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Bromination of 1-Cyclopent-1-en-1-ylbenzene and 1-(5-Bromocyclopent-1-en-1-yl)benzene and Theoretical Investigation of the Products

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The bromination of 1-cyclopent-1-en-1-ylbenzene (**4**) in different solvents and at different temperatures was accompanied by the evolution of hydrogen bromide and yielded 1-(5-bromocyclopent-1-en-1-yl)benzene (**8**). Further bromination of **8** gave exclusively 2R(S),5R(S)-1-(1,2,5-tribromocyclopentyl)benzene (**11**). The experimental results were compared with the theoretical ones based on semi-empirical (MM+ and AM1), Hartree-Fock (HF) and density functional theory (DFT). The formation of **11** was explained by the formation of a weakly bridged bromoniun ion of type **9**.

Key Words: Bromination, Olefins, MM+, AM1, Hartree-Fock (HF) and Density Functional Theory (DFT) calculations.

Introduction

Allenes are an important class of unsaturated hydrocarbons containing two cumulated double bonds in an orthogonal geometry. The synthesis and isolation or trapping of highly strained molecules, such as cyclic allenes, has been an area of extensive research during the past three decades[1,2]. Cyclohexa-1,2-diene and higher homologies have been synthesized or trapped successfully[2]. Experimental evidence for cyclopenta-1,2-diene has remained elusive. However, the generation of a derivative of **1** has recently been reported[3].

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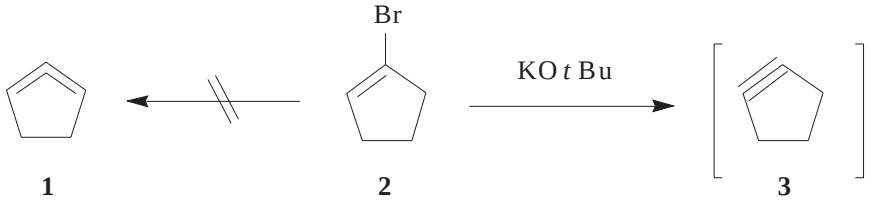
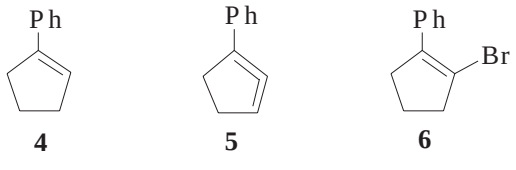


Scheme 1

One of the most efficient methods for the generation of cyclic strained allenes is the reaction of the corresponding vinylhalides with bases. Favorski first attempted to prepare 1,2-cyclopentadiene (**1**) by treatment of vinylbromide **2** with KO*t*Bu and obtained cyclopentyne **3** rather than allene **1** (Scheme 1)[4,5].

Montgomery et al. examined the reaction of 1-chlorocyclopentene with phenyllithium[6]. They showed that the coupling product, 1-cyclopent-1-en-1-ylbenzene (**4**) is formed by way of an elimination-addition mechanism proceeding via cycloalkyne intermediate.

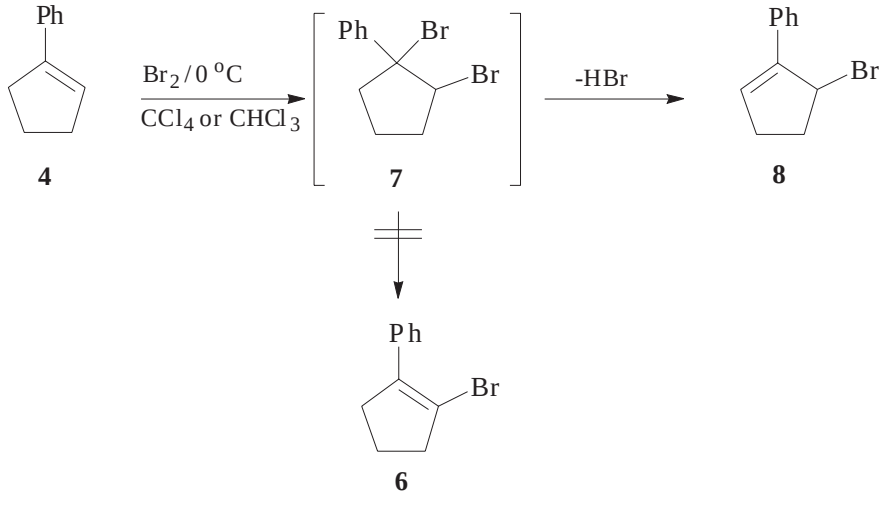


Since bromide is a better leaving group than chloride we thought that the vinyl bromide **6** might be a better potential candidate to generate the five-membered ring allene **5** upon treatment with a base. For that reason, we have attempted the synthesis of **6** via bromination of the alkene **4**.

