Regioselectivity and Mechanism of Dihalocarbene Addition to Benzocyclopropene

Marina Khrapunovich, Ekaterina Zelenova, Lillian Seu, Alexis N. Sabo, Aidan Flaherty, and Dina C. Merrer*

Department of Chemistry, Barnard College, 3009 Broadway, New York, New York 10027
dmerrer@barnard.edu

Received June 6, 2007

Dihalocarbenes add regioselectively to aryl-substituted benzocyclopropenes to produce dihalobenzocyclobutenes. The regioselectivity of addition is not due to steric effects but depends on the electronic donor or acceptor ability of the substituent. B3LYP/6-31G* calculations show preferential :C Cl2 addition to substituted benzocyclopropene through electrophilic attack on the benzocyclopropene π-system (Ea = 1.1–2.4 kcal/mol) rather than C–C σ-bond insertion into the cyclopropenyl moiety (Ea = 5–24 kcal/mol). π-Addition proceeds regioselectively through a single transition state to xylylene intermediates or directly to benzocyclobutene products.

Introduction

Although the cyclopropanation of unstrained alkenes with singlet carbenes has been well studied and the concerted nature of its mechanism widely accepted,1–11 experimental and computational investigations of singlet carbenes additions to small-ring olefins are fewer in number.12–15 Dibromo- and dichloro-

![Chemical Structure](image)

Regioselectivity and Mechanism of Dihalocarbene Addition to Benzocyclopropene

Marina Khrapunovich, Ekaterina Zelenova, Lillian Seu, Alexis N. Sabo, Aidan Flaherty, and Dina C. Merrer*

Department of Chemistry, Barnard College, 3009 Broadway, New York, New York 10027
dmerrer@barnard.edu

Received June 6, 2007

Dihalocarbenes add regioselectively to aryl-substituted benzocyclopropenes to produce dihalobenzocyclobutenes. The regioselectivity of addition is not due to steric effects but depends on the electronic donor or acceptor ability of the substituent. B3LYP/6-31G* calculations show preferential :C Cl2 addition to substituted benzocyclopropene through electrophilic attack on the benzocyclopropene π-system (Ea = 1.1–2.4 kcal/mol) rather than C–C σ-bond insertion into the cyclopropenyl moiety (Ea = 5–24 kcal/mol). π-Addition proceeds regioselectively through a single transition state to xylylene intermediates or directly to benzocyclobutene products.

Introduction

Although the cyclopropanation of unstrained alkenes with singlet carbenes has been well studied and the concerted nature of its mechanism widely accepted,1–11 experimental and computational investigations of singlet carbenes additions to small-ring olefins are fewer in number.12–15 Dibromo- and dichloro-

![Chemical Structure](image)

Regioselectivity and Mechanism of Dihalocarbene Addition to Benzocyclopropene

Marina Khrapunovich, Ekaterina Zelenova, Lillian Seu, Alexis N. Sabo, Aidan Flaherty, and Dina C. Merrer*

Department of Chemistry, Barnard College, 3009 Broadway, New York, New York 10027
dmerrer@barnard.edu

Received June 6, 2007

Dihalocarbenes add regioselectively to aryl-substituted benzocyclopropenes to produce dihalobenzocyclobutenes. The regioselectivity of addition is not due to steric effects but depends on the electronic donor or acceptor ability of the substituent. B3LYP/6-31G* calculations show preferential :C Cl2 addition to substituted benzocyclopropene through electrophilic attack on the benzocyclopropene π-system (Ea = 1.1–2.4 kcal/mol) rather than C–C σ-bond insertion into the cyclopropenyl moiety (Ea = 5–24 kcal/mol). π-Addition proceeds regioselectively through a single transition state to xylylene intermediates or directly to benzocyclobutene products.

