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Regioselectivity and Mechanism of Dihalocarbene Addition to Benzocyclopropene

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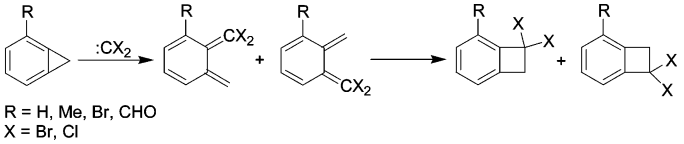

Dihalocarbenes add regioselectively to aryl-substituted benzocyclopropenes to produce dihalobenzocyclobutenes. The regioselectivity of addition is not due to steric effects but depends on the electronic donor or acceptor ability of the substituent. B3LYP/6-31G* calculations show preferential :CCl_2 addition to substituted benzocyclopropene through electrophilic attack on the benzocyclopropene π-system (E_a = 1.1−2.4 kcal/mol) rather than C−C σ-bond insertion into the cyclopropenyl moiety (E_a = 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 carbene additions to small-ring olefins are fewer in number.[12−16] Dibromo- and dichlorocarbene react with cyclopropene and cyclobutene to give, respectively, 2,3-dihalocyclobutene and 2,3-dihalocyclopentene as major products, from cationic cyclopropyl allyl (CCA) rearrangements of the likely dihalo[1.1.0]bicyclobutane and dihalo[2.1.0]bicyclopentane intermediates (eqs 1a and 2).[13] For :CX_2 (X = Br, Cl) addition to benzocyclopropene (**1a**), Kagabu and Saito invoked an analogous intermediate, **2a**, to account for the formation of dihalobenzocyclobutene **3a** (eq 3).[15] However, in none of these cases were the intermediate adducts isolated or observed spectroscopically.

Benzocyclopropene (**1a**) reacts with a variety of electrophiles in addition to :CX_2.[17] The type of intermediate involved in the addition depends upon the electrophile added. Garratt and coworkers reported the intermediacy of Wheland intermediates for the regioselective addition of HCl, Br_2, and I_2 to **1b** (eqs 4a,b); eq 4a was preferred.[18] Billups et al. determined that the reaction of **1a** with a methylene ruthenium carbenoid proceeds

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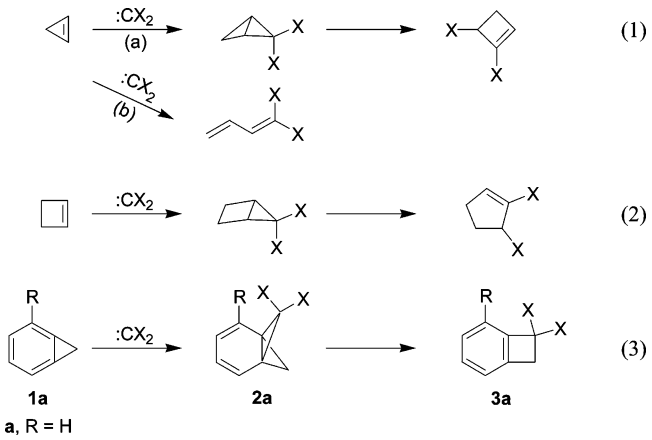
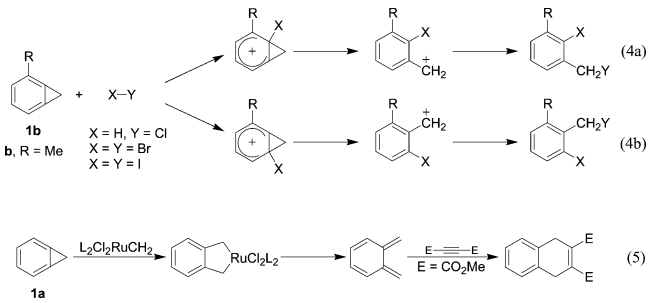


in part through a xylylene intermediate that can be trapped as a Diels−Alder adduct with dimethyl acetylenedicarboxylate (eq 5).[19] We have recently shown :CCl_2 addition to cyclopropene to proceed not only via the major bicyclo[1.1.0]butane-mediated pathway (eq 1a), but also through a minor, concerted 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.



