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Reaction of 7-carbomethoxy-cycloheptatriene with benzyne resulted in the formation of only one benzhomobarrelene isomer, **5A**. Theoretically, four addition products, **5A-D**, can be formed from this reaction. Certain molecular mechanic calculations (MM2 force field) have been undertaken on these isomers. It has been shown that the isomers **5A** and **5C** have the lowest energies. The non-existence of **5C** has been discussed in terms of a benzyne approach to a norcaradiene structure. Furthermore, MM2 calculations on two different conformers of **5A** have revealed that the bisected conformer **5AE** has the highest strain energy. However, AM1 semiempirical calculations of those conformers have shown that the conformer **5AE** possesses a lower heat of formation than the isomer **5AA**.

Introduction

Benzhomobarrelenes are interesting compounds in view of their stereochemical state following electrophilic addition[1] and di-π-methane rearrangement[2]. For this reason any approach leading to the synthesis of benzhomobarrelenes is important. There are different synthetic methods for the synthesis of these compounds, one of which is the cyclopropanation of benzobarrelene. The second is the reaction of benzyne with substituted cycloheptatriene derivatives, recently developed by Menzek and Balcı[3].

Crews and Beard[4] have examined benzyne reaction with unsubstituted cycloheptatriene, reporting the formation of two hydrocarbons, **2** and **3**. 7-Phenylcycloheptatriene results from ene-reaction. However, ycloheptatriene derivative **2** is a product of [2+2]-cycloaddition reaction. No [2+4]-cycloaddition product arising either from cycloheptatriene or norcaradiene was observed (eq. 1).


4   2   3
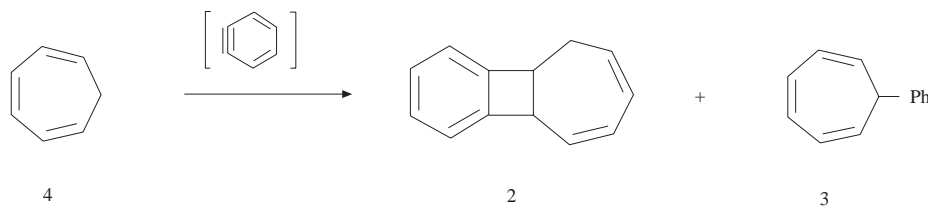
In contrast to this reaction, the cyloaddition of benzyne to the C-7 substituted cycloheptatriene derivatives 7-cyano- and 7-arbomethoxy-cycloheptatriene **4** and **6** resulted in the formation of substituted benzhomobarrelenes **5, 7** and **8**, respectively.
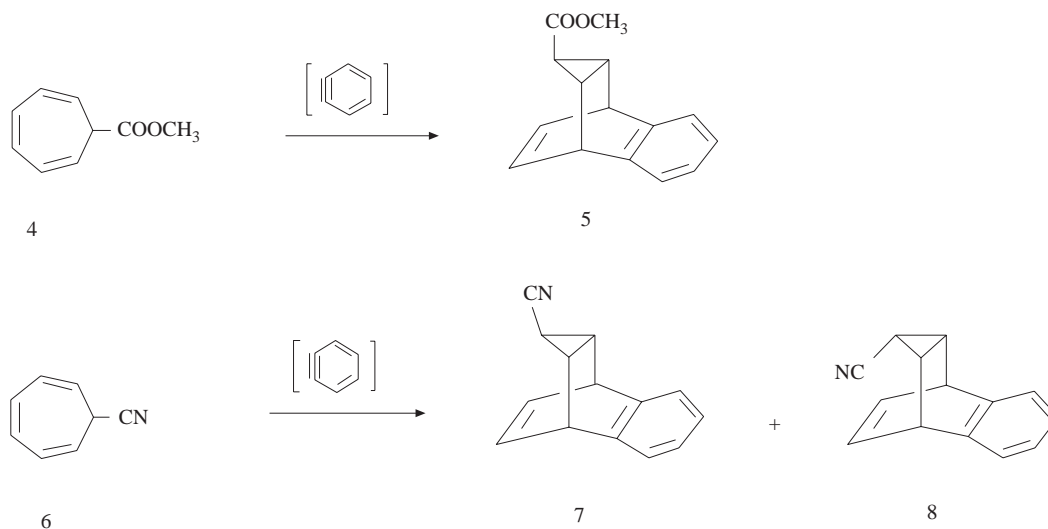
Scheme 1