Introduction

Although the cyclopropanation of unstrained alkenes with singlet carbenes has been well studied and the concerted nature of its mechanism widely accepted,1–11 experimental and computational investigations of singlet carbenes additions to small-ring olefins are fewer in number.12–15 Dibromo- and dichloro-

![Chemical Structure](image)

Regioselectivity and Mechanism of Dihalocarbene Addition to Benzocyclopropene

Marina Khrapunovich, Ekaterina Zelenova, Lillian Seu, Alexis N. Sabo, Aidan Flaherty, and Dina C. Merrer*

Department of Chemistry, Barnard College, 3009 Broadway, New York, New York 10027
dmerrer@barnard.edu

Received June 6, 2007

Dihalocarbenes add regioselectively to aryl-substituted benzocyclopropenes to produce dihalobenzocyclobutenes. The regioselectivity of addition is not due to steric effects but depends on the electronic donor or acceptor ability of the substituent. B3LYP/6-31G* calculations show preferential :C Cl2 addition to substituted benzocyclopropene through electrophilic attack on the benzocyclopropene π-system (Ea = 1.1–2.4 kcal/mol) rather than C–C σ-bond insertion into the cyclopropenyl moiety (Ea = 5–24 kcal/mol). π-Addition proceeds regioselectively through a single transition state to xylylene intermediates or directly to benzocyclobutene products.

Introduction

Although the cyclopropanation of unstrained alkenes with singlet carbenes has been well studied and the concerted nature of its mechanism widely accepted,1–11 experimental and computational investigations of singlet carbenes additions to small-ring olefins are fewer in number.12–15 Dibromo- and dichloro-

![Chemical Structure](image)
Dihalocarbene Addition to Benzocyclopropene

5. We have recently shown \( \text{CCl}_2 \) addition to cyclopropene in part through a xylylene intermediate that can be trapped as a Diels–Alder adduct with dimethyl acetylenedicarboxylate (eq 5).\(^{(19)}\) We have recently shown \( \text{CCl}_2 \) addition to cyclopropene to proceed not only via the major bicyc[1.1.0]butane-mediated pathway (eq 1a), but also through a minor, concerted route to butadiene product (eq 1b).\(^{(14)}\) These major and minor paths share a common transition state on the potential energy surface (PES) of this system and diverge at a bifurcation point, where the bifurcation is attributed to nonstatistical dynamic effects.

\[
\begin{align*}
\text{a. } R & = \text{H} \\
\text{b. } R & = \text{Me} \\
\text{c. } R & = \text{Br} \\
\text{d. } R & = \text{CHO}
\end{align*}
\]

Because the previous report of \( \text{CX}_2 \) addition to benzocyclopropene \( 1\text{a} \)\(^{(15)}\) did not provide conclusive evidence for the intermediacy of \( 2\text{a} \), and because other electrophiles (e.g., HCl/Br/Cl and Ru carbenoids) add to \( 1 \) by alternative mechanisms (i.e., involving charged\(^{(18)}\) and xylylene intermediates,\(^{(19)}\) respectively), we set out to determine the mechanism of \( \text{CX}_2 \) addition to \( 1 \). We have used experimental and computational techniques to investigate the feasibility of the following possible mechanistic routes (Scheme 1): (A) Kagabu and Saito’s original proposed pathway through intermediate \( 2\text{a} \),\(^{(15)}\) (B) initial dipolar addition through zwitierons (5 and 6) followed by rearrangement to product, analogous to Garrant et al.’s findings\(^{(18)}\) for HCl, Br\(_2\), or I\(_2\) addition to \( 1\text{b} \), (C) a mechanism involving xylylene intermediates (7 and 8) which then ring-close to benzocyclobutene products, (D) addition to form benzocyclobutenes 3 and 4 in a concerted manner, and (E) formation of xylylenes via propellane 2: \( 1 + \text{CX}_2 \rightarrow 2 \rightarrow 7 + 8 \rightarrow 3 + 4 \).

Results and Discussion

Experimental. Our experimental approach toward the elucidation of the mechanism of \( \text{CX}_2 \) addition to benzocyclopropene focused on regiochemical studies utilizing aryl-substituted benzocyclopropanes (1), where the electronic nature of \( R \) is varied (\( R = \text{H}, \text{Me}, \text{Br}, \text{CHO} \)). Constant regioisomeric product ratios 3/4, regardless of the electronic nature of \( R \), would suggest a mechanism through a more symmetric-type intermediate (i.e., 2) (Scheme 1, route A). In contrast, variations of 3/4 dependent on \( R \) would support a path(s) through an asymmetric intermediate (i.e., 5 or 6, or 7 or 8) (Scheme 1, routes B or C, respectively) or concerted formation of product (route D).