Results and Discussions

For the synthesis of **4**, bromobenzene was converted to the Grignard reagent, which was condensed with cyclopentanone. Dehydration of the crude alcohol with *p*-TsOH in benzene gave alkene **4** in 71% overall yield (Scheme 2)[7]. In the next step, we expected that the bromination of **4** followed by HBr elimination should give the target compound **6**. The addition of bromine to **4** in different solvents and at different temperatures was accompanied by the evolution of hydrogen bromide and yielded the allylic bromide **8** (Scheme 2). The structure of **8** was elucidated on the basis of NMR spectral data. Contrary to our expectations, not even a trace of the expected vinyl bromide **6** was formed in this reaction. To understand this outcome we ran some calculations on the products **6** and **8**.

The bromination of a C=C double bond is nowadays presented as a simple two-step, *trans*-addition process involving the famous bromonium ion as the key intermediate. However, bromine bridging is not general, and its magnitude depends mainly on the double bond substituents. For example, when these are strongly electron donating, i.e. able to stabilize a positive charge better than bromine, weakly bridged species of type **9** or open ions like **10** are the bromination intermediates[8].



Scheme 2

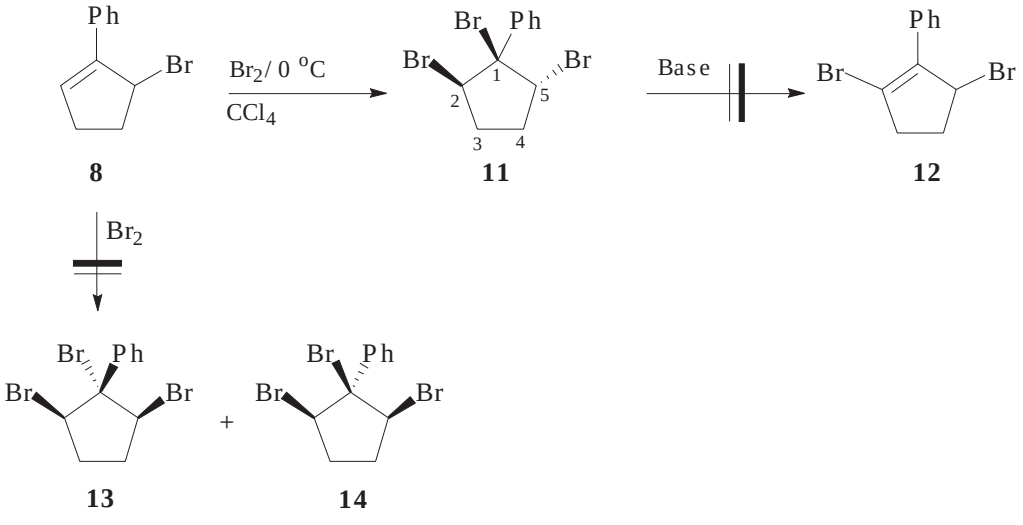
X = electron donating groups

Therefore, for the formation of **8** we suggest the following mechanism. The bromine addition to **4** leads to the initial formation of an ion pair, whose positive charge should be an unsymmetrical bridge ion type **9** (or **10**) resembling a benzylic cation more than a bromonium ion. The leaving of a proton from C-5 to give the allylic bromide **8** supports the benzylic cation character.

Afterward we studied further the bromination of the vinylbromide **8** and we hoped to obtain the dibromide **12** after base-supported elimination reaction, which might be easily converted to the vinyl bromide **6** upon reduction with $LiAlH_4$. The allylic bromide **8** was treated with bromine in CCl_4 at 0 °C and the tribromide **11** was formed as the sole product in 94% (Scheme 3). The expected symmetrical *trans,trans*-tribromide **13** and *cis,cis*-tribromide **14** were not formed. The *cis* and *trans* relation of bromine atoms in **11** was easily determined by the ^1H and ^{13}C NMR data. The protons H_2 and H_5 resonate separately as a triplet (5.06 ppm $J = 8.9$ Hz) and a doublet (5.16 ppm $J = 5.9$ Hz), respectively.

