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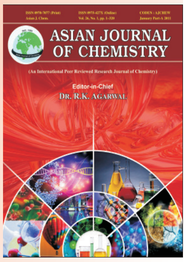

Theoretical Studies on Cyclopropanation Reaction of Aluminum Carbenoid $(CH_3)_2AlCH_2I$ with Allylic Alcohol

ZHAOHUI LI*, JINGLIN SHEN, HUIQUN HU and LIZHEN HE

Department of Chemistry and Biochemistry, Jiangxi Medical College, Shangrao 334000, P.R. China

*Corresponding author: E-mail: lich502@163.com

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The aluminum carbenoid $(CH_3)_2AlCH_2I$ promoted cyclopropanation reactions with allylic alcohol have been investigated. Two reaction channels have been found *i.e.*, the methylene transfer and carbometalation pathways. On the basis of the energetics of the reactions pathways, the methylene transfer pathway (reaction barrier of 9-10.3 kcal/mol) is favored over the carbometalation pathway (about 30 kcal/mol) in the whole reactions. Our computational results are in good agreement with the experimental results performed by Andre B. Charette.

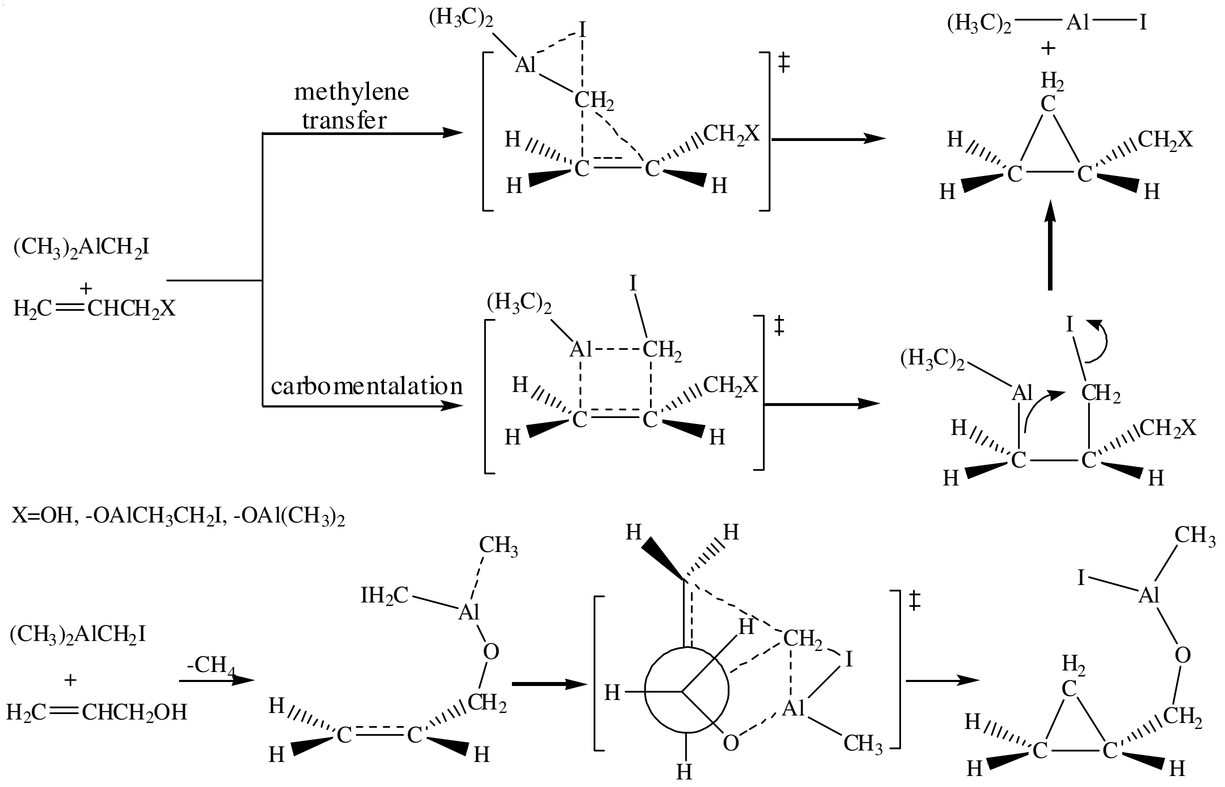
Keywords: Cyclopropanation, Density functional theory, Aluminum carbenoid, Allylic alcohol.