Furthermore, if \( \text{CX}_2 \) addition proceeds via zwitierionic intermediates (5, 6), we expect an electron-donating group (edg; e.g., \( R = \text{Me} \)) to preferentially stabilize 5, thereby regioselectively yielding 3 as the major benzocyclobutene product. In contrast, electron-withdrawing substituents (ewg; e.g., \( R = \text{Br}, \text{CHO} \)) would destabilize 5 by resonance, favoring the route 6 \( \rightarrow 4 \). We expect ewg’s to inductively destabilize 6, although we believe this effect not as detrimental as the resonance destabilization of 5.

Benzocyclopropene \( 1\text{a} \)\(^{(20)}\) and its derivatives \( 1\text{b} \sim 1\text{d} \)\(^{(22)}\) were synthesized according to literature procedures. Each of 1 was reacted with each of \( \text{CBr}_2 \) and \( \text{CCl}_2 \) generated from haloform and tert-butoxide.\(^{(3,23)}\) The yields\(^{(23)}\) of dihalocyclobutenes products decreased with decreased electron-donating strength of \( R \): when \( R = \text{Me} \), the yields of 3b \( + 4\)b were 62% (X = Br) and 44% (X = Cl), compared to yields of 29% (X = Br) and 6% (X = Cl) for 3c \( + 4\)c (i.e., when \( R = \text{Br} \)). Additionally, 1d (R = CHO) reacted with neither \( \text{CBr}_2 \) nor \( \text{CCl}_2 \) to form 3d or 4d.\(^{(24)}\) We attribute the unreactivity of 1d toward \( \text{CX}_2 \) addition in part to the reduced nucleophilicity of 1d (relative to 1a, 1b, or 1c) imparted by the more strongly electron-withdrawing formyl substituent, as well as preferential reaction of 1d with tert-butoxide.\(^{(25)}\)

In terms of the distribution of benzocyclobutenes 3 and 4, we see regioselectivity for the reaction of \( \text{CX}_2 \) with 1. When \( R = \text{Me} \), 3b/4b = 2 for addition of both \( \text{CBr}_2 \) and \( \text{CCl}_2 \). When \( R = \text{Br} \), the selectivity reverses: 3c/4c = 0.33 for addition of \( \text{CBr}_2 \) and 0.20 for \( \text{CCl}_2 \) addition.\(^{(23)}\) We used the \( ^1\text{H} \) NMR chemical shifts of the methylene and, where applicable, methyl protons to distinguish between regioisomers 3 and 4 and establish their identities. The chemical shifts of proximal addition product 3b’s methyl and methylene protons were expected to be downfield of those of 4b, and that is what was observed: for 3b-Cl, the methyl and methylene protons resonate at 2.41 and 4.07 ppm, respectively, compared to 2.22 and 4.05 ppm for 4b-Cl; for 3b-Br, the methyl and methylene protons resonate at 2.39 and 4.25 ppm, respectively, compared to 2.20 and 4.23 ppm for 4b-Br. In the case of bromo derivatives 3c vs 4c, the chemical shifts of distal addition product 4c’s methyl and methylene protons were expected to resonate downfield of those of 3c.

