Ab initio Study of Simple Mg-Ene Reactions of Propenyl Magnesium Halides and Ethylene (Type-1 Intermolecular Reaction)

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ABSTRACT

The insertion of an olefinic C=C bond into a metal-carbon bond is of potential interest as a preparative route to new products and as results of C-C coupling reactions to organic compounds. The allyl compounds of Mg, react with an olefin by inversion of the allyl group via a six center transition state. These precyclic reactions may be one of the most important classes of organic reactions. The reactions of C_3H_5MgX (X=F, Cl, Br, I) with ethylene will be discussed in light of computational studies using *ab initio* methods (RHF/6-31G*//RHF/6-31G* level). The investigation of the structural properties, theoretical thermodynamic and kinetic data i.e. $\triangle rG$, $\triangle G^{\#}$ and rate constants of the reactions at 298°K will be presented.

Keywords: Mg-ene reaction; Grignard reagents; Organometal Molecules; Ab initio calculations; Molecular modeling

INTRODUCTION

Mg-ene reaction in which transfers of "Mg" from the less-substituted allylic carbon to a carbon of the alkene function occurs simultaneously. Intermolecular Mg-ene reaction as the key step in synthesis of some important natural products has been achieved by W. Oppolzer et al. [1-4,7] The insertion of an olefinic C=C bond into a metal-carbon bond is of potential interest as a preparative route to new products and as results of C-C coupling reactions to organic compounds. The allyl compounds of Mg, react with the olefin by inversion of the allyl group via a six center transition state. These precyclic reactions may be one of the most important classes of organic reactions. The formal ene-reaction of allylic Grignard reagents to olefins has been studied by [1]H-nmr spectroscopy, and were applied for synthesis of complex molecules, such as monoterpen alkaloids, irridoids, $\Delta^{9(12)}$-capnellene and polymers.[1-7]

If the Mg-C bond at the beginning is much more reactive than the Mg - C bond of the first insertion product, the reaction would terminate after the first step. [4] The free energies ($\Delta G^{\#}$ and $\Delta_r G$) of the reactants, transition states and products in the reactions of C_3H_5MgX (X=F, Cl, Br, I) with ethylene are recorded by using RHF/6-31G*//RHF/6-31G* calculations at 298K.

This reaction show the combination of the ethylene with C_3H_5MgX for reaching to a Mg-$\Delta^{9(12)}$-capnellene **(II)** derivative as the favored product of the exothermic reaction are the main motive forces of these [Mg]-ene reaction.

COMPUTATIONAL DETAILS AND CALCULATIONS

The *ab initio* molecular orbital calculations were performed with the gaussian 98 program. Geometries for all structures were fully optimized by means of analytical energy gradients in RHF level with the 6-31G* basis

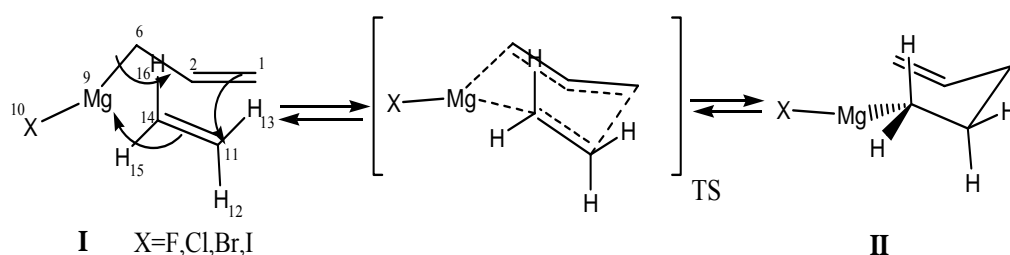*Corresponding author: avatarman.taherpour@gmail.com;
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1