INTRODUCTION

Cyclopropane-containing molecules can exhibit important biological activites. They can also be used as inhibitors and versatile synthetic intermediates[1-14]. Cyclopropane-containing molecules can be produced from carbenoid-promoted cyclopropanation reaction. Therefore, much effort has been invested to develop carbenoid reagents which can make cyclopropanes from olefins with high efficiency and stereoselectivity[1-22]. Winstein *et al.*[23] reported the first application of the Simmons-Smith (SS) reaction to an allylic alcohol, which represents an early example of the use of a heteroatom group as a directing group. This has motivated a large number of research groups to develop new and wide-ranging methods to produce similar reagents. Such as, there have been experimental reports of using Sm carbenoid to make cyclopropanated allylic alcohol by Molander and co-workers[24-26]. Several reactions of the metal (Zn, Sm, Al) reagents have also been reported for cyclopropanation of allylic alcohol[16a,17b,25]. Simmons-Smith reaction with an allylic alcohol has distinct advantages over a simple olefin in relation to reaction rate and stereoselectivity. For example, Rickborn *et al.*[27] reported that the Simmons-Smith reactions of allylic alcohol are much faster than those of simple olefins (about > 1000 times) and the reaction with a cyclic allylic alcohol proceeds through a hydroxyl group resulted from the cyclopropane ring on the same side. There are not as many theoretical reports of the Simmons-Smith carbenoids compared to the large number of experimental investigations for their cyclopropanation reactions with allylic alcohol. Recently, a systematic investigation of the reaction of the $ClZnCH_2Cl$ and CH_3SmCH_2I with an allylic alcohol were performed by the density functional theory (DFT) methods[27]. However, to our best of knowledge, the mechanism of the reaction of the Al carbenoid with allylic alcohol has still not been studied. In this paper, we describe the mechanism (**Scheme-I**) of the cyclopropanation reactions of allylic alcohol promoted aluminum carbenoid. This is similar to previously investigated Sm carbenoids[27]. Two reaction channels *i.e.*, methylene transfer and carbometalation were studied. The methylene transfer pathway is favored and competition of carbometalation pathway is very small. This is in good agreement with experiments[16(d)].

COMPUTATIONAL DETAILS

The density functional method[28,29] of B3LYP has been used to investigate the cyclopropanation reaction mechanisms of the Al carbenoids with allylic alcohol. The stationary structures of the potential energy surfaces were fully optimized at B3LYP level of theory. The analytical frequency calculations at the same level were performed in order to confirm to the optimized structures to either a minimum or a first-order saddle-point as well as to obtain the zero-point energy correction. Furthermore IRC calculations[30] were performed to confirm the optimized transition state correctly connects the relevant reactants and products. Geometry optimization for all reactants, intermediates, transition states and products as well as the frequency calculations were carried out with the 6-311G** basis set for all atoms of reaction[31]. To consider the solvent effect on the title reaction, the polarized continuum model (PCM) was



Scheme-I

applied. Single-point energy calculations were done at the B3LYP/PCM/6311G** level. All calculations were carried out using the Gaussian 98 and Gaussian 03 program suite[32].

RESULTS AND DISCUSSION

The optimized stationary structures (minima, saddle points) on the potential energy surfaces of the reaction are depicted schematically in Figs. 1-6 with selected key geometry parameters (bond lengths and bond angles) are also shown in Figs. 1-6.