The structure of the benzhomobarrelenes formed were determined by means of NMR spectral data. However, the results were not accurate enough to assign the correct configuration of these isomers. Therefore, special proton NMR experiments (NOE measurements) have been undertaken for the configurational determination and studies of the electronic structure of these molecules.[5]
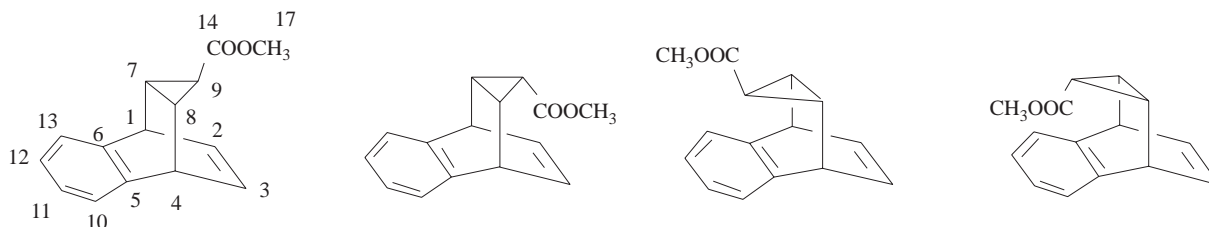
Theoretically, four addition products can be expected from the addition reaction of benzyne to **4** and **6**. In the case of **4**, we isolated only one isomer, and in the case of **6**, two isomers. In order to explain this unusual product distribution, we undertook certain molecular mechanic and semiempirical AM1 calculations on the four possible addition products arising from the reaction of **4** with benzyne.

Methods

Theoretical calculations: In order to estimate the stabilities and calculate the geometries of the isomers, conformational analyses were performed using a molecular mechanics method (MM2 force field)[6]. The full geometry optimization of the MM2 method was carried out by the Newton-Rabson algorithm with a gradient norm below 0.00001 kcal/mol.Angstrom. Furthermore, the full geometry optimization of the isomers was performed by the RHF/AM1 semiempirical method[7] with the Fletcher-Reeves algorithm with a gradient

norm below 0.01 kcal/mol.Angstrom, and the electronic properties were investigated. All calculations were made with HyperChem 3.0 on an IBM PC/AT DX4-100 computer.

Table 1. Strain energies for benzhomobarrelene derivatives **5A-D** from MM2 calculations (in kcal/mol)

Configuration	Total	Bond	Angle	Torsional	Van der Waals	Strech bend	Electrostatic
5A anti-exo	27.05	1.69	12.13	4.33	11.57	-0.94	-0.73
5B anti-endo	33.08	1.76	18.18	4.27	11.36	-0.77	-0.77
5C syn-exo	27.08	1.71	12.07	4.43	11.55	-0.95	-1.71
5D syn-endo	33.01	1.78	18.95	4.44	10.34	-0.79	-1.71

Table 2. The values (MM2) and AM1 of the calculated geometrical parameters for conformer **5AE**

Bond Distances (Å)	MM2	AM1	Bond Distances (Å)	MM2	AM1
C(1)-C(2)	1.5150	1.513	C(1)-C(6)	1.5175	1.514
C(1)-C(7)	1.5357	1.530	C(2)-C(3)	1.3424	1.346
C(3)-C(4)	1.5150	1.513	C(4)-C(5)	1.5175	1.514
C(4)-C(8)	1.5357	1.530	C(5)-C(6)	1.4003	1.419
C(5)-C(10)	1.3943	1.385	C(6)-C(13)	1.3943	1.385
C(7)-C(8)	1.4995	1.519	C(7)-C(9)	1.4902	1.513
C(8)-C(9)	1.4902	1.513	C(9)-C(14)	1.4702	1.479
C(10)-C(11)	1.3974	1.402	C(11)-C(12)	1.3983	1.391
C(12)-C(13)	1.3974	1.402	C(14)-O(15)	1.114	1.234
C(14)-O(16)	1.3479	1.371	O(16)-C(17)	1.4066	1.428