Because the previous report of :CX_2 addition to benzocyclopropene **1a**[15] did not provide conclusive evidence for the intermediacy of **2a**, and because other electrophiles (e.g., HCl/Br_2/I_2 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 :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**,[15] (B) initial dipolar addition through zwitterions (**5** and **6**) followed by rearrangement to product, analogous to Garratt et al.'s findings[18] for HCl, Br_2, or I_2 addition to **1b**, (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** + :CX_2 → **2** → **7** + **8** → **3** + **4**.

Results and Discussion

Experimental. Our experimental approach toward the elucidation of the mechanism of :CX_2 addition to benzocyclopropene focused on regiochemical studies utilizing aryl-substituted benzocyclopropenes (**1**), where the electronic nature of R is varied (R = H, Me, Br, 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 :CX_2 addition proceeds via zwitterionic intermediates (**5**, **6**), we expect an electron-donating group (edg; e.g., R = Me) to preferentially stabilize **5**, thereby regioselectively yielding **3** as the major benzocyclobutene product. In contrast, electron-withdrawing substituents (ewg; e.g., R = Br, CHO) would destabilize **5** by resonance, favoring the route **6** → **4**. We expect ewg's to inductively destabilize **6**, although we believe this effect not as detrimental as the resonance destabilization of **5**.

Benzocyclopropene (**1a**)[20] and its derivatives **1b**−**d**[21,22] were synthesized according to literature procedures. Each of **1** was reacted with each of :CBr_2 and :CCl_2 generated from haloform and *tert*-butoxide.[3,23] The yields[23] of dihalobicyclobutene products decreased with decreased electron-donating strength of R: when R = Me, the yields of **3b** + **4b** were 62% (X = Br) and 44% (X = Cl), compared to yields of 29% (X = Br) and 6% (X = Cl) for **3c** + **4c** (i.e., when R = Br). Additionally, **1d** (R = CHO) reacted with neither :CBr_2 nor :CCl_2 to form **3d** or **4d**.[24] We attribute the unreactivity of **1d** toward :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.[24]

In terms of the distribution of benzocyclobutenes **3** and **4**, we see regioselectivity for the reaction of :CX_2 with **1**. When R = Me, **3b**/**4b** = 2 for addition of both :CBr_2 and :CCl_2. When R = Br, the selectivity reverses: **3c**/**4c** = 0.33 for addition of :CBr_2 and 0.20 for :CCl_2 addition.[23] We used the ^{1}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 methylene protons were expected to resonate downfield of those of **3c**

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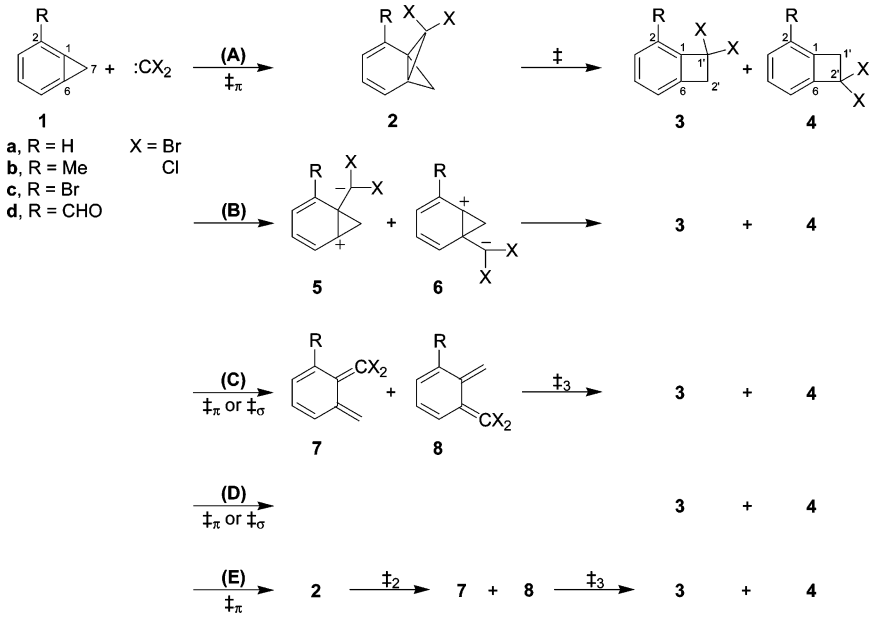
(23) Yields of **3** + **4** were calculated relative to unreacted **1** by integration of the ^{1}H NMR of the product mixtures. The product ratios **3**/**4** were obtained from comparison of their ^{1}H NMR integrations of the product mixtures; these spectra are included in the Supporting Information. Full experimental details are provided in the Experimental Section and Supporting Information.