Cyclopropanation reaction of $(CH_3)_2AlCH_2I$ with the allylic alcohol: Fig. 1. displays the calculated geometry found for Al carbenoid $(CH_3)_2AlCH_2I$ and the reactant complex RC1, RC2 and transition states (TS1, TS2) for reactions of allylic alcohol through two different pathways to produce cyclopropane (c-C_4H_8OH) and $(CH_3)_2AlI$. When $(CH_3)_2AlCH_2I$ and allylic alcohol approach each other, a complex may be formed between them. A transition state (TS1) was found on the way to cyclopropane (c-C_4H_8OH) and $(CH_3)_2AlI$. The Al carbenoid $(CH_3)_2AlCH_2I$ approaches allylic alcohol from above the molecular plane in an asymmetric manner. In the transition structure TS1, allylic alcohol molecule has shifted its planar structure with a significant pyramidalization of about 13.1° for C^2, which indicates that the $sp^2 \rightarrow sp^3$ rehybridization is necessary for cyclopropane formation; whereas the pyramidalization of C^3 is only 1.1°. There is another significant evidence for the asynchronous approach of the allylic alcohol molecule in the methylene transfer mechanism that the C^1-C^3 distance in TS1 is 2.220 Å, which is 0.320 Å shorter than the C^2-C^3. The interaction of the $(CH_3)_2AlCH_2I$ moiety with the π-olefin orbital are mainly responsible for the slight lengthening of C^1=C^2 bond and C^3-Al bond from the reactant complex (RC1) to the transition state (TS1) where C^1=C^2 bond length is elongated by 0.016 Å and the C^3-Al bond length is elongated by 0.029 Å, respectively. Relatively large changes are associated with the ∠I-C^3-Al, the ∠I-Al-C^3, the C^3-I and Al-C^3 distances that vary from 101.9°, 41.7°, 2.235 Å, 1.998 Å in RC1, to 65.7°, 71.1°, 2.711 Å, 2.030 Å in TS1, respectively, as shown in Fig. 1. Notably, in the transition state TS1, the C^3-I bond becomes nearly broken and the electron-rich I atom is attracted by the metal center nearly resulted in a complete Al-I bond. These changes in the bond lengths and angles are attributed to partial formation of the $(CH_3)_2$ AlI byproduct in the transition state. The Al-I interaction is believed to give a sufficient compensation to the weakening of the Al-C^3 bond from RC1 to TS1. As shown in Fig. 1, the methylene transfer pathway has a barrier of 10.3 kcal/mol in $(CH_3)_2AlCH_2I$ and is exothermic by about 38.9 kcal/mol at the B3LYP level, indicating that the cyclopropanation reaction of $(CH_3)_2AlCH_2I$ with allylic alcohol proceeds easily (with a barrier of 10.3 kcal/mol). Vibrational analysis showed that the TS1 structure is the first-order saddle point with only one imaginary frequency of 317i cm^{-1} and the IRC calculations confirmed that the TS1 connects the corresponding reactant RC1 and products (c-C_4H_8OH) and $(CH_3)_2AlI$. Thus, it is evident that TS1 is the transition states of the concerted reaction of $(CH_3)_2AlCH_2I$ with allylic alcohol through the methylene transfer pathway.

Compared with the methylene transfer pathway, the carbomentalation pathway has larger changes in the geometry from the reaction complex to the transition state. The Al-C1 interaction increases significantly from 2.901 Å in RC2 to 2.022 Å in TS2. And the C^2-C^3 forms to a significant extent going from