(23) Yields of 3 + 4 were calculated relative to unreacted 1 by integration of the \( ^1\text{H} \) NMR of the product mixtures. The product ratios 3/4 were obtained from comparison of their \( ^1\text{H} \) NMR integrations of the product mixtures; these spectra are included in the Supporting Information. Full experimental details are provided in the Experimental Section and Supporting Information.
(24) The reactions of 1d + KOtBu + CHX\(_3\) yielded very complex mixtures of products, none of which appear to be the result of \( \text{CX}_2 \) addition to 1d. However, many of the products appear to be the result of reactions of 1d with tert-butoxide, as evidenced by the mass spectra of said products containing fragment ions with \( m/z = 105 \) (PhCO\(^+\)) and 57 (MeC\(^+\)). In the CHCl\(_3\) reactions, we detected very small amounts of \( \text{CCl}_3 \) addition to 1d, presumably at the formyl moiety, as well. No such \( \text{CBr}_2 \) + 1d addition products were detected, however.


because of the expected deshielding effect of the aryl bromine substituent. Again, our prediction was borne out: for 3c-Cl, the methylene protons have a chemical shift of 4.05 ppm, compared to 4.09 ppm for 4c-Cl; 3c-Br’s methylene protons resonate at 4.20 ppm, versus 4.25 ppm in 4c-Br.

That these reactions are regioselective supports proposed mechanistic routes B and C (Scheme 1), which proceed through asymmetric intermediates 5 (or 6) and 7 (or 8), respectively, or concerted route D. Furthermore, the regioselectivity would not seem to support paths A or E through intermediate 2, which is expected to be nonselective in its ultimate rearrangement to 3 and 4. To distinguish between mechanisms B and C, conclusive evidence for the intermediary of xylylenes 7 and 8 could be obtained via Diels–Alder trapping of these species with dimethyl acetylenedicarboxylate (DMAD) (eq 6), as Billups et al. did in their 1a + Ru carbenoid studies.19

Because 1b (R = Me) yielded the most carbene addition products 3 and 4, we reacted 1b with each of CHX3/KOt-Bu (X = Br, Cl) in the presence of DMAD.23 Unfortunately, none of 9b or 10b was observed. In the case of attempted trapping of proposed xylylene intermediates for the addition of :CB2 to 1b, the yield and ratios of benzocyclobutene products 3c-Br and 4c-Br were produced in the same yield and ratio as previously obtained in the absence of DMAD. It does also appear that :CB2 has reacted with excess DMAD. In the :CCl2 reactions (i.e., 1b + KOtBu + CHCl3 + DMAD), carbene addition products 3c-Cl and 4c-Cl were formed in extremely low yields, with unreacted 1b recovered. Additionally, it does not appear that :CCl1 reacted with DMAD; instead, DMAD seems to have reacted with KOtBu, forming a complex mixture of products. The absence of xylylenes 5 and 8 from the attempted trapping experiments does not preclude their formation, only that they are too short-lived to be trapped. Further discussion and resolution of these issues follows in our computational investigations.

Computational.25–28 We have seen experimental evidence of regioselectivity for the reaction of substituted 1 with :CX2 (X = Br, Cl). To rule out the effect of the steric bulk of R on the selectivity of benzocyclobutene products 3 vs 4, we conducted a computational Hammett study. The B3LYP/6-31G* level of theory using Gaussian98 or 03 unless otherwise noted. All stationary points were confirmed by frequency analyses. The reported energies include ZPE corrections that were scaled by 0.9806 (ref 29).

(25) All calculations were carried out at the B3LYP/6-31G* level of theory using Gaussian98 or 03 unless otherwise noted. All stationary points were confirmed by frequency analyses. The reported energies include ZPE corrections that were scaled by 0.9806 (ref 29).


311G* energy differences between 3 and 4 (ΔΔH₂₋₄, X = Cl) were plotted against Hammett σ-values for a wide range of substituents R (Figure 1).¹¹

The correlation in Figure 1 is linear, except when R = tert-butyl. Unless R is quite large, its effect on the stability of 3 vs 4 is purely electronic in nature: 3 is stabilized when R = edg; 4 is stabilized when R = edg. Therefore, we can rule out steric effects on the preferential formation of 3 vs 4. In addition, if steric factors were to affect product stability, we would have predicted similar values of 3/4 for R = Me and Br, as the sizes of these groups are approximately equal.²² However, as seen earlier, this was not the case: 3/4 = 2 when R = Me, compared to 3/4 = 0.20–0.33 when R = Br.