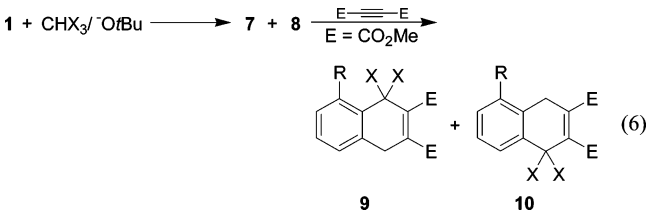
(24) The reactions of **1d** + KOtBu + CHX_3 yielded very complex mixtures of products, none of which appear to be the result of :CX_2 addition to **1d**. However, many of the products appear to be the result of reactions of **1d** with *tert*-butoxide, as evidenced by the mass spectra of said products containing fragment ions with m/z = 105 ($PhCO^+$) and 57 (Me_3C^+). In the $CHCl_3$ reactions, we detected very small amounts of $^-CCl_3$ addition to **1d**, presumably at the formyl moiety, as well. No such $^-CBr_3$ + **1d** addition products were detected, however.

SCHEME 1. Proposed Mechanisms of :CX_2 Addition to Benzocyclopropene (1)



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 intermediacy 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]



(6)

Because **1b** (R = Me) yielded the most carbene addition products **3** and **4**, we reacted **1b** with each of CHX_3/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 :CBr_2 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 $^{-}CBr_3$ has reacted with excess DMAD. In the :CCl_2 reactions (i.e., **1b** + KOtBu + $CHCl_3$ + 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 $^{-}CCl_3$ 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.[25−29] We have seen experimental evidence of regioselectivity for the reaction of substituted **1** with :CX_2 (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-

(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).

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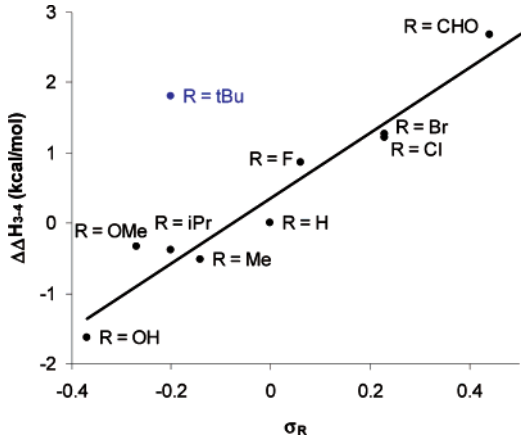


FIGURE 1. Hammett plot of the energy differences between benzocyclobutenes **3** and **4** ($\Delta\Delta H_{3-4}$; X = Cl) for various R (B3LYP/6-311G* with scaled ZPE correction).

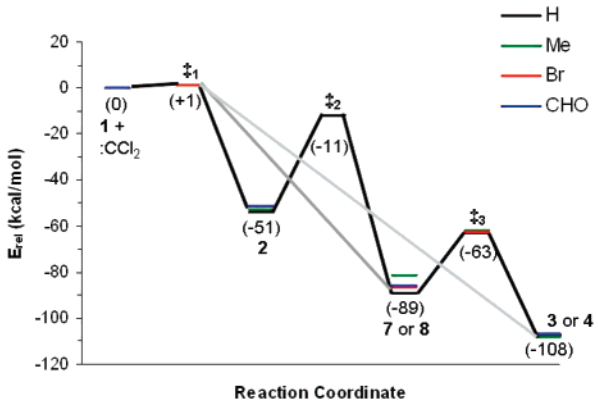


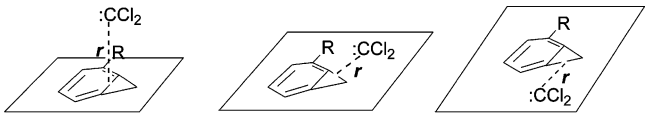
FIGURE 2. Potential energy surface for :CCl_2 + benzocyclopropene **1**. Relative energies are in kilocalories per mole at B3LYP/6-31G* and are ZPE-corrected (ZPEs are scaled by 0.9806). See Table S1 in the Supporting Information for all E_{rel} values.

