Addition of Dichloro- and Dibromocarbene to 1,2-Diphenylcyclobutene

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1,2-Diphenylcyclobutene (**7**) was reacted with dibromo- and dichlorocarbene, both generated *via* three different methods. 1,3-Diphenyl-2-halocyclopenta-1,3-dienes **12** were isolated which result from addition of the dihalocarbenes to the cyclobutene double bond of **7**. A cationic cyclopropyl-allyl rearrangement (CCA) in *gem*-dihalobicyclopentanes **8** leads to 2,3-dihalocyclopentenes **9**, which under the reaction conditions are dehydrohalogenated to **12**. A second carbene addition and rearrangement afford aromatic compounds **11** and **16**.

The most common and thoroughly investigated reaction of carbenes is the addition to carbon-carbon double bonds. Although vast literature concerning dihalocarbene reactions with open chain and cyclic alkenes larger than four-membered rings[1-3] exists, only a few studies with small-ring alkenes have been reported.[4-6]

Since the pioneering work of Skell and Woodworth[7,8] and Doering,[9] it is generally accepted that the singlet carbene addition occurs by a one-step process in which two new σ-bonds are formed simultaneously. Although this type of addition proceeds in a concerted fashion, it cannot be synchronous, due to orbital symmetry considerations.[1,10]

In 1956, Skell and Garner[11] suggested that the addition of dibromocarbene to several alkenes would lead to a transition state with complete charge separation, but the intermediacy of a complex "as a partially formed cyclopropane that has some carbonium ion character developed on one of the carbons of the double bond" was never proven. Later on, Yang and Marolewski[12] proposed a stepwise addition of photochemically generated monoiodo- and monochlorocarbenes to 1,2-dimethyl-cyclobutene in order to explain the formation of the 2-(1-methylcyclopropyl)-1-halopropenes found. Jones et al.[13] suggested for this reaction the involvement of a biradical, which would result from addition of a triplet carbene. Due to the small energy gap between the singlet ground state and the triplet state of monohalo- and some dihalocarbenes, an equilibrium was postulated. In order to explain the formation of the products, however, the rate of reaction of the triplet carbene must be much larger than that of the singlet.

Recently, for the reactions of dihalocarbenes with 1,2-diphenylcyclopropenes **1**, a two-step mechanism involving dipolar or polarized activated complexes, such as **2**, has been suggested (Scheme 1) to explain the formation of the 1,3-butadienes **3**.[4]

Moreover, **1** can react with dihalocarbenes to afford the putative bicyclo[1.1.0]butane **4**. After cleavage of the central bond in **4** and loss of one halide, the homoaromatic cyclobutenyl cation **5** is generated.[14] Recombination of **5** with the halogen anion gives cyclobutene **6** as the major product.

The high reactivity of strained cyclopropene **1** towards dihalocarbenes is clearly reflected by the narrow gaps of the

differential orbital energies (LUMO$_{carbene}$–HOMO$_{alkene}$).[4] Consequently, based on determination of differential orbital energies,[15] one might predict a similar reactivity for the addition of dihalocarbenes to 1,2-diphenylcyclobutene (**7**).

Scheme 1.
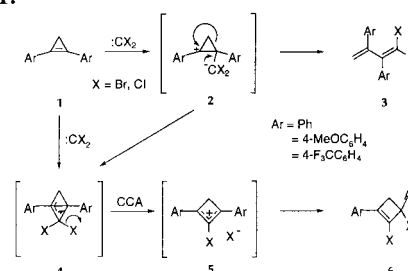
Only very few dihalocarbene additions to cyclobutenes are known.[5,6] To provide further evidence for the proposed mechanism (Scheme 1), 1,2-diphenylcyclobutene (**7**)[16] was treated with dibromo- and dichlorocarbene (Scheme 2). The dihalocarbenes were generated by three different ways, using the methods of Doering and Hoffmann (KOᵗBu/CHX$_3$),[17] Seyferth (PhHgCX$_3$/refluxing benzene)[18] and Xu (ultrasound).[19,20]

The *gem*-dihalovinylcyclopropanes **14** (Scheme 2) which, among other compounds, were expected to be formed in the reactions, were synthesized independently. To this end, Horner-Wadsworth-Emmons reactions were performed on (1-phenylcyclopropyl)phenyl ketone[21] and the corresponding diethyl-1,1-dihalomethylphosphonate[22] at room temperature which afforded **14** (**a** and **b**) in 13% yield each.