The B3LYP/6-31G* PES of :CCl₂ addition to 1a – c (according to the mechanistic routes depicted in Scheme 1) is shown in Figure 2. (Table S1 in the Supporting Information contains values for all stationary points shown in Scheme 1 and Figure 2.) We considered two modes of :CCl₂ addition to 1a - c in our calculations: (1) addition to the π-system of 1a – c to yield propellane intermediate 2a – c, zwitterionic intermediates 5a – c and 6b – c, xylylene intermediates 7a – c and 8b – c, or benzocyclobutenes 3a – c and 4b – c as the initial intermediates or products of :CCl₂ addition, and (2) addition to the σ-system of 1a – c’s cyclopropenyl moiety to produce either xylylenes 7a – c and 8b – c or benzocyclobutenes 3a – c and 4b – c directly. To find the transition states for each of these approaches to each of these products, we used a combination of two techniques: (a) we optimized the :CCl₂-1a – c geometries at varying distances of r (1.0 – 3.5 Å, in 0.1-Å increments), where r was the distance between the carbene carbon and the midpoint of the C1–C6 π-bond of 1a – c, and where r was the distance between the carbene carbon and the midpoint of the C1–C6 π-bond of 1a – c, a method previously used with success for the investigation of :CCl₂ addition to cyclopropene and to 1-butene (Scheme 2), and (b) the quadratic synchronous transit method.

The optimized transition states for :CCl₂ addition to the π-system of 1a – c, 𝜂₂ (Figure 3a), are 1.1–2.4 kcal/mol higher in energy than the starting materials, in accord with 0–2 kcal/mol activation energies calculated for :CCl₂ addition to cyclopropene and to 1-butene. Notably, these lone transition states lead from starting materials to each of propellane 2a – c, xylylenes 7a – c and 8b – c, and benzocyclobutenes 3a – c and 4b – c. For :CCl₂ addition to the σ-system of 1a – c, through transition state 𝜂₃, activation barriers of 5–24 kcal/mol are computed (Figure 3b). Just as 𝜂₂ was found to be the lone transition state for π-addition, 𝜂₃ is the only transition state for σ-addition, and 𝜂₃ also leads to multiple products: to xylylenes 7a – c and 8b – c as well as to benzocyclobutenes 3a – c and 4b – c.

All 𝜂₂ and 𝜂₃ relative energies are compiled in Table S1 in the Supporting Information.

The phenomenon of a single transition state leading to multiple products on PESs containing flat reaction plateaus has been observed previously in other systems.¹⁴–²³ These include cyclopropene stereomutation,²⁴ the vinylecyclopropane–cyclopentane rearrangement,²⁵ and the degenerate rearrangement of...
The most relevant of these to benzocyclopropene is the common transition state for CCl₂ addition to cyclopropene, yielding dihalobicyclo[1.1.0]butane and dihalobutadiene products (eq 1). In the current study of CCl₂ + 1, intermediate propellane 2 corresponds to the bicyclobutane in the simpler CCl₂ + cyclopropene case, and xylylenes 7 and 8 are analogous to butadiene (Scheme 3).

As far as calculation of the remainder of the mechanistic routes shown in Scheme 1 is concerned, the previously proposed mechanism for CX₂ + 1a suggests that intermediate adduct 2a rearranges directly to benzocyclobutene product 3a (route A). Attempts at finding a transition state connecting 2a to benzocyclobutene product 3a in a concerted manner were unsuccessful. Rather, if intermediate 2a is indeed formed during the reaction of 1a with CCl₂, it must first rearrange, over a 40–41 kcal/mol barrier (‡2), to xylylene 7a, as in mechanistic route E, before proceeding to 3a. Electroyclic ring closure with rearomatization of 7a- → 8b,c → 3a + 4b,c occurs with Eₐ = 20–25 kcal/mol via ‡3.

Lest zwitterions 5 and 6 be neglected, these species are also proposed as possible intermediates in this system. The generation of 5 and 6 could also account for the observed experimental regioselectivity of CX₂ addition to 1; however, attempts at finding 5a (R = H) as an energy minimum on the PES of this system were unsuccessful. That 5a is not an energy minimum is not surprising, as we had previously shown analogous zwitterions for CCl₂ addition to cyclopropene not to be minima on that PES either.

