Pergamon

Tetrahedron Letters 41 (2000) 9633–9637

TETRAHEDRON
LETTERS

Addition of dihalocarbenes to corannulene. A fullerene-type reaction[†]

Dorin V. Preda and Lawrence T. Scott*

Boston College, Merkert Chemistry Center, Chestnut Hill, MA 02467-3860, USA

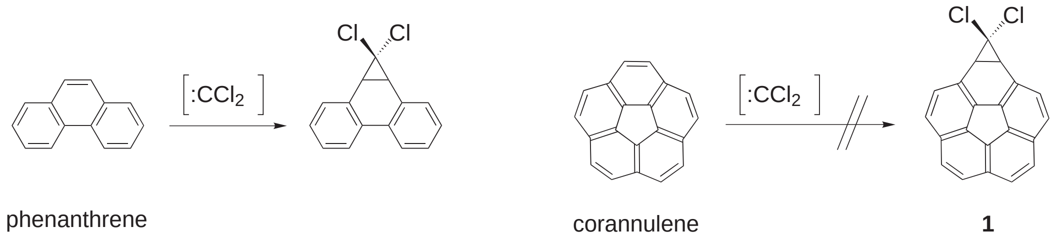
Received 31 August 2000; accepted 29 September 2000

Abstract

Dihalocarbenes (:CCl_2, :CBr_2, and :CI_2) add preferentially to one of the radial double bonds of corannulene, rather than to the rim. These cyclopropanations strongly resemble the additions of dihalocarbenes to fullerenes, which likewise occur at 6:6-double bonds, destroy the cyclic conjugation in two adjacent benzene rings, and give 'closed' adducts. An explanation is offered for the abnormally high reactivity of the interior carbon atoms of corannulene. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: carbenes; cyclopropanation; orbital effects; polycyclic aromatic compounds.

The pronounced bond length alternation around the six-membered rings of the bowl-shaped corannulene molecule resembles that seen in the central ring of phenanthrene.[1] It would be natural to assume, therefore, that the cyclopropanation of corannulene with dichlorocarbene should mimic that of phenanthrene[2] to give adduct **1** (Scheme 1). We find, however, that this mode of addition does not occur, despite the fact that formation of **1** would preserve the greatest possible number of benzene rings and would introduce the least additional strain into the corannulene skeleton.



Scheme 1.

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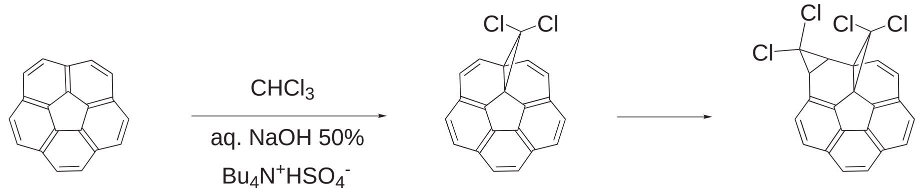
* Corresponding author. Fax: 617-552-2705; e-mail: lawrence.scott@bc.edu

[†] We dedicate this paper to Professor Harry Wasserman on the occasion of his 80th birthday.

PII: S0040-4039(00)01734-2

Instead of adding to one of the perimeter bonds of corannulene, dichlorocarbene adds exclusively to one of the radial bonds, giving adduct **2** as the primary product.[3,4] As the reaction proceeds, the reactive olefinic bonds in **2** begin to compete with corannulene for the carbene, and a 2:1 adduct (**3**) starts to accumulate as a secondary product (Eq. (1)).[5] The reaction can be conveniently monitored by NMR spectroscopy, but at no time do we ever see any evidence for adduct **1**.



2 **3**

(1)

Because the 1:1 adduct (**2**) goes on to the 2:1 adduct (**3**) at a rate similar to that of its formation, the concentration of **2** never reaches a high level. Nevertheless, by careful chromatography we were able to obtain a relatively pure sample of **2**, contaminated by only ca. 5% of residual corannulene. The ^{1}H NMR spectrum of **2** (Fig. 1) shows the expected singlet and two doublets in the region for aromatic hydrogens and two doublets in the region for olefinic hydrogens.