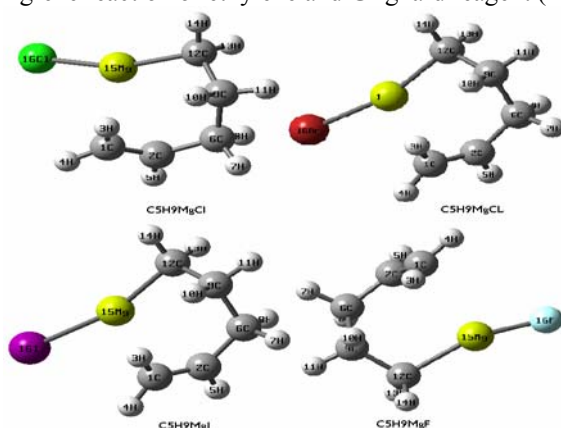**Fig. 1.** The Mg-ene reaction of ethylene and Grignard reagent (x=F, Cl, Br, I)

Fig. 2. The product of the Mg-ene Grignard reactions of C_3H_5MgX (X=F, Cl, Br, I) with ethylene.
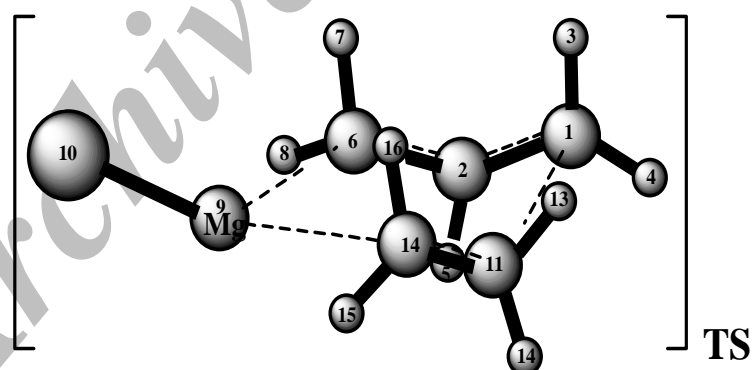

Fig. 3. The transition state of the Mg-ene Grignard reactions of C_3H_5MgX (X=F, Cl, Br, I) with ethylene.

set.[8] The synchronous Transit-guided Quasi-Newton (STQN) method was used to locate transition states and products, which were confirmed to have zero and one imaginary frequent cy, respectively. The frequencies were scaled by a factor of 0.8929 and used to compute the free energies ($\Delta G^{\#}$) and the free energies changes of reaction ($\Delta_r G$) at 298°K by equations:

$\Delta G^{\#} = \sum G_{TS} - \sum G_{Reactants}$ Eq.-1

$\Delta_r G = \sum G_{products} - \sum G_{reactants}$ Eq.-2

Also, rate constants were calculated with the Eyring equation, derived from transition state theory:[9]

$k = k_B T/h \exp(-\Delta G^*/RT)$ Eq.-3

$\Delta G^{\#}$ is the free energy difference between transition state and reactants. The imaginary reactions were studied in the method: RHF/6-31G*//RHF/6-31G*. In this study, the most conformations of the simple cycloalkynes (**I-1** to **I-4**) were investigated in the 1,3-dipolar cycloaddition reactions with Ethylene.

2

RESULT AND DISCUSSION

The selected structural parameters, the heats of formation in kcal mol^{-1} and the results of the reactions of C_3H_5MgX (X=F, Cl, Br, I) with ethylene will be discussed in light of computational studies using RHF/6-31G*//RHF/6-31G* method and the transition states of the conversion from the reactants to the organometal products are summarized in Table-1 to Table-4 and Fig.-1 to Fig. 3. The energy surface and the barrier energy for the reactions were investigated in detail by changing the position and distances between appropriate atoms in the reaction pathway. The diagram of the free energies ($\Delta G^{\#}$) and the free energies changes of reaction ($\Delta_r G$) at 298°K for in the intermolecular Mg-ene reactions of C_3H_5MgX (X=F, Cl, Br and I) with ethylene for producing the product C_5H_9MgX ($\Delta G^{\#}$ and $\Delta_r G$ in kcal mol^{-1}) and kinetic (rate constants=k in $M^{-1}Sec^{-1}$ and relative constants=k´) data, by: RHF/6-31G*//RHF/6-31G* method are shown in Fig.4 to Fig. 7. The free energies of the reactants, transition states and products in the reactions are listed in Tab. 1 to Tab. 4 The results show the treatment the electron correlation gives more stable energies.