Valence Angles (∘)	MM2	AM1	Valence Angles (∘)	MM2	AM1
C(2)-C(1)-C(5)	102.14	105.34	C(2)-C(1)-C(7)	110.66	108.34
C(5)-C(1)-C(7)	104.66	104.21	C(1)-C(2)-C(3)	114.48	114.53
C(2)-C(3)-C(4)	114.48	114.53	C(3)-C(4)-C(6)	102.14	105.34
C(3)-C(4)-C(8)	110.66	108.33	C(5)-C(4)-C(8)	104.66	104.22
C(4)-C(5)-C(10)	126.19	126.61	C(1)-C(6)-C(5)	113.23	113.01
C(1)-C(6)-C(13)	126.21	126.60	C(5)-C(6)-C(13)	120.55	120.39
C(1)-C(7)-C(8)	110.95	110.74	C(1)-C(7)-C(9)	120.21	120.42
C(8)-C(7)-C(9)	59.80	59.87	C(4)-C(8)-C(7)	110.95	110.74
C(4)-C(8)-C(9)	120.21	120.45	C(7)-C(8)-C(9)	59.79	59.86
C(7)-C(9)-C(8)	60.41	60.27	C(7)-C(9)-C(14)	111.61	117.16
C(8)-C(9)-C(14)	116.66	117.16	C(2)-C(10)-C(11)	118.93	118.97
C(10)-C(11)-C(12)	120.53	120.64	C(11)-C(12)-C(13)	120.53	120.64
C(6)-C(13)-C(12)	118.92	118.97	C(9)-C(14)-C(15)	122.84	129.82
C(9)-C(14)-O(16)	116.01	112.66	C(15)-C(14)-O(16)	121.15	117.93
C(14)-O(16)-C(7)	117.76	114.61	H-C(9)-C(14)	116.15	112.35

Torsional Angle (○)	MM2	AM1	Torsional Angles (○)	MM2	AM1
C(1)-C(2)-C(3)-C(4)	0.0	0.045	C(1)-C(6)-C(13)-C(12)	179.73	179.75
C(1)-C(7)-C(8)-C(4)	0.0	0.03	C(1)-C(7)-C(9)-C(4)	-158.56	-154.97
C(2)-C(3)-C(4)-C(5)	-57.23	-55.20	C(1)-C(2)-C(3)-C(6)	-124.03	-125.63
C(4)-C(5)-C(10)-C(11)	-179.73	-179.74	C(4)-C(8)-C(9)-C(14)	158.66	154.99
C(5)-C(4)-C(8)-C(9)	123.92	124.59	C(5)-C(6)-C(1)-C(7)	59.03	59.71
C(5)-C(10)-C(11)-C(12)	0.18	0.13	C(6)-C(1) C(7)-C(9)	-123.92	-124.62
C(7)-C(9)-C(14)-C(15)	-33.15	-34.12	C(7)-C(9)-C(14)-C(16)	146.48	145.88
C(8)-C(9)-C(14)-C(15)	32.39	34.58	C(8)-C(9)-C(14)-C(16)	-147.64	-145.42
C(9)-C(14)-C(16)-C(17)	-179.98	-179.99	H-C(9)-C(14)-O(15)	179.64	179.77
H-C(9)-C(14)-O(16)	-0.39	-0.23			

Table 3. Total energy E_{tot} (in kcal/mol), formation heat ΔH (in kcal/mol) ionization potential IP (in eV), frontial MO energies, $\mathcal{E}_{HOMO}$ and $\mathcal{E}_{LUMO}$ (in eV) and dipol moment μ_D (in Debye) of benzhomobarrelene derivatives **5A-D** (AM1)

| Isomers	$E_{tot.}$	ΔH	IP	$\mathcal{E}_{HOMO}$	$\mathcal{E}_{LUMO}$	μ_D
5A (anti-exo)	-63452.2	10.207	9.307	-9.307	0.399	1.594
5B (anti-endo)	-63443.3	19.068	9.238	-9.238	0.342	1.570
5C (syn-exo)	-63452.1	10.283	9.341	-9.341	0.309	1.648
5D (syn-endo)	-63439.5	22.866	9.185	-9.185	0.379	1.590

Results and Discussions

Electron-accepting substituents such as -CHO, -COOR, and -CN on the C-7 carbon atom tend to shift the equilibrium to norcaradiene.[8] In the case of C-7 substituted cycloheptatriene derivatives, we observe two conformational isomers.[9] Ring inversion takes place between quasi-axial and quasi-equatorial conformers, as shown in Scheme 2. The existence of two isomers has been detected by addition of dienophiles to cycloheptatriene derivatives to give two configurational isomers of norcaradiene.[10]