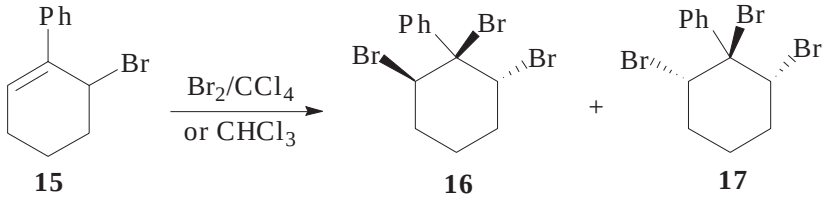
To understand these different coupling modes we performed AM1 calculations on **11** in order to determine the corresponding dihedral angles. The dihedral angle between H_2 and H_{3trans} is 99^o whereas the dihedral angle between the protons H_2 and H_{3cis} is 19^o, which indicates clearly the doublet splitting of the resonance signal of H_2 AM1 calculations indicate that the dihedral angle between the protons H_5 and H_{4cis} is approximately 30^owhereas the dihedral angle between H_5 and H_{4trans} is 150^o. These geometrical data are responsible for the triplet splitting of the resonance signal of the H_5-proton.

Attempted dehydrohalogenation reactions of **11** with different bases NH_3/KOtBu, THF/KOtBu, $NaNH_2$/KOtBu and DBU at different temperatures to obtain **12** failed.



Scheme 3

The interesting feature of this bromination reaction was the absence of other isomers **13** and **14**. Bellucci et al.[9] have studied the addition of bromine to 1-(6-bromocyclohex-1-en-1-yl)benzene (**15**) and obtained two isomers, *trans,trans* and *cis,trans*1-(1,2,6-tribromocyclohexyl)benzene **16** and **17** (Scheme 4). The product distribution was strongly influenced by the reaction conditions. While bromine in chloroform favored the formation of the isomer **17**, pyridine perbromide as the bromination agent afforded an excess of **16**.



Scheme 4

To understand the different behavior of these homologues **8** and **15** against the bromination reaction (the sole formation of **11**, from **8** and the formation of a mixture of **16** and **17** from **15**) we carried out some calculations.

Computational Methods

All calculations were performed by Gaussian 98 package[10] on Pentium IV 1.5 GHz and Pentium III 733 MHz computers. For each molecule investigated, stable geometry and vibrational frequencies were calculated. The latter were used to verify the character of the stationary points found in the geometry optimizations. The computational research was divided into three parts. In the first part, the geometries of **6** and **8** were optimized using three different types of theory; semi-empirical (MM+ and AM1), Hartree-Fock (HF) and density functional theory (DFT)[11] in order to obtain more stable geometry and eliminate doubt. In calculations with the HF method, the basis set increased from minimal basis set (STO-3G) to 3-21G and 6-31G(d) split valance basis sets to obtain best geometry for each species. In DFT calculations, Becke's

3-parameter exchange hybrid functional[12] with the Lee, Yang, Parr correlation functional[13] (B3LYP) and 6-31G(d) basis set was used.

Table 1 lists the absolute energies (in a.u.) and absolute energy differences, ΔE, (in kcal/mol) between isomers **6** and **8**, where $\Delta E = E_1 - E_2$. In Table 1, MM+, RHF/3-12G, RHF/6-31G(d), and RB3LYP/6-31G(d) levels of theory support the experimental outcome and indicate that isomer **8** is more stable. It is obvious that AM1 and RHF/STO-3G levels give the incorrect results because of the fact that as the level and basis set increases, the reliability of computational results increases.

In the second part of this work we calculated the energies of all possible open carbocations **18-21** that can be formed by the addition of a bromonium ion to **8**. The calculations were performed again in three different levels of theory to find the most stable isomer among **18-21**. Table 2 illustrates the absolute energies of these isomers. We found that isomers **20** and **21** do not have stable geometries as expected (**20** converged to **19**; **21** converged to **18)**.