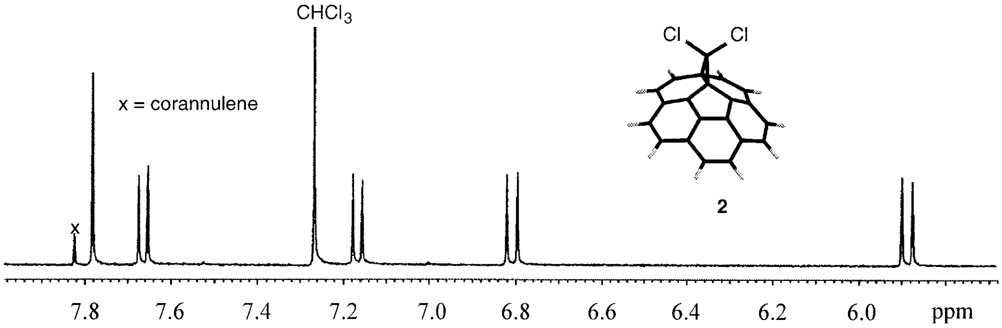
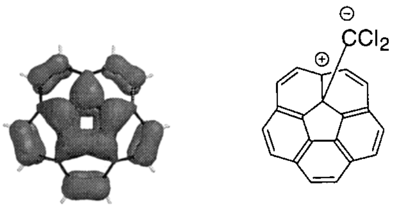


Figure 1. ^{1}H NMR spectrum of the 1:1 adduct (**2**)

The large coupling constant observed for the two high field signals ($J_{\text{vic}}=9.6$ Hz) is consistent with a 'closed' propellane-type structure for **2** that has an intact cyclopropane ring and two localized double bonds. Density functional calculations (pBP/DN**//AM1)[6] likewise favor the closed structure over an 'open' structure (cf. 1,6-methano[10]annulene) as the global energy minimum for **2**. The dichlorocarbene adduct of corannulene thus resembles the dichlorocarbene adduct of C_{60}, in which the carbene has added to a 6:6-double bond and the cyclopropane ring remains closed.[7]

Why does dichlorocarbene add to the radial bond of corannulene when that mode of addition (**2**) disrupts the cyclic conjugation in *two* benzene rings, rather than in only one, and clearly introduces more strain than the perfectly reasonable alternative mode (**1**) would have? Like most carbene additions, this one is almost certainly irreversible under the reaction conditions employed, i.e. we are dealing with a kinetically controlled process (discussed further below). Recent computational studies and kinetic isotope effect measurements[8] indicate that the transition state for dichlorocarbene addition to a double bond is very unsymmetrical, the

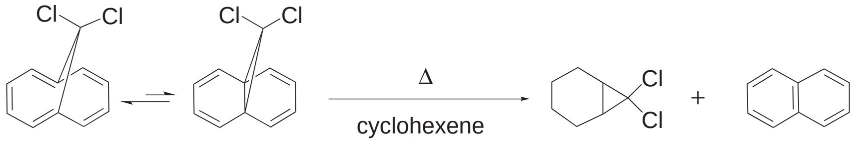
LUMO of the electrophilic carbene interacting most strongly with the largest HOMO coefficient it can find in the π-system. In extreme cases, there is even experimental evidence that the process may be stepwise.[9] When dichlorocarbene approaches corannulene, therefore, it seeks out the site where the highest occupied molecular orbital (HOMO) coefficient is the largest. MO calculations reveal that the HOMO of corannulene is doubly degenerate and that both orbitals have their largest coefficients at the *interior* carbon atoms (Fig. 2). Dichlorocarbene is thus drawn to the five-membered ring of corannulene by a strong HOMO–LUMO interaction. If the addition were stepwise, the zwitterionic intermediate would have structure **4**. Regardless of whether the reaction is concerted and asynchronous or completely stepwise, once bonding between the carbene and an interior carbon atom of corannulene has begun, the formation of adduct **1** ceases to be an option.