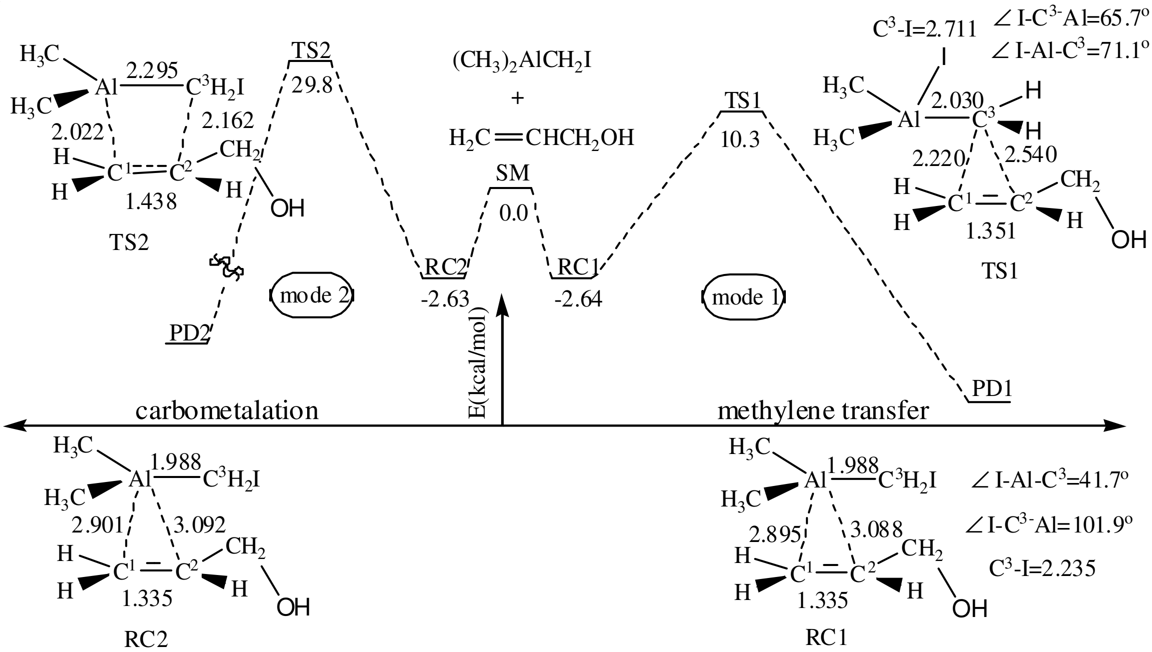


Fig. 1. Structures and energies of cyclopropanations reaction of allylic alcohol with $(CH_3)_2AlCH_2I$ *via* methylene transfer and carbometalation. Bond lengths are shown in angstroms.energies relative to the separated reactants are shown in kilocalories per mole

a distance 3.092 Å in RC2 to 2.162 Å in TS2. This is accompanied by the weakening of C^3-Al bonds from 1.998 Å in RC2 to 2.295 Å in TS2. It is interesting that the C^3-I bond length and the Al-I interaction only change slightly during the process from RC2 to TS2, indicating that, different from the methylene transfer pathway, the Al-I interaction contribute little to the weakening of the C^3-Al of TS2 in the carbometalation process. Thus, it requires more energy to overcome the barrier of carbometalation pathway from RC2 to TS2. The reaction barrier height at the B3LYP/6-311G** level for the reaction system of $(CH_3)_2AlCH_2I$ and allylic alcohol, is calculated to be 29.8 kcal/mol, as shown in Fig. 1. The barrier height of 29.8 kcal/mol predicts that the reaction does not occur easily under room-temperature conditions. Vibrational analysis found that the optimized TS2 structure had one imaginary frequency of 381i cm^{-1} and was confirmed to connect the corresponding reactants and products by IRC calculations. To examine bulky solvation effect, the polarized continuum model (PCM) was utilized for dichloromethane ($\varepsilon = 8.93$). All single-point energy calculations were done at the B3LYP/PCM/6-311G** level for the reaction systems (RC, TS). The reaction barriers from RC to TS were computed with ZPE corrections. The barriers decrease by 0.5 kcal/mol and 0.3 kcal/mol for the methylene transfer and the carbometalation, respectively, indicating that the dichloromethane solvent has a positive effect on the chemical reactivity.

