.* **1989**, *90*, 2154.

(35) (a) Cizek, J. *Adv. Chem. Phys.* **1969**, *14*, 35. (b) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910. (c) Scuseria, G. E.; Janssen, C. L. Schaefer, H. F., III. *J. Chem. Phys.* **1988**, *89*, 7382. (d) Scuseria, G. E.; Schaefer, H. F., III. *J. Chem. Phys.* **1989**, *90*, 3700. (e) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968. (f) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem. Symp.* **1989**, *23*, 199.