The reasonably deep calculated potential well in which 7a resides was met with some concern, given our inability to trap any sort of xylylene intermediate experimentally (vide supra). Precedents for similar behavior of seemingly stable (i.e., isolable under other reaction conditions) yet untrappable, intermediate compounds were observed in the :CX₂ + 1,2-disubstituted cyclopropene systems. For :CX₂ + 1,2-diarylcyclopropanes, the major experimental reaction path is through intermediate 1,1-dihalo-2,4-diarylbicyclo[1.1.0]butanes to 2,3-dihalo-1,3-diarylcyclobutenes via CCA rearrangement (eq 1), as reported by Brinker et al. This CCA rearrangement was calculated for :CCl₂ addition to cyclopropene not to be minima on that PES either.


(37) Transition state ‡2 was calculated three separate times, obtaining structurally and energetically similar species, all providing Eₐ values of 39.7–41.4 kcal/mol for 2a → 7a → 3a.

1,2-disubstituted cyclopentenes (i.e., the rearrangement of 1,1-dichloro-2,4-disubstituted bicyclo[1.1.0]butanes to 2,3-dichloro-1,3-disubstituted cyclobutenes) to require 11–34 kcal/mol of activation energy (Scheme 2).14 Bicyclobutanes are well known, can be readily synthesized by other methods,39 and are generally stable. However, for the approximately 110 kcal/mol exothermic reaction of :CCl 2 + cyclopropene first to bicyclobutane and subsequently to cyclobutene product,14 the bicyclobutane intermediate is not observed, nor isolated, experimentally in solution, even with diaryl substitution.13

Yu and Muckerman investigated the reaction of singlet methylene and acetylene by reaction dynamics calculations in the gas phase.38 The initial “product” of 1CH 2 + C 2H 2 is cyclopropene, which subsequently rearranges with equal probability to either propene (E a = 37 kcal/mol) or allene (E a = 45 kcal/mol). As with bicyclobutanes, cyclopentenes can be synthesized by a variety of methods and stored in solution at low temperatures for several days.40 However, Yu and Muckerman calculated the lifetime of cyclopropene as formed by 1CH 2 addition to C 2H 2 to be only 3.2 ps. They attributed cyclopropene’s fleeting lifetime, despite its existence in a reasonably deep potential well (87 kcal/mol back to 1CH 2 + C 2H 2 and 37–45 kcal/mol to propyne or allene), to its “highly energized”38 state. Upon initial 1CH 2 addition to the acetylene triple bond, the total potential energy of the system drops by a large amount. The potential and kinetic energies then exchange as the cyclopropene is formed. During this time, the kinetic energy strongly oscillates, meaning that the cyclopropene “lives” as a very energized species. Subsequent rearrangement of the energetic cyclopropene over ~40 kcal/mol barriers to propyne or allene is therefore facile.

With these related examples in mind, we draw comparisons between the current investigation of :CX 2 + benzocyclobutene 1 with :CCl 2 + cyclopropene and 1CH 2 + acetylene. Although the 1CH 2 + acetylene case was calculated for the gas phase,38 where dynamic effects are expected to be enhanced, the experimental investigations of :CX 2 + 1,2-diarylcyclopentenes were conducted in solution,13 where vibrationally hot molecules have more ways of releasing excess energy (particularly with two aryl substituents), and yet bicyclobutane intermediates were still unisolable; only the cyclobutene products were found. Therefore, taking together here the experimental results in solution, which demonstrate regioselective product formation of benzocyclobutenes 3 and 4 via an asymmetric intermediate, and our computed PES, we conclude that a pair of regioisomeric xylylene intermediates (7 and 8) may intervene in the mechanism of this reaction. We propose that 7 and 8 are not trappable because of the excess energy with which they are generated, resulting in short lifetimes and rapid rearrangement to products 3 and 4. It is possible that propellane intermediate 2 is formed upon initial addition of :CX 2 to 1 and is followed by rearrangement to 7 and 8 (i.e., Scheme 1, route E). However, we think this less likely than addition of :CX 2 and 1 directly to 7 and 8 in a concerted manner (Scheme 1, route C) because regioselectivity is established during the initial addition of :CX 2.