Table 1. Selected structural parameters of C_3H_5MgX (X=F, Cl, Br and I)[a]

Parameters	X=F	X=Cl	X=Br	X=I
Bond Length(BA)				
1C - 2C	1.325	1.325	1.325	1.321
2C - 6C	1.49	1.49	1.49	1.5
6C - 9Mg	2.10	2.09	2.08	2.06
9Mg-10X	1.77	2.21	2.38	2.57
Bond Angle(B)				
1C - 2C - 6C	127.09	127.07	126.96	126.56
2C - 6C - 9Mg	108.84	107.02	108.25	113.79
6C - 9Mg - 10X	178.86	179.02	177.77	177.52
Dihedral(B)				
1C - 2C - 6C-9Mg	-95.88	-92.74	-93.21	0
2C - 6C-9Mg-10X	23.46	33.1	-177.84	180

[a] RHF/6-31G*//RHF/6-31G*

Table 2. Selected structural parameters of the intermolecular Mg-ene reactions of C_3H_5MgX (X=F, Cl, Br and I) with ethylene

Parameters	TS(X=F)	TS(X=Cl)	TS(X=Br)	TS(X=I)
Bond Length(BA)				
1C-2C	1.32	1.32	1.32	1.32
2C-6C	1.50	1.50	1.50	1.50
11C-14C	1.32	1.32	1.32	1.32
1C-11C	4.44	4.30	4.29	4.21
9Mg-10X	2.79	2.83	2.84	2.87
6C-9Mg	2.11	2.11	2.09	2.08
9Mg-10X	1.79	2.23	2.41	2.60
Bond Angle(B)				
1C-2C-6C	126.74	126.29	126.27	126.15
2C-6C-9Mg	113.16	110.55	110.35	109.10
6C-9Mg-10X	155.05	161.42	161.32	161.84
Dihedral(B)				
1C - 2C - 6C-9Mg	88.28	78.47	78.02	74.82
2C - 6C-9Mg-10X	23.24	33.54	33.61	35.821

3

Table 3. Selected structural parameters of the intermolecular Mg-ene reactions
of C_3H_5MgX (X=F, Cl, Br and I) with ethylene for producing the product C_5H_9MgX.[a]

Parameters	Products (C_5H_9MgX)			
	X=F	X=Cl	X=Br	X=I
Bond Length(BA)				
1C - 2C	1.33	1.33	1.33	1.33
2C-6C	1.51	1.51	1.51	1.51
6C-9C	1.53	1.53	1.53	1.53
9C-12C	1.54	1.54	1.54	1.54
12C-15Mg	2.11	2.10	2.09	2.09
15Mg-16X	1.78	2.23	2.40	2.60
Bond Angle(B)				
1C-2C-6C	127.10	127.19	127.05	127.09
2C-6C-9C	116.15	116.16	109.84	99.15
6C-9C-12C	113.11	112.95	115.92	112.74
9C-12C-15Mg	110.39	110.41	112.98	110.47
12C-15Mg-16X	161.58	159.71	162.97	162.04
Dihedral(B)				
1C-2C-6C-9C	-31.29	-29.00	-30.49	-29.99
2C-6C-9C10C	-64.52	-64.98	-64.68	-64.81
6C-9C10C-15Mg	49.78	48.19	49.05	49.48
9C10C-15Mg-16X	176.68	179.99	174.34	172.35

a: RHF / 6-31G* // RHF / 6-31G*

Table 4. The free activation energies changes in the intermolecular Mg-ene reactions of C_3H_5MgX (X=F, Cl, Br and I) with ethylene for producing the product C_5H_9MgX ($\Delta G^{\#}$ and $\Delta_r G$ in kcal mol^{-1}) and kinetic (rate constants=k in M^{-1}Sec^{-1} and relative constants=k´) data, by: RHF/6-31G*//RHF/6-31G* method