Cyclopropanation reaction of monomeric(allyloxy) $AlCH_3CH_2I$: It is known experimentally that the Simmons-Smith cyclopropanation of free allylic alcohol takes place through initial formation of an allylic alkoxide[16c,21]. We examined the monomeric reaction pathway of the cyclopropanation of allyl alcohol, as shown in Fig. 2. As seen from Fig. 2, the attack between $(CH_3)_2AlCH_3CH_2I$ and the OH group of the allylic alcohol leads to the allylic alkoxide RC3 and CH_4 molecule which may be formed when the H atom cleavaged from the OH group of allylic alcohol with the CH_3 radical. The product(PD3), cyclopropylmethoxide, forms from RC3 through the transition state of TS3. Inspection of Fig. 2 shows that the angle O-Al-C^3, Al-O-C in RC3 is 119.2°, 114.2° and that in TS3 is 100.3°, 138.4°. From RC3 to TS3, the distances of C^1-Al and C^2-Al have larger changes. One can conjecture that such a large structural change causes a large deformation energy and raises the activation energy. The calculated activation energy is 22.6 kcal/mol for mode 3 ,which indicate that the mode 3 is energetically unfavorable and cannot be used to explain the experimental result that appreciable reaction could occur at a temperature of -40 °C.

Cyclopropanation reaction of $(CH_3)_2AlCH_2I$ with the monomeric (allyloxy)$Al(CH_3)CH_2I$: Because of relatively high barriers found for the mode 3, it further motivated us to investigate the well-establlished DFT approach to interpretate on the mechanism of the cyclopropanation reaction of the CH_3AlCH_2I with the monomeric (allyloxy) $Al(CH_3)CH_2I$. Fig. 3 displays the optimized geometry and energetics of model 4 and 5. Fig. 3 shows that the reaction possibly occurs *via* two pathways *i.e.*, methylene transfer and carbometalation Similar to intermolecular reaction of the $(CH_3)_2AlCH_2I$ with the allylic alcohol, the separated reactants $(CH_3)_2AlCH_2I$ and Monomeric (allyloxy)$Al(CH_3)CH_2I$ start with the reactant complex RC4 (model 4) and RC5 (model 5). In model 4 of methylene transfer, the final product PD4 is formed *via* a transition state TS4 with activation energy of 10.7 kcal/mol, which is a three-membered transition state. However, a four-membered transition state in model 5 of carbometalation gives a final product PD5. Inspecting the structures of both transition states suggests that TS4 is earlier than TS5, for example, the distance of C^1 -C^2 has a smaller change of 0.015 Å in TS4 from 1.336 to 1.351 Å than that of 0.106 Å in TS5 from 1.335 to 1.441 Å as going from reactant complex to transition state. This indicates that less energy is required for the formation of C^1-C^2 bond in model 4

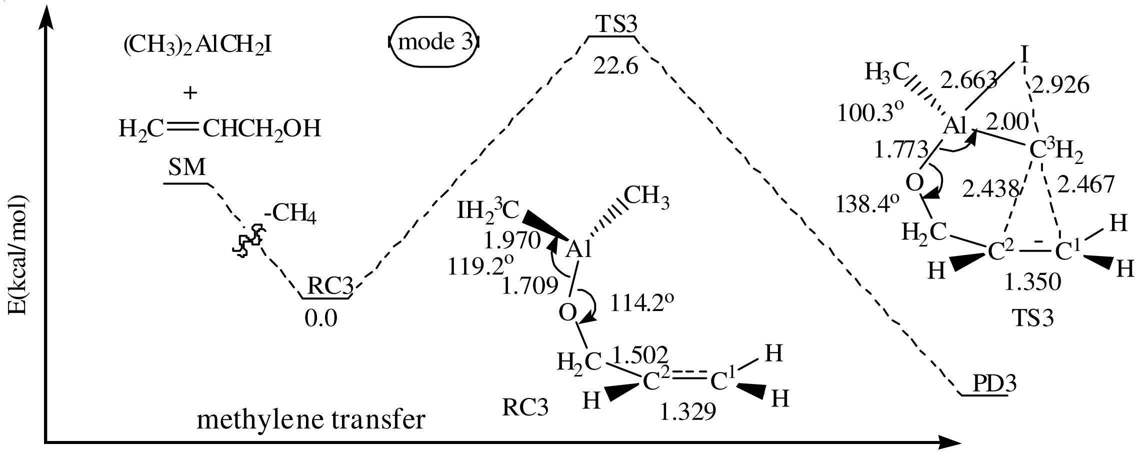


Fig. 2. Structures and energies of intramolecular cyclopropanations reactions of monomeric(allyloxy)AlCH$_3$CH$_2$I. Bond lengths are shown in angstroms.energies relative to the separated reactants are shown in kilocalories per mole