Alternatively, the other proposed mechanistic path that accounts for both the experimental regioselectivity and the computational results is route D. Here, :CX 2 may add directly, via π-attack on 1, to yield benzocyclobutene products 3 and 4 in a concerted fashion. Because the same transition state 2f leads to xylylenes 7a–c and 8b,c or benzocyclobutenes 3a–c and 4b,c, it is entirely possible that either or both routes C and/or D are operative. If it is indeed true that both paths lead to products, and because the xylylene intermediates appear to be untrappable when produced in this way, it would be virtually impossible to distinguish which path predominates without conducting a complete reaction dynamic study on the :CX 2-benzocyclobutene system.

Conclusions

Dibromo- and dichlorocarbene add to 2-substituted benzocyclobutenes (1) regioselectively, where R = edg yields benzocyclobutene 3b as the major product and R = ewg favors the formation of product 4c. The calculated transition state for initial π-addition of :CCl 2 reaction to benzocyclobutene 1 is shared among three reaction paths that yield different intermediates or products: propellane 2, xylylenes 7 and 8, and benzocyclobutenes 3 and 4 (via routes A and E, C, and D, respectively). Zwitterions 5 and 6 (route B) are not believed to intervene in the mechanism of :CX 2 + 1, as 5a was not shown to be a minimum on the PES of this reaction. The calculated PES for .CCl 2 + 1 does not rule out propellane intermediate 2 (routes A and E) as part of the addition mechanism, but if 2 is indeed formed, it does not convert directly to products 3 and 4, but rearranges first to xylylenes 7 and 8 (route E), which subsequently ring-close and rearomatize to 3 and 4. However, the experimental regioselectivity of carbene addition disfavors the intermediacy of 2, thus discounting paths A and E. Although xylylenes 7 and 8 (route C) were not able to be trapped as Diels–Alder adducts, their untrappability is attributed to the highly energized states in which they are expected to exist because of the very exothermic way in which they are generated in this system, similar to Brinker et al.’s inability to isolate bicyclobutane intermediates in their solution-phase experiments of :CX 2 + 1,2-diarylcyclopentenes.13 Therefore, the mechanistic routes that account for the experimental and computational results reported herein involve formation of products 3 and 4 either in a concerted fashion (route D) or via xylylenes 7 and 8 (route C). To definitively distinguish the prevalent mechanistic path, C or D, would require a thorough reaction dynamic study of this system.

Experimental Methods

General Procedure for Dihalocarbene Additions to Benzo-
cyclopentenes 1. Into a 25-mL, 3-necked round-bottom flask were placed 0.150–0.155 g (1.3 mmol) of potassium t-butoxide, 5 mL of anhydrous pentane, and a solution of 0.0275 g (0.26 mmol) of 1 dissolved in 2.5 mL of anhydrous pentane. The reaction mixture was stirred and cooled to 0 °C, and to it was added 0.05 mL (0.57 mmol) of CHX 3 (X = Br or Cl) dropwise via syringe over 1 min. Once the CHX 3 had been added, the reaction flask was allowed to warm to room temperature and stirred overnight. After stirring for 12 h at room temperature, the reaction was quenched by the addition of 5–7 mL of water. The products were then extracted with ether, and the ether extracts were combined and washed with brine and


dried over Na2SO4. The reaction mixtures were analyzed by GC/MS and 1H NMR. Regioisomeric product ratios were calculated by 1H NMR via integration of the methylene (and methyl, in the case of 3b and 4b) protons on the benzocyclobutene products.

Attempted Trapping of Xylylenes 7b and 8b by DMAD. The procedure for 3C5H4 addition to 1b was followed as above, but into the reaction flask was added 0.141–0.142 g (1.0 mmol) of DMAD along with 1b, before CH2Cl2 (X = Br or Cl) addition.