X in C_3H_5Mg-X	$\Delta G^{\#}$	$\Delta_r G$	k ×10^{-10}	k′
F	3.28	-9.12	2.45	1
Cl	2.99	-10.42	4.49	1.83
Br	2.87	-10.68	4.87	1.98
I	1.66	-12.8	37.84	15.43

Structures for the synchronous transition state are obtained with mean bond length values of C-Mg and C-C bonds in transition states of C_3H_5MgX (X=F, Cl, Br, I) with ethylene. The bond length values of C6-Mg(9) for the transition states are 2.11, 2.11, 2.09 and 2.08 in Å for the reactions of C_3H_5MgX (X=F, Cl, Br, I) with ethylene, respectively. The calculated Mg-X bonds for C_3H_5MgX (X=F, Cl, Br, I), the transition states and the product C_5H_9MgX, are: [X=F: 1.77, 1.79, 1.78], [X=Cl: 2.21, 2.23, 2.23], [X=Br: 2.38, 2.41, 2.40] and [X=I: 2.57, 2.60, 2.60], respectively. Tables 1-3 show the selected structural parameters of the reactions and the

changes of the bond lengths, bond angles and the dihedral angles of **I**, TS and **II** of the reactions. By increasing the size of halogen (X) the bond lengths of Mg-X for **I**, TS and **II** have increased. For each intermolecular Mg-ene reactions of C_3H_5MgX (X=F, Cl, Br, I) with ethylene (**I**), the thermodynamic and kinetic stabilities of are related to the character of the halogen, Mg-X (X=F, Cl, Br, I) bond lengths and the structural characters particularly around the [C6…Mg9(X,10)...C14C11] of the transition states. The kinetic stabilities were decreased by increasing the size of halogens, subsequently increasing the bond length strain of Mg-X in **I**

4

and TS. Table-4 shows the calculated rate constants (k, in $M^{-1}Sec^{-1}$) by utilizing the RHF/6-31G*//RHF/6-31G* (k) methods and the Eyring equation (Eq.-3). The chemical affinity and the calculated rate constants in the method increased by decreasing the size of the Mg-X in **I**. The rate constants with RHF/6-31G*//RHF/6-31G* for the reactions of C_3H_5MgX (X=F, Cl, Br, I) with ethylene **(I)** are 2.45E-10, 4.49E-10, 4.87E-10 and 37.84E-10, respectively. The results demonstrated that the rate constant show a grate different when the halogen was Iodide (X=I). The rate constant in this condition is almost 10 times more than the other halogens X=F, Cl and Br in Mg-X bonds. The free energy differences between transition states and reactants ($\Delta G^{\#}$ in kcal mol^{-1}) by RHF/6-31G*//RHF/6-31G* for the reactions **I** , are 3.28, 2.99, 2.87 and 1.66, respectively. The results in RHF/6-31G*//RHF/6-31G* level show decrease in the $\Delta G^{\#}$ of the reactions of **I** by increasing the atomic number of halogen. The free energy