4

Figure 2. Left: Superimposed maps of the two degenerate highest occupied molecular orbitals of corannulene (pBP/DN**//AM1). Right: The intermediate to be expected if the carbene addition were completely stepwise

One case in which a dichlorocarbene cyclopropanation has been observed to proceed thermally in the reverse direction bears an intriguing structural resemblance to our adduct **2**. Vogel et al. found that propellane **6**, though less stable than the 'open' 11,11-dichloro-1,6-methano[10]annulene **5**, can be formed reversibly by heating **5** and that it slowly extrudes dichlorocarbene at 50°C.[10] When cyclohexene was present to trap the carbene, 7,7-dichloronorcarane (**7**) and naphthalene were obtained as the major products (Eq. (2)).



5 **6** **7**

(2)

Motivated by this example, we heated adduct **2** in cyclohexene and observed a slow increase in the amount of corannulene (NMR with an internal standard). The absence of 7,7-dichloronorcarane (**7**) in the reaction mixture (NMR and GC/MS), however, argues against carbene extrusion as the pathway leading back to corannulene. What we did observe instead of **7** was a substantial amount of the dimer of cyclohexenyl radical (3,3′-dicyclohexenyl). These results suggest a stepwise decomposition pathway[11] in which **2** first breaks only one bond to give a diradical analogous to **4**; a hydrogen atom transfer from cyclohexene to the CCl_2 radical center would account for the formation of cyclohexenyl radical, and subsequent loss of a $CHCl_2$ radical would generate corannulene. Thus, the cyclopropanation of corannulene with dichlorocarbene does not appear to be thermally reversible, at least not as a concerted process.

Dibromocarbene, generated from bromoform by the same phase transfer method as in Eq. (1), behaves the same as dichlorocarbene toward corannulene, affording a 1:1 adduct of type **2** and a 2:1 adduct of type **3**.[12] To allay concerns that the 1:1 adduct might be arising from nucleophilic addition of the initially formed trihalomethyl anion, rather than from a true carbene cycloaddition, we generated dibromocarbene independently from Seyferth's reagent ($PhHgCBr_3$)[13] in the presence of corannulene under neutral conditions in refluxing benzene. The same 1:1 adduct of type **2** was obtained from this reaction; no evidence could be seen, however, for any 2:1 adduct. The exclusive formation of a 1:1 adduct of type **2** in this reaction confirms that free dihalocarbenes exhibit a kinetic preference for cyclopropanation of the radial bonds of corannulene. The absence of any 2:1 adduct in this case suggests that the concentration of 1:1 adduct never built up to a high enough level to compete with corannulene for the carbene. Control experiments confirm that the 1:1 dibromocarbene adduct of type **2** decomposes readily in refluxing benzene.

Diiodocarbene generated from iodoform by the same phase transfer method as in Eq. (1) likewise gives a 1:1 adduct of type **2** in low yield.[14] No 2:1 adduct of type **3** was seen in this case, perhaps owing to the steric demands of the iodine atoms, although this might also be just a consequence of the low concentration of 1:1 adduct.

In conclusion, the addition of dihalocarbenes to corannulene provides a striking example of the reactivity of *interior* carbon atoms of open geodesic polyarenes. The only prior examples of dihalocarbene additions to polycyclic π-systems that destroy simultaneously the cyclic conjugation in two benzene rings are the additions of dihalocarbenes to fullerenes[7] and to diindenochrysene, a bowl-shaped alkene-centered $C_{26}H_{12}$ fullerene fragment that also exhibits fullerene-like reactivity.[15]

Acknowledgements

Financial support from the National Science Foundation is gratefully acknowledged.