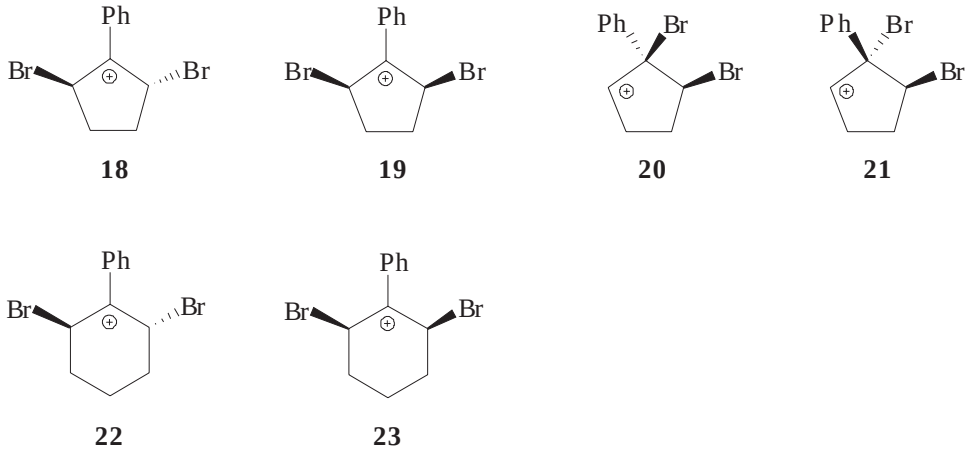


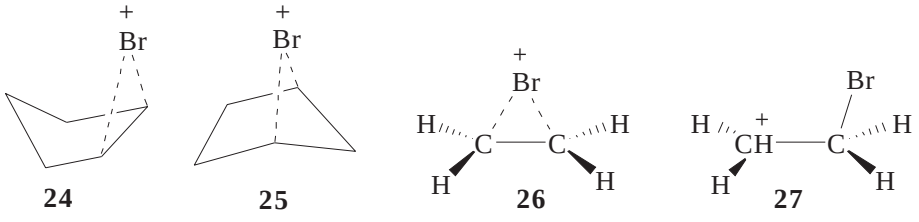
Table 1. Results of calculations at given levels of theory for isomers **6** and **8**. $E_6$and E_8 are the absolute energies in a.u., ΔE is the difference in absolute energies in kcal/mol.

Method	E_6 (a.u.)	E_8 (a.u.)	ΔE (kcal/mol)
MM+	0.024806	0.012891	7.48
AM1	0.050055	0.054747	-2.94
RHF/STO-3G	-2962.529271	-2962.523180	-3.82
RHF/3-12G	-2980.652964	-2980.654745	1.12
RHF/6-31G*	-2992.839518	-2992.843624	2.58
RB3LYP/6-31G*	-2997.494005	-2997.498663	2.92

Table 2. The relative energies of the isomers **18** and **19** in AM1, RHF/STO-3G, RHF/3-12G levels of theory.

Method	**18**	**19**
	E_{rel} (kcal/mol)	E_{rel} (kcal/mol)
AM1	0.00	0.16
RHF/3-12G	0.00	2.50
RB3LYP/3-12G	0.00	3.13

We found that the most stable (having the lowest energy) is open ion **18**. We assume that the nucleophile, the bromide anion, can attack the stable cation **19** from the two faces of this ion to give the single product **11**.



24 **25** **26** **27**

The formation of a 1,2-bridged bromonium ion **24** or a 1,3-bridged bromonium ion **25** were not considered as the possible intermediates. It is well documented that the bridged bromonium ion **26** is more stable than 1-bromoethyl cation **27** by 0.4 kcal/mol. However, in cyclic systems, the stability of cyclic bromonium ions is reduced. Recently, Sigalas et al.[14] showed that 1,2-bridged cation **24** is only 0.1 kcal/mol more stable than 1-bromocyclopentylium, whereas 1,3-bridged cation **25** is 14 kcal/mol higher in energy due to the strain in the molecule. In the case of substituted cyclopentene derivatives, 1,2-bridged cation **24** is less stable than the open cation.

Table 3. The absolute energies (a.u.) and relative energies of **23** and **24** in different levels of theory.

Method	E_{22} (a.u.)	E_{23} (a.u.)	$Erel_{22}$ (kcal/mol)	$Erel_{23}$ (kcal/mol)
AM1	0.3296860	0.3290879	0.00	-0.38
RHF/3-12G	-5579.287883	-5579.2857045	0.00	1.37
RB3LYP/3-12G	-5585.910876	-5585.9068978	0.00	2.50

To explain why the bromination of **15** gives two isomers, the structures **16** and **17,** the possible intermediates **22** and **23** were also optimized at the same levels of theory to be able to compare the behavior of five- and six-membered ring structures. The optimization results are given in Table 3. Optimizations in RHF/3-21G and B3LYP/3-21G levels of theory show that **22** is more stable than **23**, as we determined in the case of **19** and **20**. On the basis of these results ($\Delta E = 2.50$ kcal/mol for **22/23** and $\Delta E = 3.13$ for **18/19**) it is very difficult to explain the formation of an isomeric mixture of **16** and **17** upon the bromination of **15**.