changes of reactions ($\Delta_r G$) are shown in Table-4. The values of $\Delta_r G$ were obtained by the use of two RHF methods and Eq.-2. The values of $\Delta_r G$ by RHF/6-31G*//RHF/6-31G* method for the exothermic reactions of **I**, are -9.12, -10.42, -10.68 and -12.80, respectively. The gaps in the free energies between reactants and products have been increased by the thermodynamic stability of bigger halogen. See Tab. 4 and Fig. 4. to Fig. 7. The results of the calculations show just a difference in the Mg-ene reactions of C_3H_5MgX (X=F, Cl, Br, I) with ethylene, in comparison with the other reactions in this group. See the results of X=I. The calculated data of relative constants (k´) in RHF/6-31G*//RHF/6-31G* were shown in Table-4. These results suggest that, the relative constants of reaction rates decreased by increasing the size of the halogen and increasing the bond length of Mg-X and also chemical affinity of reactants to take part in the Mg-ene reactions of **I** to produce of the Mg-$\Delta^{9(12)}$-capnellene **(II)** derivatives.
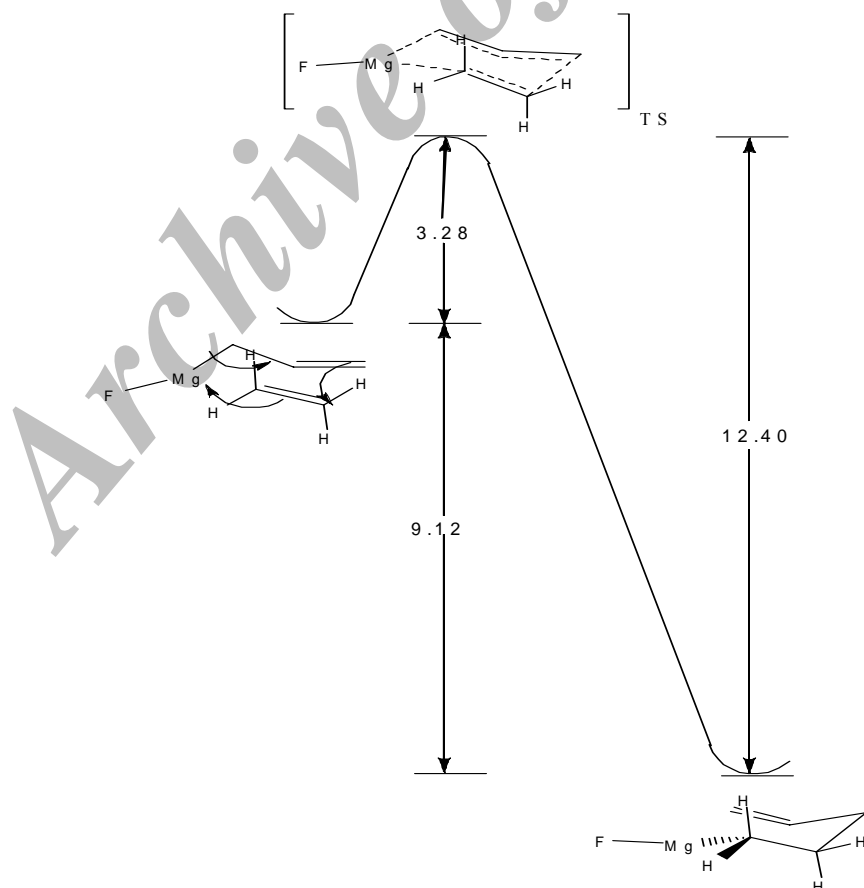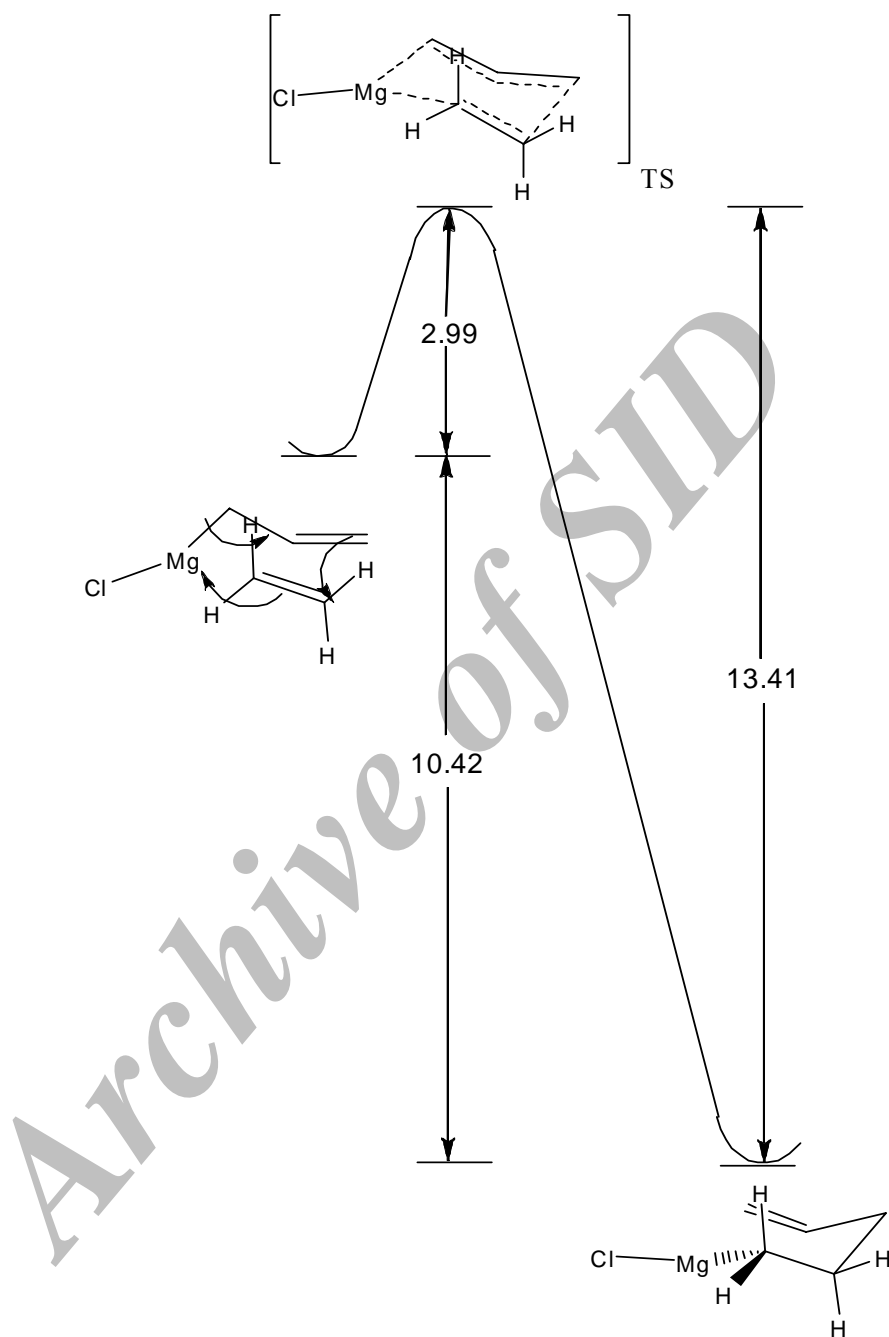