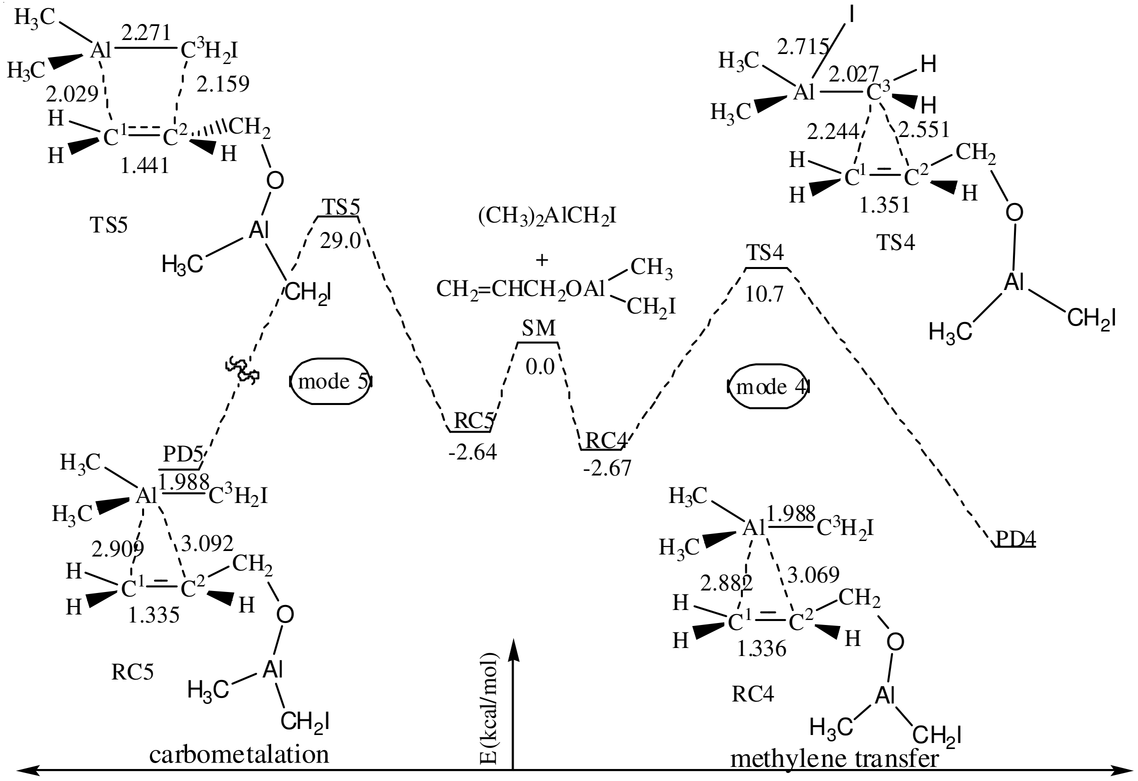


Fig. 3. Structures and energies of intermolecular cyclopropanation reaction of (CH$_3$)$_2$AlCH$_2$I with monomeric(allyloxy)AlCH$_3$CH$_2$I via methylene transfer and carbometalation. Bond lengths are shown in angstroms.energies relative to the separated reactants are shown in kilocalories per mole

than in model 5. Our calculated reaction barriers have a good agreement with above analysis. For example, they are 10.7 kcal/mol in methylene transfer model and 29 kcal/mol in carbometalation path, respectively. The lower barrier for mode 4 suggests that cyclopropanation reaction of the (CH$_3$)$_2$AlCH$_2$I with the monomeric(allyloxy)AlCH$_3$CH$_2$I is likely to occur on a methylene transfer pathway. The competition from carbometalation pathway is negligible.

