10th International Electronic Conference on Synthetic Organic Chemistry (ECSOC-10). 1-30 November 2006. http://www.usc.es/congresos/ecsoc/10/ECSOC10.htm & http://www.mdpi.org/ecsoc-10/

[g013]

THE EFFECT OF BENZO-ANNULATION ON RING OPENNING OF CYCLOPROPYLIDENE TO CYCLIC ALLENE: *DFT STUDY*

Akin Azizoglu

Department of Chemistry, University of Balikesir, TR-10100 Balikesir, Turkey

e-mail address for correspondence: azizoglu@balikesir.edu.tr

Abstract: Density functional theory computations elucidated the ring opening of benzo-annulated derivatives of bicycle[4.1.0]hept-7-ylidene (**6**). The B3LYP geometry optimizations and single-point energies employed a 6-31G (d) basis set. The ring opening barrier leading to cycloallenes, **11** and **15** is predicted to be 11.11 and 9.52 kcal/mol, respectively, which are lower than that for the ring opening of cyclopropylidene **6** (15.1 kcal/mol). This explains that **11** and **15** could be generated if Doering-Moore-Skattebol reaction is carried out for this purpose.

Keywords: cyclic allenes, cumulenes, carbenes, DFT methods, ring opening reaction

Introduction

The cyclic allenes with eight or less skeletal C-atoms, known as highly strained organic compounds, has attracted organic and computational chemists because of their enhanced reactivity and their unusual physical properties [1-11]. They are non-planar, chiral allenes rather than planar zwitterionic or carbene-like species, even in the case of the highly strained cyclohexa-1,2-diene and cyclohepta-1,2-diene [5].

Over the years the Doering-Moore-Skattebol method [6], briefly the treatment of 1,1-dihalocyclopropanes with alkyllithium reagents, has been used to prepare a range of

cyclic allenes [7] (*Figure 1*). Although this method is the most efficient for the generation of cyclohexa-1,2-diene **3** [8], paradoxically, it was not successful for the higher homologue **9**. A tricyclic hydrocarbon **7** and **8** mixture was isolated from the reaction of **5** with methyllithium [9] (*Scheme 1*).

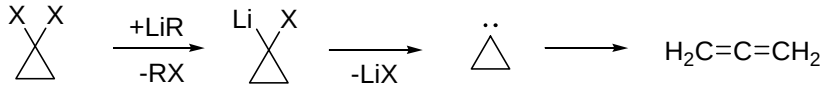
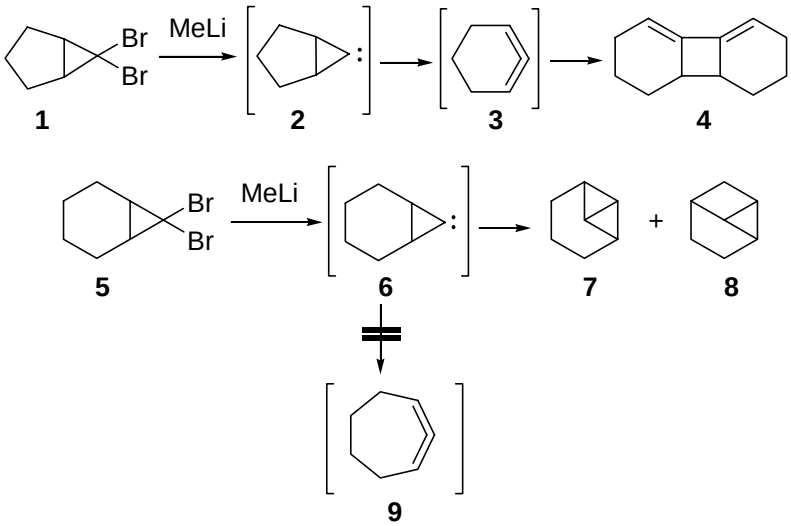