Fig. 4. The diagram of the free energies ($\Delta G^{\#}$) and the free energies changes of reaction ($\Delta_r G$) at 298°K for the intermolecular Mg-ene reaction **(I)** of C_3H_5MgF with ethylene by using RHF/6-31G*//RHF/6-31G* method.
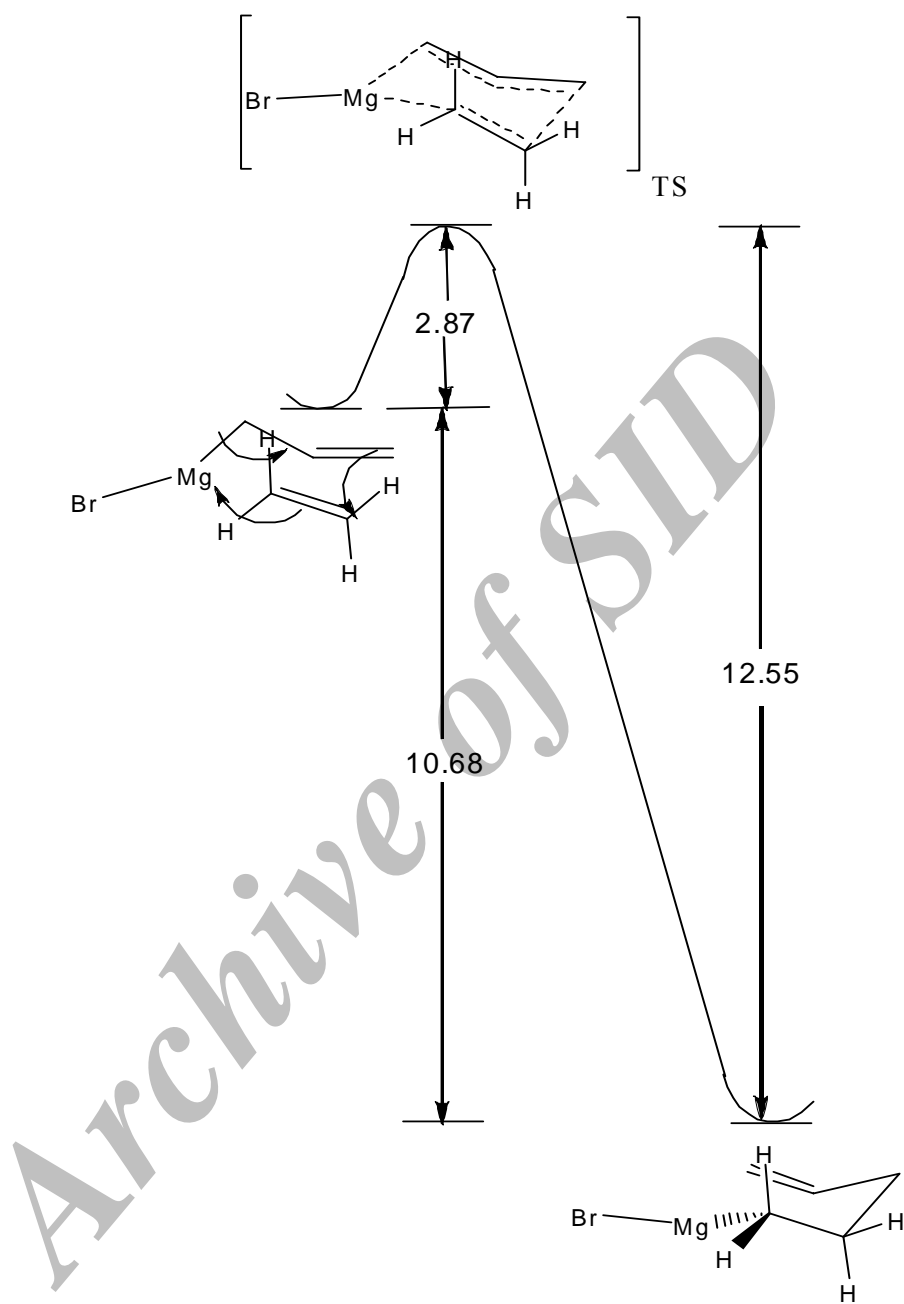
5