We assume that an open ion **22** (like **18**) is not involved during bromination reactions. A weakly bridged species of type **9** may be involved as the intermediate, which could determine the product distribution. For that reason, we have calculated the absolute energies (a.u.) and relative energies (kcal/mol) of the products **11/13** and **16/17** in order to see whether or not product stability plays a determining role in product distribution.

Table 4 tabulates the absolute energies (a.u.) and relative energies (kcal/mol) of **11** and **13** in different levels of theory. In the AM1 method, structure **13** seems to have slightly less energy than **11**. In contrast, structure **11** has lower energy than structure **13** in RHF/3-21G and B3LYP/3-21G levels of theory.

Table 5 shows the absolute and relative energies of **16** and **17**, the six-membered ring analogous of **11** and **13**. Unlike the five-membered ring case, structures **16** and **17** can be considered to degenerate energetically in RHF/3-21G and B3LYP/3-21G levels of theory. For these structures, AM1 results mistakenly show that **17** is more stable than **16**.

Table 4. The absolute energies (a.u.) and relative energies of **11** and **13** in different levels of theory.

Method	E_{13} (a.u.)	E_{11} (a.u.)	$Erel_{13}$ (kcal/mol)	$Erel_{11}$ (kcal/mol)
AM1	0.0468866	0.0475025	-0.39	0.00
RHF/3-12G	-8100.7833274	-8100.7857824	1.54	0.00
RB3LYP/3-12G	-8108.8874954	-8108.8903453	1.79	0.00

On the basis of these results we assume that the weakly bridged bromonium ions are involved in the bromination reaction of **8** and **15**. The stability of the products determines the product distribution.

Experimental Section

1-(5-Bromocyclopent-1-en-1-yl)benzene 8. To a solution of alkene **4** (0.4 g, 3.47 mmol) in 20 mL of CCl_4 was added a solution of Br_2 (0.55 g, 3.47 mmol) in 20 mL of CCl_4 at 0 °C over 30 min. The mixture was washed with water (50 mL) and dried ($MgSO_4$). After removal of the solvent, the crude product was chromatographed on a florisil column (5 g) eluting with n-hexane gave bromo-alkene compound **9** (0.75 g, 77%). ^{1}H-NMR (200 MHz, $CDCl_3$) δ = 7.45 (m, 5H), 6.54 (m, 1H), 5.49 (m., 1H), 2.70 (m, 1H), 2.52 (m, 3H). ^{13}C-NMR (50 MHz, $CDCl_3$) δ = 144.9, 133.9, 132.6, 129.0 (2C), 128.3, 126.7 (2C), 58.9, 37.5, 32.0. Anal. Calcd for $C_{11}H_{11}Br$: C, 59.22; H, 4.97. Found: C, 59.01; H, 5.05.

Table 5. The absolute energies (a.u.) and relative energies of **16** and **17** in different levels of theory.

Method	E_{17} (a.u.)	E_{16}(a.u.)	$Erel_{17}$ (kcal/mol)	$Erel_{16}$ (kcal/mol)
AM1	0.0349633	0.0373399	-1.49	0.00
RHF/3-12G	-8139.610447	-8139.610377	-0.04	0.00
RB3LYP/3-12G	-8147.998139	-8147.999053	0.57	0.00

1-(1,2/5-Tribromocyclopentyl)benzene 11. To a solution of bromoalkene **8** (1 g, 4.48 mmol) in 25 mL CCl_4 was added a solution of Br_2(0.72 g, 4.5 mmol) in 25 mL CCl_4 at 0 °C, and stirred for 1 h. After removal of the solvent, the crude product was chromatographed on a silica gel column (20 g) eluting with n-hexane gave compound **11** as the sole product (colorless liquid, 1.6 g, 94%). ^{1}H-NMR (200 MHz, $CDCl_3$) δ = 7.65 (m, 2H), 7.40 (m, 3H), 5.16 (d, J= 5.9 Hz, 1H), 5.06 (t, J = 8.9 Hz, 1H), 3.20 (m, 1H), 2.86 (m, 1H), 2.46 (m, 2H). ^{13}C-NMR (50 MHz, $CDCl_3$) δ = 140.6, 129.2, 128.8 (2C), 128.3 (2C), 81.7, 60.6, 51.5, 34.4, 33.5. IR (NaCl, film, cm^{-1}) 3080, 3020, 2980, 2840, 1445, 1300, 1180, 1060, 1030, 900, 690, 640. Anal. Calcd for $C_{11}H_{11}Br_3$: C, 34.50; H, 2.90. Found : C, 34.13; H, 2.98.

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