311G* energy differences between **3** and **4** ($\Delta\Delta H_{3-4}$; X = Cl) were plotted against Hammett σ-values[30] (σ_R) for a wide range of substituents R (Figure 1).[31]

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 = ewg. 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.[32] 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 :CCl_2 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 E_{rel} values for all stationary points shown in Scheme 1 and Figure 2.) We considered two modes of :CCl_2 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 :CCl_2 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 :CCl_2-**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 C_1–C_6 π-bond of **1a**−**c**, and where *r* was the distance between the carbene carbon and the midpoint of the C_1–C_7 σ-bond of **1a**−**c**, a method previously used with success for the investigation of :CCl_2 addition to cyclopropene[14] and to 1-butene[6] (Scheme 2), and (b) the quadratic synchronous transit method.

SCHEME 2. π- and σ-Addition of :CCl_2 to Benzocyclopropene 1



The optimized transition states for :CCl_2 addition to the π-system of **1a**−**c**, $\ddagger_\pi$ (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 :CCl_2 addition to cyclopropene[14] and to 1-butene.[6] 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 :CCl_2 addition to the σ-system of **1a**−**c**, through transition state $\ddagger_\sigma$, activation barriers of 5−24 kcal/mol are computed (Figure 3b). Just as $\ddagger_\pi$ was found to be the lone transition state for π-addition, $\ddagger_\sigma$ is the only transition state for σ-addition, and $\ddagger_\sigma$ also leads to multiple products: to xylylenes **7a**−**c** and **8b**,**c** as well as to benzocyclobutenes **3a**−**c** and **4b**,**c**. All $\ddagger_\pi$ and $^\ddagger_\sigma$ 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.[14,33−36] These include cyclopropane stereomutation,[34] the vinylcyclopropane−cyclopentene rearrangement,[35] and the degenerate rearrangement of

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(31) Previous studies have attempted to correlate product ratios with Hammett σ-constants: regioisomers of 1,3-dipolar cycloadditions of p-substituted benzonitrile oxides and methyl propiolate (Ponti, A.; Molteni, G. *Chem.−Eur. J.* **2006**, *12*, 1156), and products of triplet p-substituted bis(2,6-dimethylphenyl)carbenes (Hu, Y.; Ishikawa, Y.; Hirai, K.; Tomioka, H. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 2207). These investigations showed no correlation between product ratios and Hammett constants. However, thermodynamics (ΔH and ΔS) of cis−trans isomerizations of p-substituted palladium(II)−phosphine complexes do show linear correlations with Hammett σ-constants (Verstuyft, A. W.; Nelson, J. H. *Inorg. Chem.* **1975**, *14*, 1501; Knight, L. M.; Nelson, J. H. *Inorg. Chem.* **1977**, *16*, 1317).

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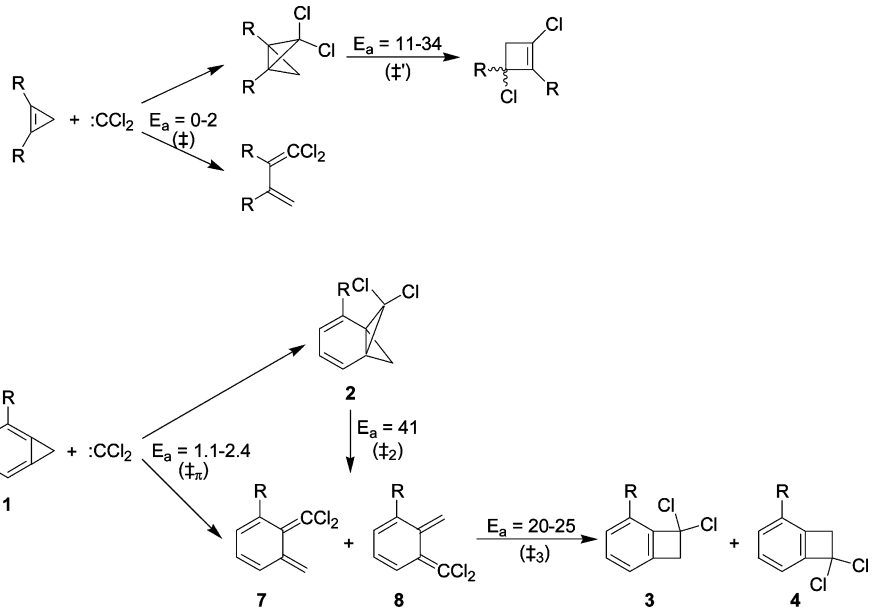
SCHEME 3. Comparison of :CCl_2 Addition to Cyclopropene and to Benzocyclopropene (1); Energies Are in Kilocalories per Mole at B3LYP/6-31G*



bicyclo[3.1.0]hex-2-ene.[36] The most relevant of these to benzocyclopropene is the common transition state for :CCl_2 addition to cyclopropene, yielding dihalobicyclo[1.1.0]butane and dihalobutadiene products (eq 1).[14] In the current study of :CCl_2 + **1**, intermediate propellane **2** corresponds to the bicyclobutane in the simpler :CCl_2 + 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