quasi-equatorial CHT   quasi-axial CHT

exo-NOR   endo-NOR
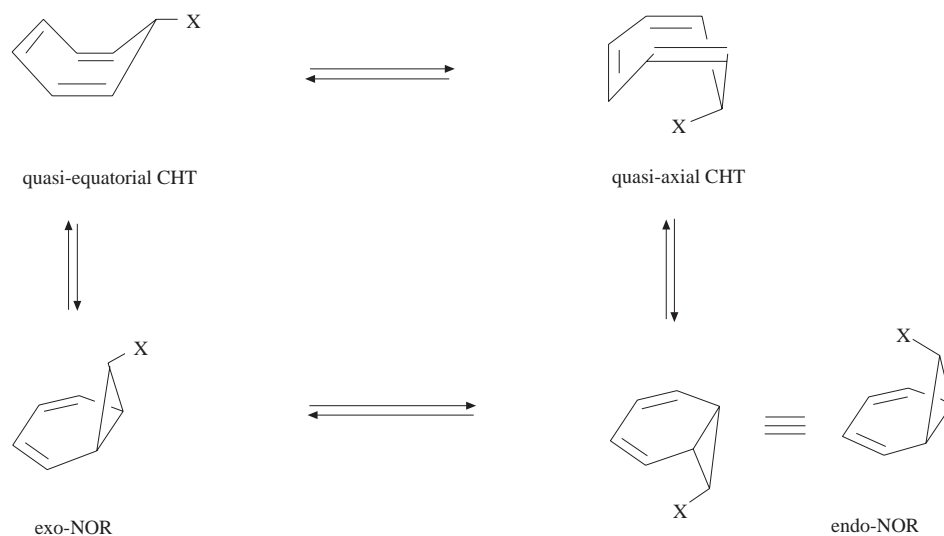
Scheme 2.

On the basis of these dynamic conformational processes, we should expect four addition products, **5A-D**, which theoretically can be formed from the reaction of 7-carbomethoxy-cycloheptatriene with benzyne. 7-carbomethoxy-cycloheptatriene can form two different norcaradiene isomers (Scheme 2). The faces of the norcaradiene isomers are not equivalent. Therefore, the benzyne molecule can approach the norcaradiene unit from two different sides (Scheme 3). In the case of endo-norcaradiene, steric repulsion due to the bulkiness of the carboxyl group can prevent the approach of benzyne from the endo-face of the molecule. In the case of exo-norcaradiene, the cyclopropyl hydrogen is aligned in the "inside" endo position. Therefore, the approach of benzyne from the endo-face is also disfavored. On the basis of these steric interactions which will occur in the transition state, the formation of **5C** and **5D** can be excluded.

endo-approach

exo-approach
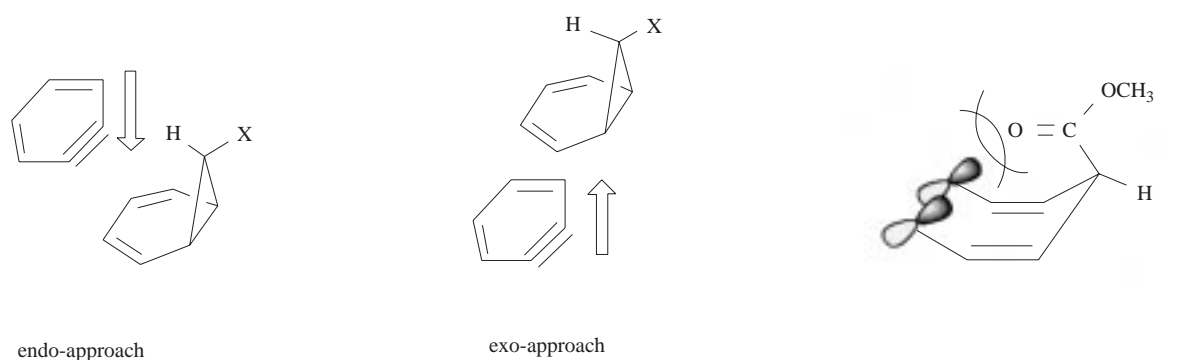
Scheme 3.

To gain further insight into these systems, we made MM2 and AM1 calculations by the semiempiric method and obtained full geometry optimization and electronic structures of these isomers **5A-D**. The strain energies (MM2) of **5A** and **5C** lie about 6 kcal/mol lower than those of the isomers **5B** and **5D** (Table 1). Structures **5A** and **5C** differed in energy by only 0.03 kcal/mol, favoring **5D** (for heat of formation energies ΔH_F see Table 3). Detailed analysis of the components of strain energies indicates that strain energy depends mainly on angle strain (angle bending) and van der Waals strain. The angle strain energies of **5B** and **5D** are higher than those of **5A** and **5C**, although their van der Waals energies are almost equal (Table 1).