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3. To a solution of corannulene (100 mg, 0.4 mmol) in 50 mL of chloroform were added 10 mL of a 50% aqueous solution of NaOH and tetrabutylammonium hydrogen sulfate (20 mg) as a phase transfer catalyst. The mixture was stirred at room temperature for 20 h. The resulting brown solution was poured into 200 mL of water and extracted with chloroform (3×15 mL). The combined organic solutions were dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure to give a dark brown solid. The crude product (ca. 105 mg) contains ca. 90% of corannulene, 8% of **2** and 2% of **3** (as determined by ^1H NMR spectroscopy). Column chromatography on neutral alumina with 6:1 pentane:ether as eluant followed by preparative TLC (on silica gel with 6:1 pentane:ether as eluant) afforded relatively pure samples of **2** and **3**.
4. Selected data for compound **2**: ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.78 (s, 2H), 7.66 (d, $J=8.8$ Hz, 2H), 7.16 (d, $J=8.8$ Hz, 2H), 6.80 (d, $J=9.6$ Hz, 2H), 5.88 (d, $J=9.6$ Hz, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ (ppm): 141.0, 138.3, 133.1, 129.3, 128.5, 128.3, 127.8, 126.0, 118.3, 93.0, 86.7, 50.1; HRMS: calcd. for $C_{21}H_{10}Cl_2$: 334.0130. Found: 334.0127.
5. Selected data for compound **3**: ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.69 (d, $J=9.0$ Hz, 1H), 7.63 (d, $J=7.8$ Hz, 1H), 7.62 (d, $J=8.4$ Hz, 1H), 7.60 (d, $J=8.7$ Hz, 1H), 7.16 (d, $J=8.4$ Hz, 1H), 7.14 (d, $J=8.4$ Hz, 1H), 6.87

(d, $J=9.6$ Hz, 1H), 6.07 (d, $J=9.6$ Hz, 1H), 3.07 (d, $J=10.2$ Hz, 1H), 2.95 (d, $J=10.2$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 145.3, 142.5, 138.9, 137.6, 136.7, 132.7, 130.9, 129.5, 120.9, 128.2, 127.5, 126.8, 125.4, 120.5, 63.6, 62.5, 46.7, 43.3, 36.5, 35.7 (20 signals seen out of 22 expected); HRMS: calcd. for $C_{22}H_{10}Cl_4$: 414.9615. Found: 414.9615.

6. Minimum energy molecular geometries were optimized at the AM1 level of theory, and single point energies were calculated at the pBP/DN** level of theory using the computational chemistry programs implemented in Spartan 5.0 (Wavefunction, Inc., Irvine, CA 92612).
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12. Selected data for dibromocarbene adducts: *1:1 adduct*: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.77 (s, 2H), 7.66 (d, $J=8.4$ Hz, 2H), 7.15 (d, $J=8.4$ Hz, 2H), 6.84 (d, $J=9.6$ Hz, 2H), 5.88 (d, $J=9.6$ Hz, 2H); *2:1 adduct*: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.68 (d, $J=9.2$ Hz, 1H), 7.64 (d, $J=8.8$ Hz, 1H), 7.62 (d, $J=8.8$ Hz, 1H), 7.59 (d, $J=9.2$ Hz, 1H), 7.17 (d, $J=8.4$ Hz, 1H), 7.13 (d, $J=8.4$ Hz, 1H), 6.92 (d, $J=9.6$ Hz, 1H), 6.11 (d, $J=9.6$ Hz, 1H), 3.09 (d, $J=10.0$ Hz, 1H), 3.04 (d, $J=10.0$ Hz, 1H).
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14. Selected data for the diiodocarbene adduct: *1:1 adduct*: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.74 (s, 2H), 7.65 (d, $J=8.8$ Hz, 2H), 7.13 (d, $J=8.8$ Hz, 2H), 6.94 (d, $J=9.6$ Hz, 2H), 5.82 (d, $J=9.6$ Hz, 2H).
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