Fig. 5. The diagram of the free energies ($\Delta G^{\#}$) and the free energies changes of reaction ($\Delta_r G$) at 298°K for the intermolecular Mg-ene reaction (**I**) of C_3H_5MgCl with ethylene by using RHF/6-31G*//RHF/6-31G* method.

Fig. 6. The diagram of the free energies ($\Delta G^{\#}$) and the free energies changes of reaction ($\Delta_r G$) at 298°K for the intermolecular Mg-ene reaction (**I**) of C_3H_5MgBr with ethylene by using RHF/6-31G*//RHF/6-31G* method.
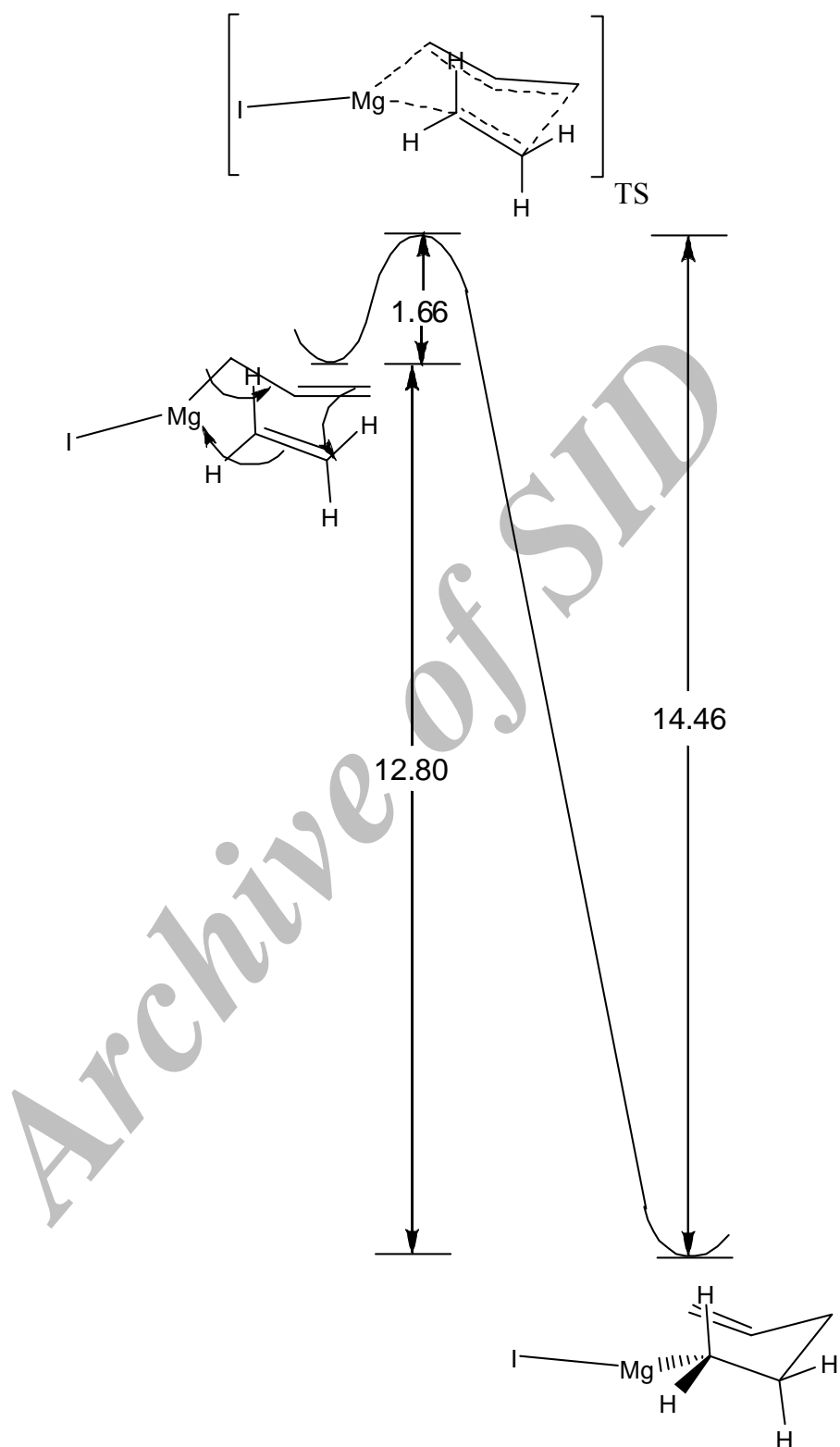
Fig. 7. The diagram of the free energies ($\Delta G^{\#}$) and the free energies changes of reaction ($\Delta_r G$) at 298°K for the intermolecular Mg-ene reaction **(I)** of C_3H_5MgI with ethylene by using RHF/6-31G*//RHF/6-31G* method.

CONCLUSION

Comparing results show that in the Mg-ene Grignard reactions of C_3H_5MgX (X=F, Cl, Br, I) with ethylene (I) to producing the Mg-$\Delta^{9(12)}$-capnellene (II) derivatives, the rate constant increases as increasing the size of the halogen and the free energies changes in reactions decreases. The comparison of the thermodynamic and kinetic data of the reactions I showed that the chemical affinity of I increases by increasing the bond length of Mg-X. The free energies ($\Delta G^{\#}$ and $\Delta_r G$) of the reactants, transition states and products in the reactions of the Mg-ene reactions are recorded by using RHF/6-31G*//RHF/6-31G* calculations at 298°K. The kinetic data (rate constants= k in M^{-}

^{1}Sec^{-1} and relative constants=k´) were calculated by the Eyring equation, which is derived from transition state theory. In these exothermic reactions, the k and k´ of the reactions increased by increasing the size of X and the bond length of metal-halogen bond for producing the Mg-$\Delta^{9(12)}$-capnellene (II) derivatives.

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