Scheme 2.
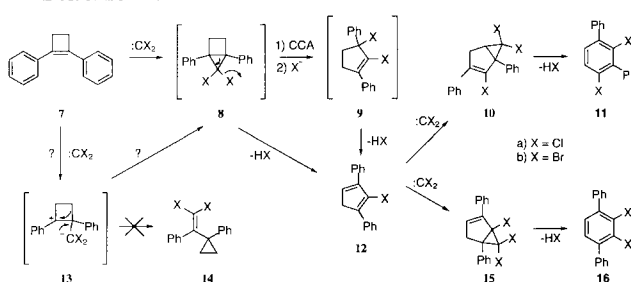
In the dichloro- and dibromocarbene additions to 1,2-diphenylcyclobutene (**7**), the intermediate adduct **8** could never be isolated nor spectroscopically observed without doubt. Instead, 1,3-diphenyl-2,3-dihalocyclopentene (**9**), deriving from a CCA rearrangement **8** → **9**,[10,14] is believed to be formed. Under all three conditions applied, however, **9** is rapidly dehydrohalogenated to afford 1,3-diphenyl-2-halocyclopenta-1,3-diene (**12**). In addition, the hitherto unknown aromatic compounds **11** and **16** were produced. Therefore, under these conditions, cyclopentadiene **12** underwent a second carbene addition. This reaction is favored at the sterically less hindered and more

electron-rich double bond, yielding 1,3-diphenyl-2,6,6-trihalo-bicyclo[3.1.0]hex-2-ene (**10**). It occurs also, in lower yield, at the other double bond of **12** to give 2,5-diphenyl-1,6,6-trihalo-bicyclo[3.1.0]hex-2-ene (**15**). After ring opening and concomitant dehydrohalogenation, **10** is converted to **11**. The aromatization of **15** → **16** proceeds in the same manner.

In a typical experiment, under Doering-Hoffmann conditions no reaction occured, and starting material **7** was recovered completely. In contrast, when ultrasound was applied to the reaction mixture,[20] after 35 min about 30% of **11a**, 10% of **16a** and small amounts of 1,3-diphenyl-2,6,6-trichlorobicyclo[3.1.0]hex-2-ene (**10a**) could be isolated (Table 1, entry 1). If, under the same conditions, ultrasonication was extended to 60 min (entry 3), almost no starting material could be detected, but 45% of **11a** along with 26% of **16a** were observed. In order to avoid basic conditions and prevent any subsequent dehydrohalogenation of **9**, **10** and **15**, Seyferth´s method was used (entries 4 - 6). Still, no 1,3-diphenyl-2,3-dihalocyclopentenes (**9**) could be detected. Interestingly, **10a** could be isolated as main product (entry 5), whereas with PhHgCBr₃ only the aromatic compound **11b** was formed (entry 6). Bromide is a better leaving group than chloride and that might be responsible for this result.

Table 1.

Entry	Source of carbene	Isolated yield of compounds /%					
		7	10	11	12[c]	15[c]	16
1	NaOH/CHCl₃/TEBA/35 min/◖◗[a]	38	1.5	29.5	2	0.5	9.5
2	NaOH/CHCl₃/TEBA/45 min/◖◗[a]	22	2.5	40	5	0.5	16
3	NaOH/CHCl₃/TEBA/60 min/◖◗[a]	7.5	7	45	1.5	1	26
4	PhHgCCl₃, benzene, reflux[b]	41	1.5	1	trace	trace	trace
5	PhHgCBrCl₂, benzene, reflux[b]	45.5	23	8	2	6	2
6	PhHgCBr₃, benzene, reflux[b]	50	0	8	0	0	0

[a] Ultrasonication at 35 kHz. [b] Reflux for 25 minutes. [c] Determined by means of GC MS and ¹H NMR. TEBA = triethylbutylammonium chloride.

It is noteworthy, that no *gem*-dihalovinylcyclopropane **14** resulting from a rearrangement of **13** could be observed with any of the examined dihalocarbene additions to 1,2-diphenylcyclobutene (**7**). While there is evidence that dihalocarbenes can undergo a stepwise addition to 1,2-diphenylcyclopropenes **1**,[4] bearing electron-pushing or electron-pulling substituents at the *para* position of one phenyl group, at this point, there is no support for such a mechanism in the corresponding carbene reactions with 1,2-diphenylcyclobutene (**7**). The structural differences between **1** and **7**[23] could certainly be one reason. A stronger argument, however, is based on the enormous difference in strain energy of parent cyclopropene (55.2 kcal/mol[24]) and cyclobutene (28.4 kcal/mol[24]). In the reaction of dihalocarbenes with cyclobutene forming bicyclo[2.1.0]pentane, the ring strain increases by 26 kcal/mol; on the other hand, the calculated increase for cyclopropene forming bicyclo[1.1.0]butane is only about 9 kcal/mol. The larger build-up of strain energy in the case of cyclobutene **7** seems to impede the ease of this reaction. Indeed, when compared with the reaction of dichlorocarbene and **1**, under otherwise identical conditions, a slower reaction was observed for the corresponding addition to **7**. Furthermore, while in the concomitant rearrangement of bicyclobutane to cyclobutene about 36 kcal/mol of total strain ener-

gy are released, almost all strain energy (ca. 51 kcal/mol) is set free in the corresponding rearrangement of bicyclopentane to cyclopentene. Moreover, if the carbene addition to **7** would proceed *via* **13**, i.e. in a stepwise fashion, as has been suggested for **1**,[4] to give *gem*-dihalovinylcyclopropanes **14**, almost no ring strain is lost. In contrast, there is considerable driving force in the corresponding reaction **2** → **3**, due to the formation of strain-free butadienes **3**. These energy considerations clearly show the exceptionally high reactivity of cyclopropenes and the importance of ring strain in the reaction pathways of carbene additions.

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