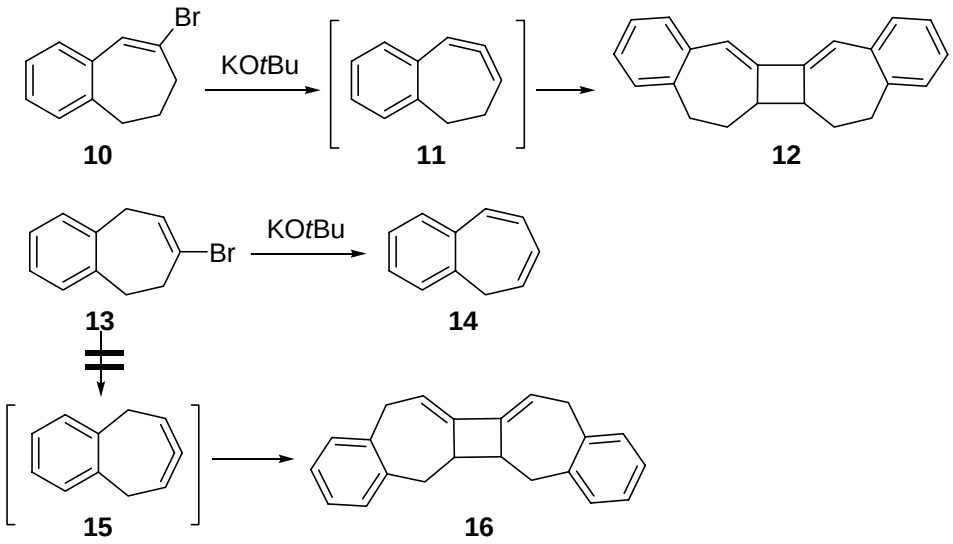
Figure 1. General Description of Doering-Moore-Skattebol method.

Recently, Scheleyer et. al. [10] have have elucidated the ring opening of carbenes **2** and **6** to the corresponding cyclic allenes using density functional theory computations. For the cyclopropylidene **2**, the barrier to ring opening leading to allene **3** was found to be 0.2 kcal/mol. However, the activation barrier of **6** for the isomerization to cyclohepta-1,2-diene **9** was found to be 14.6 kcal/mol. The half-chair conformation of the cyclohexane ring in **6** is not suitable for the ring-opening reaction and the needed change to the chair conformation during the reaction is responsible for this high activation barrier. On the other hand, the activation barriers for intramolecular CH-insertions to yield **7** and **8** were found to be 6.4 and 9.1 kcal/mol, respectively (*Scheme1*).



Scheme 1

Due to the inexplicability of Doering-Moore-Skattebol approach for the synthesis of seven-membered ring allene, Balci et. al. [11] applied the base-catalyzed elimination method using the appropriate vinylcycloalkenes, **10** and **13**, to generate the benzene annulated-six membered ring allenes **11** and **15**. Although they succeeded to isolate the dimer **12** confirming the formation of cycloallene **11**, the reaction of **10** with base gave the hydrocarbon **14**, instead of the expected allene **15** (*Scheme 2*).



Scheme 2

Hence, we have performed density functional theory (DFT) calculations to investigate the effect of benzo-annulation on the ring opening of bicyclo[4.1.0]hept-7-ylidene (**6**). It will be helpful to the chemists who consider synthesizing the cyclic allenes, **11** and **15**, using Doering-Moore-Skattebol reaction.

Computational Methods:

All calculations reported herein were performed using the GAUSSIAN 03W program package [12]. Density functional theory (DFT) [13] has been applied to optimize all of the structures and to predict harmonic vibrational frequencies. Becke's three-parameter non-local exchange functional along with the Lee–Yang–Parr non-local correlation function (B3LYP) [14] was employed. The 6-31G (d) basis set was used throughout. Stationary points were characterized as minima or transition structures by analytic evaluation of harmonic vibrational frequencies at the level of geometry optimization.

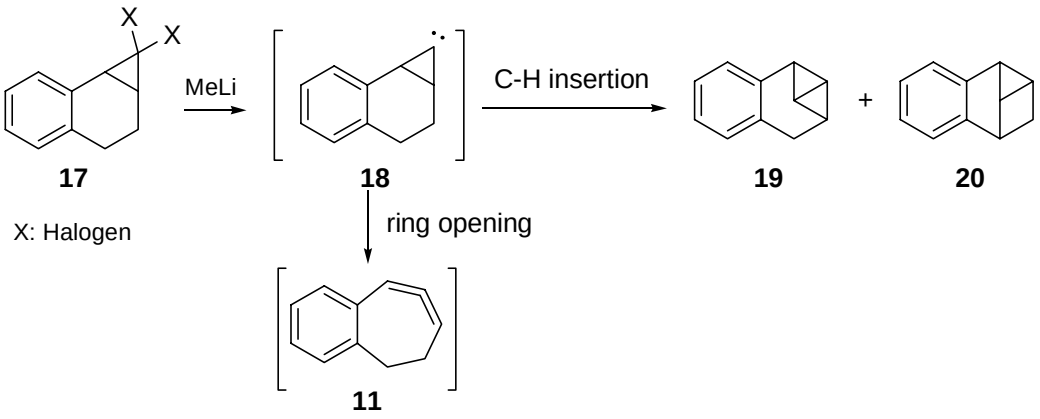
Results and Discussions:

The chosen computational method has been very successful in modeling the ring opening of cyclopropylidenes [3,10]. The ring-opening barrier leading to allene for bicycle[4.1.0]hept-7-ylidene (**6**) is found to be 15.1 kcal/mol, which is almost same as the reported literature values given in Table 1. The activation barriers for the C-H insertion products, **7** and **8** are found to be 6.2 and 9.6 kcal/mol, respectively. These results explain the barrier for ring opening cannot be overcome, whereas the intramolecular C-H insertion reactions are preferred.