1,1′-Dichlorobenzocyclobutene (3a-Cl): 1H NMR (300 MHz, CDCl3) δ 7.47–7.35 (m, 3H), 7.2 (m, 1H), 4.05 (s, 2H). GC/MS (EI): m/z (relative intensity) 260/262/264 [0.0/1.00/0.0, M+/(M+ + 2)/(M+ + 4)], 181/183 [62/0.60/0.7, (M+ − 79)/(M+ + 2) − 79)], 102 (100, M+ − 160), 75 (26.7, M+ − 186).

2-Methyl-1,1′-dichlorobenzocyclobutene (3b-Cl): 1H NMR (300 MHz, CDCl3) δ 7.38–6.98 (m, 3H), 7.08 (d, J = 7.8 Hz, 1H), 7.18 (t, J = 0.7 Hz, 1H), 4.23 (s, 2H), 2.20 (s, 3H). GC/MS (EI): m/z (relative intensity) 186/188/190 [27/16.8/9.00, M+/(M+ + 2)/(M+ + 4)], 151/153 [85/0.45/0.5, (M+ − 35)/(M+ + 2) − 35)], 115 (77.5, M+ − 80), 89 (15.0, M+ − 96).

2-Methyl-2′,1′-dichlorobenzocyclobutene (4b-Cl): 1H NMR (300 MHz, CDCl3) δ 7.38–6.98 (m, 3H), 4.05 (s, 2H), 2.22 (s, 3H). GC/MS (EI): m/z (relative intensity) 186/188/190 [27/16.8/9.00, M+/(M+ + 2)/(M+ + 4)], 151/153 [85/0.45/0.5, (M+ − 35)/(M+ + 2) − 35)], 115 (100, M+ − 70), 89 (18.9, M+ − 96).

2-Methyl-1′,1′-dibromobenzocyclobutene (3b-Br): 1H NMR (300 MHz, CDCl3) δ 7.31 (t, J = 7.6 Hz, 1H), 7.14 (dt, J = 7.8, 0.8 Hz, 1H), 6.96 (dt, J = 7.3, 0.7 Hz, 1H), 4.25 (s, 2H), 2.39 (s, 3H). 13C NMR (75 MHz, CDCl3) δ 147.9, 136.7, 133.5, 123.6, 130.0, 120.9, 59.7, 47.9, 14.8. HRMS (EI): calcld, 273.8993; found, 273.9000. GC/MS (EI): m/z (relative intensity) 274/276/278 [0.5/1.0/0.5, M+/(M+ + 2)/(M+ + 4)], 195/197 [100/100, M+ − 79]/(M+ + 2) − 79)], 116 (16.5, M+ − 160), 89 (16.5, M+ − 186).

2-Methyl-2′,2′-dibromobenzocyclobutene (4c-Br): 1H NMR (300 MHz, CDCl3) δ 7.28 (d, J = 7.5 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.08 (d, J = 7.4 Hz, 1H), 4.23 (s, 2H), 2.20 (s, 3H). 13C NMR (75 MHz, CDCl3) δ 150.0, 135.2, 134.4, 132.4, 130.0, 118.6, 59.4, 47.1, 16.8. HRMS (EI): calcld, 273.8993; found, 273.9000.

Acknowledgment. We are grateful to the NSF (CHE-0517876, CHE-0234660, DUE-99952633), PRF (37969-GB4), Research Corporation (CC5551), and Barnard College for financial support. We thank the Howard Hughes Foundation (to E.Z.) and the Bernice G. Segal Fund of Barnard College (to M.K.) for fellowships, the Women Chemists Committee and the Division of Organic Chemistry of the ACS for travel awards to E.Z. and L.S., respectively, and Dr. Yasuhiro Itagaki (Columbia University) for high-resolution mass spectrometric analyses. D.C.M. thanks Professors Westen T. Borden, Richard P. Johnson, Maitland Jones, Paul R. Rablen, and Daniel A. Singleton for helpful discussions, and Anthony Condo and Dr. John Decatur for valuable NMR suggestions.