The Al carbenoid (CH$_3$)$_2$AlCH$_2$I approaches the monomeric (allyloxy) AlCH$_3$CH$_2$I from above the molecular plane in an another manner. As shown in Fig. 4, the mode 6 and the mode 7 are likely occur. the transition state (TS6) (299i cm^{-1}) was found for the reaction of mode 6 on the methylene transfer pathway to c-C$_4$H$_8$OAlCH$_3$CH$_2$I and (CH$_3$)$_2$AlI. The geometry of TS6 is similar to that of TS4. the reaction has barrier of 10.3 kcal/mol at the B3LYP/6311G** level. As for the carbometalation pathway, the geometry of TS7 is similar to that of TS5. the reaction has barrier of 24.4 kcal/mol at the B3LYP level of theory, As shown in Fig. 4. the barrier of mode 7 is little lower than that of mode 5, probably due to reason that I atom like a bridge,which partially connects Al atom and C^3 atom, could significantly stablize the TS7 and RC7 in the reaction. Simlar to mode 4,5 methylene transfer pathway is favored and the competition from carbometalation pathway is negligible.

Cyclopropanation reaction of (CH$_3$)$_2$AlCH$_2$I with the monomeric (allyloxy)Al(CH$_3$)$_2$: The decomposition reaction of allylic alcohol with (CH$_3$)$_2$AlCH$_2$I to produce the

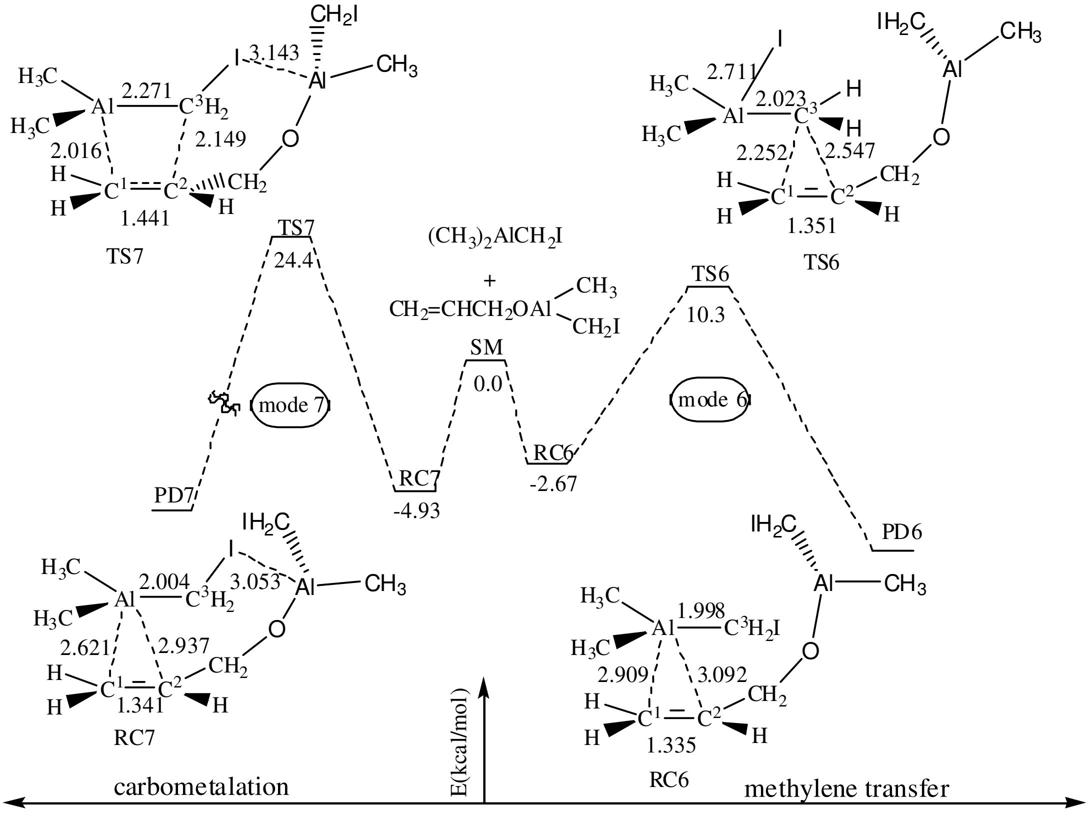


Fig. 4. Structures and energies of intermolecular cyclopropanation reaction of $(CH_3)_2AlCH_2I$ with monomeric(allyloxy)$AlCH_3CH_2I$ *via* methylene transfer and carbometalation. Bond lengths are shown in angstroms.energies relative to the separated reactants are shown in kilocalories per mole