Table 1: Energies Relative to the Corresponding Carbene Ground State Including Zero-Point Corrections (in kcal/mol) for the Corresponding Insertion and Allene Products and Related Transition States.

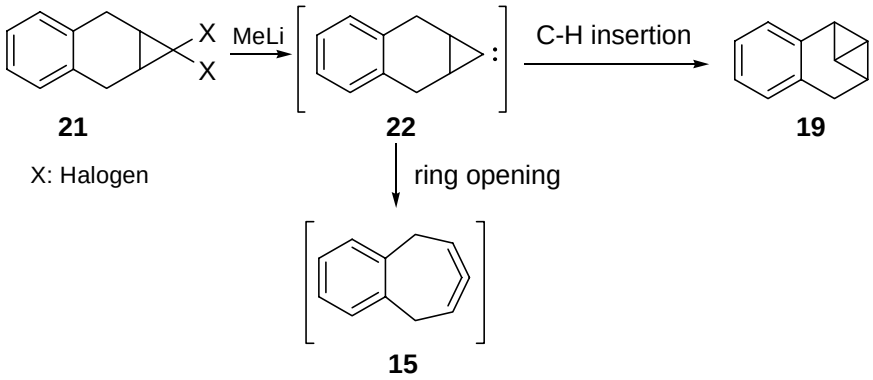
	Relative Energy Values	
	B3LYP/6-31G(d)	B3LYP/TZP[10]
7	6.2	6.4
8	9.6	9.1
9	15.1	14.6

To investigate the effect of benzo-annulation on the ring opening and CH-insertion reactions, we considered two *gem*-dihalocyclopropanes **17** and **21**, for the possible precursors of cyclopropylidenes, **18** and **22**, respectively (Scheme 3 and 4). Three possible products can be considered for the reaction of cyclopropylidene **18**. Two of them are the intramolecular CH-insertion reaction of **18** resulting in the tricyclic hydrocarbons **19** and **20**. The computed activation energy barriers (kcal/mol) for internal C-H insertions are found to be 4.81 (**TS1**) for **18→19** and 11.39 (**TS2**) for **18→20** (Table 2 and Figure 2). On the other hand, the activation barrier for the disrotatory ring-opening of **18** forming the cycloallene **11** is predicted to be 11.11 kcal/mol, which is as low as that of the insertion reaction, **18→20**. According to these results, the formation of insertion product **20** and allene **11** are in equal opportunity and seems to be possible, whereas **19** can be easily formed during the reaction of cyclopropylidene **18**.



Scheme 3

Then, we elucidated the possible reaction products of **22**. One is the intramolecular CH-insertion product **19**, which is the same product resulting from the insertion reaction of cyclopropylidene **18**. The activation energy barrier (**TS4**) is computed to be 3.70 kcal/mol for **22→19**. On the other hand, the activation barrier (**TS5**) for the disrotatory ring-opening reaction forming allene, **22→15**, is predicted to be 9.52 kcal/mol, which is much lower than that for the ring opening of cyclopropylidene, **6→9** (Table 1 and 2). This explains that the insertion product **19** has greater chance for the formation than the allene product **15**, whereas both could be isolated if the Doering-Moore-Skattebol reaction is carried out for this purpose.



Scheme 4

Table 2: Absolute Energies (*E*, in hartree/particle), Number of Imaginary Frequencies [in brackets], Zero-Point Vibrational Energies (ZPVE, in kcal/mol), and Energies Relative to the Corresponding Carbene Ground State Including Zero-Point Corrections (in kcal/mol) for the Corresponding Insertion and Allene Products and Related Transition States at the level of B3LYP/6-31G(d).