According to the calculations of geometrical parameters in endo-isomers **5B** and **5D**, C(1)-C(7)-C(9), C(2)-C(1)-C(7), and C(7)-C(9)-C(14), angles differ considerably from the tetrahedral angle. For anti-endo isomer **5B** C(1)-C(7)-C(9), C(2)-C(1)-C(7), and C(7)-C(9)-C(14), the angles are 126.5, 113.8, and 115.8°, respectively. Angle increase in the endo-isomers can be explained in terms of steric effects associated with the carbonyl group and double bond (or benzene ring).

The energies of different conformations in connection with the rotation around the C(9)-C(14) bond were calculated. The most stable conformation for **5A** was found to be the bisected conformation **5AE** (for the structural parameter see Table 2). Although conformer **5AE** has higher strain energy than conformer **5AA**, its formation heat (ΔH_F = -1.773 kcal/mol) is 1.509 kcal/mol lower than that of conformer **5AA** (Heat of formation ΔH_F = -0.264 kcal/mol). Bisected conformer **5AE** is the most stable conformer.

This stabilization can be explained in terms of the interaction of the vacant π^*-orbital of carbonyl group with the cyclopropane 3E Walsh-type orbital. This is because the transfer of electron density from the 3E Walsh orbital into the vacant π^* orbital decreases the antibonding electron density in the distal bond (Figure 2). In the case of **5AA**, this kind of electronic interaction is out of the question because of the lack of an adequate geometrical arrangement.
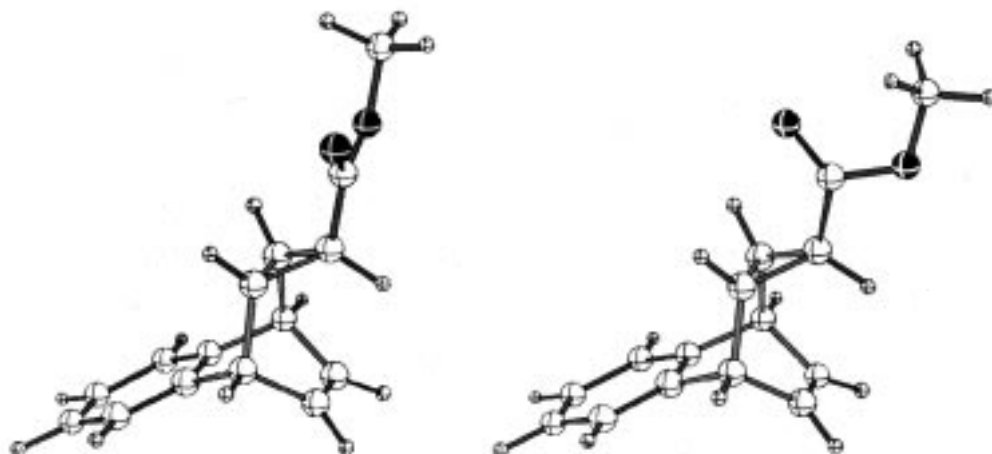
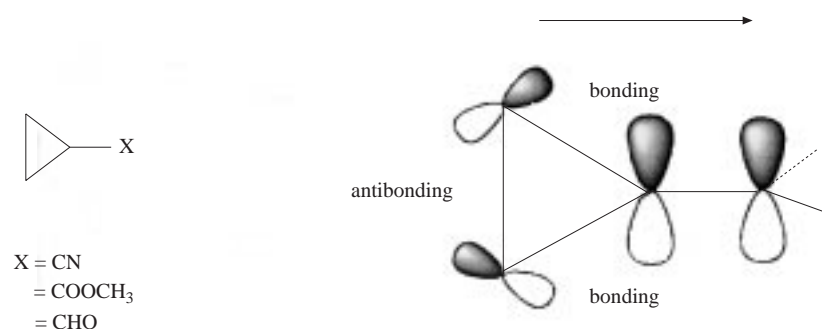**Figure 1.** Optimized geometries for conformer **5AA**, and **5AE**.

Figure 2. Interaction of cyclopropane HOMO 3E' with vacant π^* orbital.

Finally, we conclude that the reaction of benzyne with 7-carbomethoxy-cycloheptatriene should from **5A** and **5C** on the basis of MM2 force field calculations. This two isomers differ in energy by only 0.03 kcal/mol. The non-existence of isomer **5C** can be rationalized in terms of steric repulsion occurring between the cyclopropyl proton and benzyne molecule by approach to exonorcaradiene from the endo-face.

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