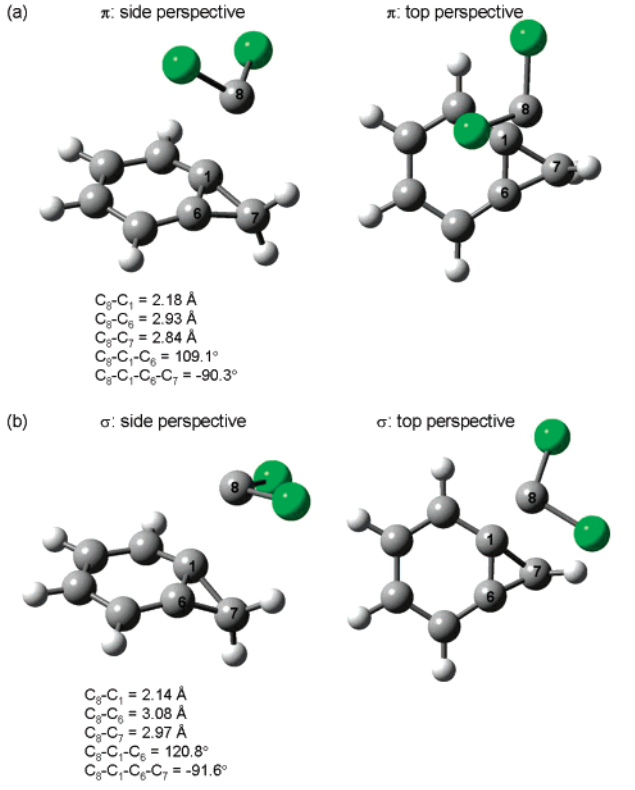


FIGURE 3. B3LYP/6-31G*-optimized transition states for :CCl_2 + benzocyclopropene **1a** by (a) π-attack ($‡_\pi$) and (b) σ-attack ($‡_\sigma$).

mechanism for :CX_2 + **1a** suggests that intermediate adduct **2a** rearranges directly to benzocyclobutene product **3a** (route A).[15] 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 :CCl_2, it must first rearrange, over a 40−41 kcal/mol barrier ($‡_2$),[37] to xylylene **7a**, as in mechanistic route E, before proceeding to **3a**. Electrocyclic ring closure with rearomatization of **7a**−**c** + **8b**,**c** → **3a** + **4b**,**c** occurs with E_a = 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 :CX_2 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 :CCl_2 addition to cyclopropene not to be minima on that PES either.[14]

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 :CX_2 + 1,2-disubstituted cyclopropene[13,14] and $^1CH_2$ + acetylene[38] systems.

For :CX_2 + 1,2-diarylcyclopropenes, 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.[13] This CCA rearrangement was calculated for :CCl_2 addition to a variety of

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(37) Transition state $‡_2$ was calculated three separate times, obtaining structurally and energetically similar species, all providing E_a values of 39.7−41.4 kcal/mol for **2a** → $‡_2$ → **7a**.

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1,2-disubstituted cyclopropenes (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, cyclopropenes 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 $:CX_2$ + benzocyclopropene **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-diarylcyclopropenes 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 $\ddagger_\pi$ 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 $:CX_2$-benzocyclopropene system.

Conclusions

Dibromo- and dichlorocarbene add to 2-substituted benzocyclopropenes (**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 benzocyclopropene **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-diarylcyclopropenes.[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 Benzocyclopropenes 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

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dried over Na_2SO_4. The reaction mixtures were analyzed by GC/MS and ^{1}H NMR. Regioisomeric product ratios were calculated by ^{1}H 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 $:CX_2$ 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 CHX_3 (X = Br or Cl) addition.