	E	***ZPVE***	***E+ZPVE***	***ΔE***
18	-425.03108 [0]	108.52	-424.85815	0.00
19	-425.11921 [0]	110.28	-424.94347	-53.54
20	-425.12337 [0]	110.76	-424.94685	-55.66
11	-425.11427 [0]	109.71	-424.93944	-51.01
TS1 (18→19)	-425.02149 [1]	107.31	-424.85048	4.81
TS2 (18→20)	-425.01038 [1]	106.92	-424.83999	11.39
TS3 (18→11)	-425.01290 [1]	108.22	-424.84044	11.11
22	-425.02569 [0]	108.30	-424.85310	0.00
19	-425.11921 [0]	110.28	-424.94347	-56.7
15	-425.10311 [0]	109.53	-424.92857	-47.36
TS4 (22→19)	-425.01835 [1]	107.39	-424.84721	3.70
TS5 (22→15)	-425.01031 [1]	108.17	-424.83794	9.52

As a conclusion, the benzo-annulation on cyclopropylidene **6** decreases drastically the activation barriers for the formation of insertion product **19** and allene products, **11** and **15**. However, there is no observed change for the formation of insertion product **20**.

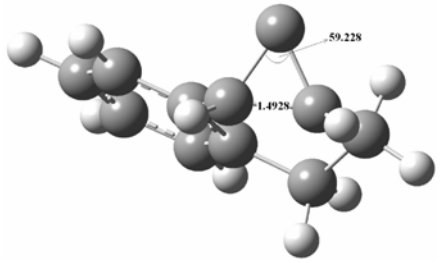
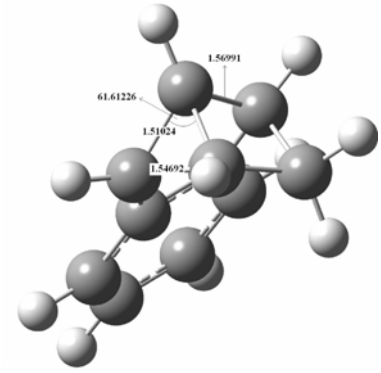
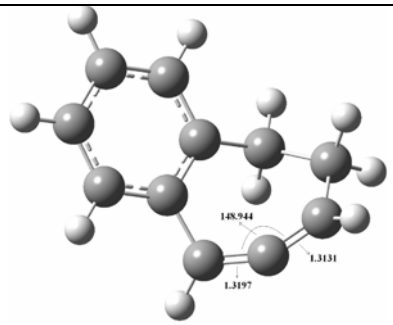
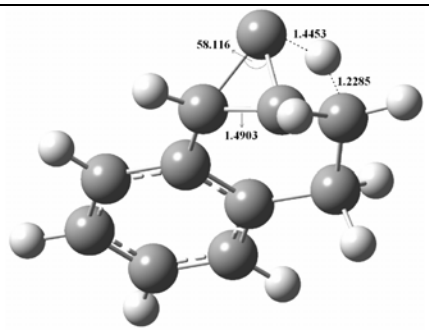
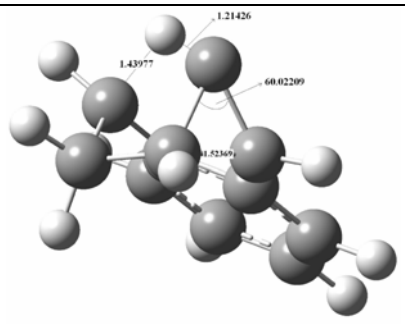
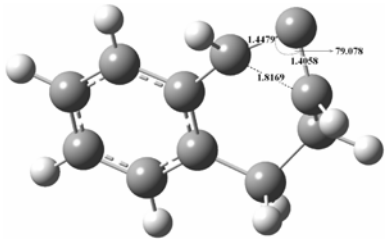
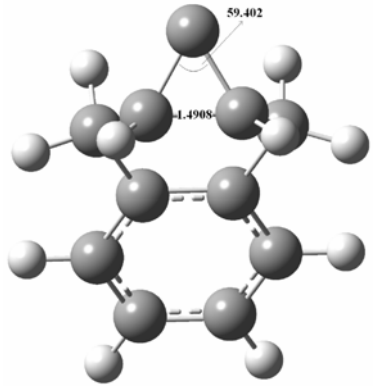
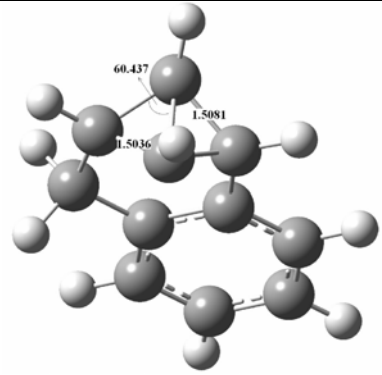
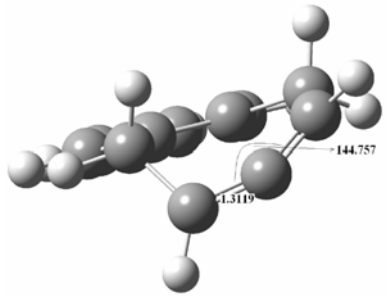
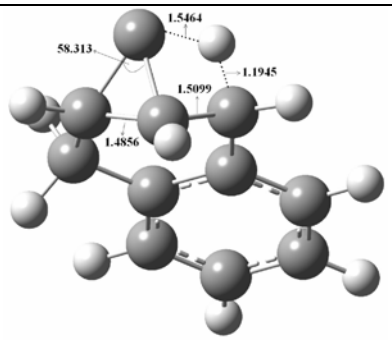
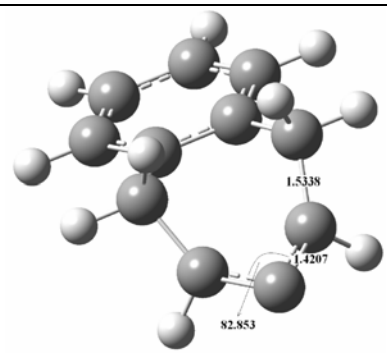
		