1′,1′-Dichlorobenzocyclobutene (3a-Cl):[15] ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.47−7.35 (m, 3H), 7.2 (m, 1H), 4.12 (s, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 148.8, 138.1, 132.6, 129.6, 124.6, 120.9, 79.7, 57.9. GC/MS (EI): *m/z* (relative intensity) 172/174/176 [23.7/15.7/2.3, $M^+/(M^+ + 2)/(M^+ + 4)$], 137/139 [100/35.7, $(M^+ - 35)/((M^+ + 2) - 35)$], 101 (58.3, $M^+ - 70$), 75 (31.1, $M^+ - 96$).

1′,1′-Dibromobenzocyclobutene (3a-Br):[15] ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.42 (m, 2H), 7.30 (m, 1H), 7.18 (m, 1H), 4.30 (s, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 151.1, 137.2, 132.6, 129.7, 124.4, 121.5, 60.4, 48.2. GC/MS (EI): *m/z* (relative intensity) 260/262/264 [0.0/1.0/0.0, $M^+/(M^+ + 2)/(M^+ + 4)$], 181/183 [62.0/60.7, $(M^+ - 79)/((M^+ + 2) - 79)$], 102 (100, $M^+ - 160$), 75 (26.7, $M^+ - 186$).

2-Methyl-1′,1′-dichlorobenzocyclobutene (3b-Cl): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38−6.98 (m, 3H), 4.07 (s, 2H), 2.41 (s, 3H). GC/MS (EI): *m/z* (relative intensity) 186/188/190 [19.2/13.3/1.7, $M^+/(M^+ + 2)/(M^+ + 4)$], 151/153 [100/30.8, $(M^+ - 35)/((M^+ + 2) - 35)$], 115 (77.5, $M^+ - 70$), 89 (15.0, $M^+ - 96$).

2-Methyl-2′,2′-dichlorobenzocyclobutene (4b-Cl): ^{1}H NMR (300 MHz,) 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 [27.6/18.9/0.0, $M^+/(M^+ + 2)/(M^+ + 4)$], 151/153 [85.0/45.7, $(M^+ - 35)/((M^+ + 2) - 35)$], 115 (100, $M^+ - 70$), 89 (18.9, $M^+ - 96$).

2-Methyl-1′,1′-dibromobenzocyclobutene (3b-Br): ^{1}H NMR (300 MHz, CD_2Cl_2) 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). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 147.9, 136.7, 133.5, 132.6, 130.0, 120.9, 59.7, 47.9, 14.8. HRMS (EI): calcd, 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 (4b-Br): ^{1}H NMR (300 MHz, CD_2Cl_2) 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). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 150.0, 135.2, 134.4, 132.4, 130.0, 118.6, 59.4, 47.1, 16.8. HRMS (EI): calcd, 273.8993; found, 273.8999. GC/MS (EI): *m/z* (relative intensity) 274/276/278 [0.7/1.4/0.7, $M^+/(M^+ + 2)/(M^+ + 4)$], 195/197 [77.1/72.9, $(M^+ - 79)/((M^+ + 2) - 79)$], 116 (100, $M^+ - 160$), 89 (26.4, $M^+ - 186$).

2-Bromo-1′,1′-dichlorobenzocyclobutene (3c-Cl): ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.55 (dd, 1.3, 7.5 Hz, 1H), 7.32−7.25 (m, 2H), 4.05 (s, 2H). GC/MS (EI): *m/z* (relative intensity) 250/252/254/256 [12.5/23.8/11.3/0.0, $M^+/(M^+ + 2)/(M^+ + 4)/(M^+ + 6)$], 215/217/219 [60.0/77.5/21.3, $(M^+ - 35)/((M^+ + 2) - 35)/((M^+ + 4) - 35)$], 136/138 [100/35.0, $(M^+ - 115)/((M^+ + 2) - 115)$], 99 (28.8, $M^+ - 150$), 75 (46.3, $M^+ - 176$).

2-Bromo-2′,2′-dichlorobenzocyclobutene (4c-Cl): ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.48 (dd, J = 0.74, 8.2 Hz, 1H), 7.33 (dd, J = 7.3, 8.2 Hz, 1H), 7.17 (dd, J = 0.73, 7.3 Hz, 1H), 4.09 (s, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 146.1, 140.8, 134.1, 132.4, 123.4, 114.2, 78.9, 57.6. HRMS (EI): calcd, 249.8952; found, 249.8957. GC/MS (EI): *m/z* (relative intensity) 250/252/254/256 [16.5/28.0/14.0/1.3, $M^+/(M^+ + 2)/(M^+ + 4)/(M^+ + 6)$], 215/217/219 [75.0/100/23.8, $(M^+ - 35)/((M^+ + 2) - 35)/((M^+ + 4) - 35)$], 136/138 [72.5/23.8, $(M^+ - 115)/((M^+ + 2) - 115)$], 99 (16.5, $M^+ - 150$), 75 (21.5, $M^+ - 176$).