18	**20**	**11**
		
TS1 (18→19)	**TS2 (18→20)**	**TS3 (18→11)**
		
22	**19**	**15**
		
TS4 (22→19)	**TS5 (22→15)**	

Figure 2: The optimized structures of **11**, **15**, **18**, **19**, **20**, **22** and the transition structures, **TS1**, **TS2**, **TS3**, **TS4**, and **TS5**. (Bond lengths are in angstrom and bond angles are in degree)

Acknowledgment:

The author wishes to thank the Scientific and Technical Research Council of Turkey (Grant: TUBITAK-TBAG104T371) for their financial support.

References

[1] Christl, M., in *Modern Allene Chemistry*, Krause, N., Hashmi, S.K., Ed.; Wiley-VCH, **2004**, Vol.1, pp 242-357.

[2] Daoust, K. J.; Hernandez, S. M.; Konrad, K. M.; Mackie, I. D.; Winstanley, J., Jr.; Johnson, R. P., *J.Org.Chem.*, **2006**, 71, 5708-5714.

[3] Kilbas, B., Azizoglu, A., Balci, M., *Helv.Chim.Acta*, **2006**, 89, 1449-1456.

[4] Azizoglu, A.; Ozen, R.; Hokelek, T.; Balci, M., *J.Org.Chem.*, **2004**, 69, 1202-1206.

[5] a) Schmidt, M.W., Angus, R.O., Johnson, R.P., *J. Am. Chem. Soc.*, **1982**, 104, 6838. b) Balci, M., Jones, W.M., *J. Am. Chem. Soc.*, **1981**, 103, 2874-2876. c) Balci, M., Jones, W.M., *J. Am. Chem. Soc.*, **1980**, 102, 7607-7608.

[6] a) Doering, W.v.E., LaFlamme, P.M., *Tetrahedron*, **1958**, 2, 75-79. b) Moore, W.R., Ward, H.R., *J. Org. Chem.*, **1960**, 25, 2573. c) Skattebol, L., *Tetrahedron Lett.*, **1961**, 167-172.

[7] a) Sydnes, L.K., *Chem.Rev.*, **2003**, 103, 1133-1150. b) Fedorynski, M., *Chem.Rev.*, **2003**, 103, 1099-1132.

[8] Moore, W.R., Moser, W.R., *J. Am. Chem. Soc.*, **1970**, 92, 5469.

[9] Moore, W.R., Ward, H.R., Merritt, R.F., *J. Am. Chem. Soc.*, **1961**, 83, 2019.

[10] Bettinger, H.F., Schleyer, P.v.R., Schreiner, P.R., Schaefer, H.F., *J.Org.Chem.*, **1997**, 62, 9267-9275.

[11] Yildiz, Y.K., Secen, H., Krawiec, M., Watson, W.H., Balci, M., *J.Org.Chem.*, **1993**, 58, 5355-5359.

[12] Gaussian 03W, *Revision C.2*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin,

J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

[13] Parr, R.G.; Yang, W., Density Functional Theory of Atoms and Molecules; Oxford University Press; Oxford, **1989**.

[14] a) Becke, A.D., *J. Chem. Phys.*, **1993**, 98, 5648, b) Lee, C., Yang, W., Parr, R.G., *Phys. Rev. B*, **1988**, 37, 785.