2-Bromo-1′,1′-dibromobenzocyclobutene (3c-Br): ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.51 (dd, J = 1.3, 7.5 Hz, 1H), 7.32−7.24 (m, 2H), 4.20 (s, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 152.2, 137.6, 135.0, 131.8, 120.4, 116.7, 59.8, 45.2. HRMS (EI): calcd, 337.7941; found, 337.7939. GC/MS (EI): *m/z* (relative intensity) 338/340/342/344 [0.4/1.0/0.8/0.0, $M^+/(M^+ + 2)/(M^+ + 4)/(M^+ + 6)$], 259/261/263 [51.6/100/46.6, $(M^+ - 79)/((M^+ + 2) - 79)/((M^+ + 4) - 79)$], 180/182 [83.2/76.8, $(M^+ - 160)/((M^+ + 2) - 160)$], 101 (65.6, $M^+ - 240$), 75 (92.6, $M^+ - 266$).

2-Bromo-2′,2′-dibromobenzocyclobutene (4c-Br): ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.50 (dd, J = 0.70, 8.2 Hz, 1H), 7.30 (dd, J = 7.3, 8.1 Hz, 1H), 7.13 (dd, J = 0.69, 7.3 Hz, 1H), 4.25 (s, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 147.7, 139.9, 134.0, 132.4, 123.2, 115.2, 59.8, 46.2. HRMS (EI): calcd, 337.7941; found, 337.7950. GC/MS (EI): *m/z* (relative intensity) 338/340/342/344 [0.5/1.0/1.0/0.5, $M^+/(M^+ + 2)/(M^+ + 4)/(M^+ + 6)$], 259/261/263 [52.1/100/47.9, $(M^+ - 79)/((M^+ + 2) - 79)/((M^+ + 4) - 79)$], 180/182 [68.8/67.7, $(M^+ - 160)/((M^+ + 2) - 160)$], 101 (45.3, $M^+ - 240$), 75 (59.9, $M^+ - 266$).

Computational Methods. All calculations were carried out for the gas phase at the B3LYP/6-31G* level of theory using Gaussian98[27] or 03[28] unless otherwise noted. All stationary points were confirmed by frequency analyses. The reported energies include ZPE corrections scaled by 0.9806.[29] The geometries and energies of **3** and **4** used in the Hammett study (Figure 1) were calculated at B3LYP/6-311G*, and were ZPE-corrected (scaled by 0.9806).

Two modes of $:CCl_2$ addition to **1a**−**c** were calculated (Scheme 2). The first mode involved $:CCl_2$ addition to the π-system of **1a**−**c** where the reaction coordinate was defined as the distance *r* from the carbene carbon to the midpoint of the C_1–C_2 π-bond of **1a**−**c**, as per previous calculations of $:CCl_2$−alkene addition.[6,14] The second mode was $:CCl_2$ addition to the σ-system of **1a**−**c**'s cyclopropenyl moiety, where the reaction coordinate was the distance *r* from the carbene carbon to the midpoint of each of the C_1–C_3 and C_2–C_3 σ-bonds of **1a**−**c**. Distance *r* ranged from 1.0 to 3.5 Å in 0.1-Å increments for both modes of addition. To find the transition states for π- and σ-addition of $:CCl_2$, these "stepwise" techniques were used in combination with quadratic synchronous transit calculations and confirmed as transition states by frequency analyses.

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Supporting Information Available: General experimental conditions, characterization and copies of ^{1}H NMR, ^{13}C NMR, HSQC, HMBC, and EI mass spectra for compounds **3b**-Cl, **4b**-Cl, **3b**-Br, **4b**-Br, **3c**-Cl, **4c**-Cl, **3c**-Br, and **4c**-Br; ^{1}H NMR spectra of reaction mixtures of **3b**-Cl + **4b**-Cl, **3b**-Br + **4b**-Br, **3c**-Cl + **4c**-Cl, and **3c**-Br + **4c**-Br; tables of relative energies of stationary points for the PES of **1** + $:CCl_2$ and of the energy differences ($\Delta\Delta H_{3-4}$) of substituted **3** and **4**; and 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.

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