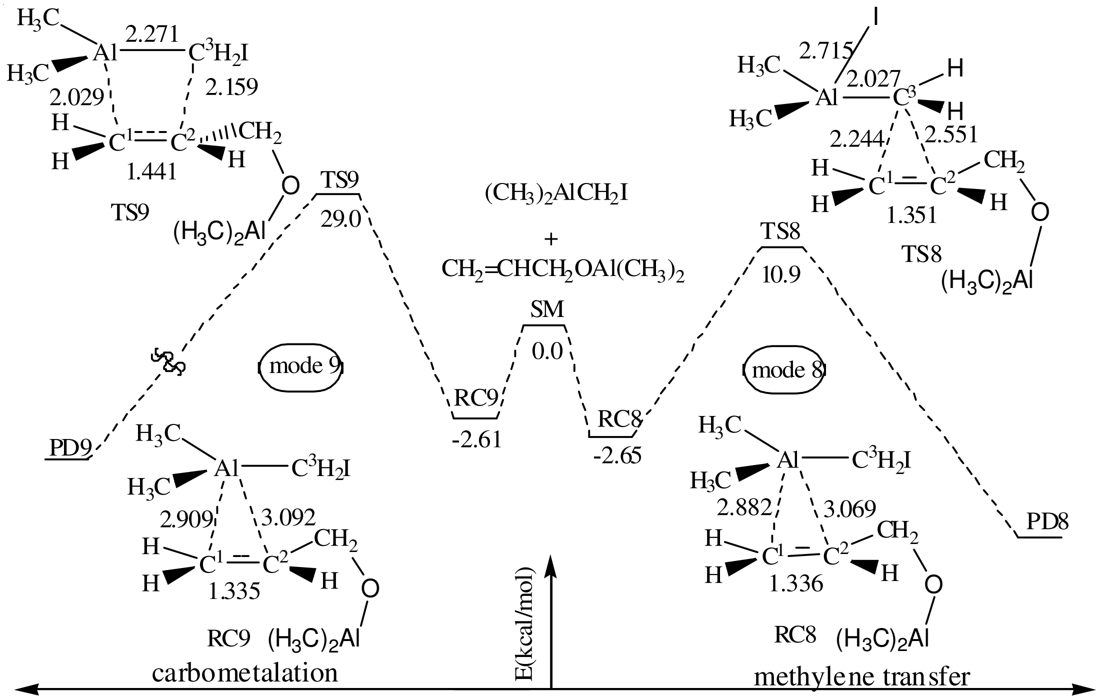


Fig. 5. Structures and energies of intermolecular cyclopropanation reaction of $(CH_3)_2AlCH_2I$ with monomeric(allyloxy)$Al(CH_3)_2$ via methylene transfer and carbometalation. Bond lengths are shown in angstroms.energies relative to the separated reactants are shown in kilocalories per mole

monomeric (allyloxy)$Al(CH_3)_2$ and CH_3I is likely to occur. This further encouraged us to investigate substituent effect on titled reaction. Figs. 5 and 6 display the optimized geometries and energies found for the reactions of intermolecular reaction of the $(CH_3)_2AlCH_2I$ with the monomeric (allyloxy)$Al(CH_3)$. The reaction of $(CH_3)_2AlCH_2I$ with the monomeric (allyloxy)$Al(CH_3)_2$ is also involved two kinds of reaction pathways of methylene transfer and carbometalation in which the RC, TS and PD are structurally similar to the corresponding ones found in the cyclopropanation of the monomeric

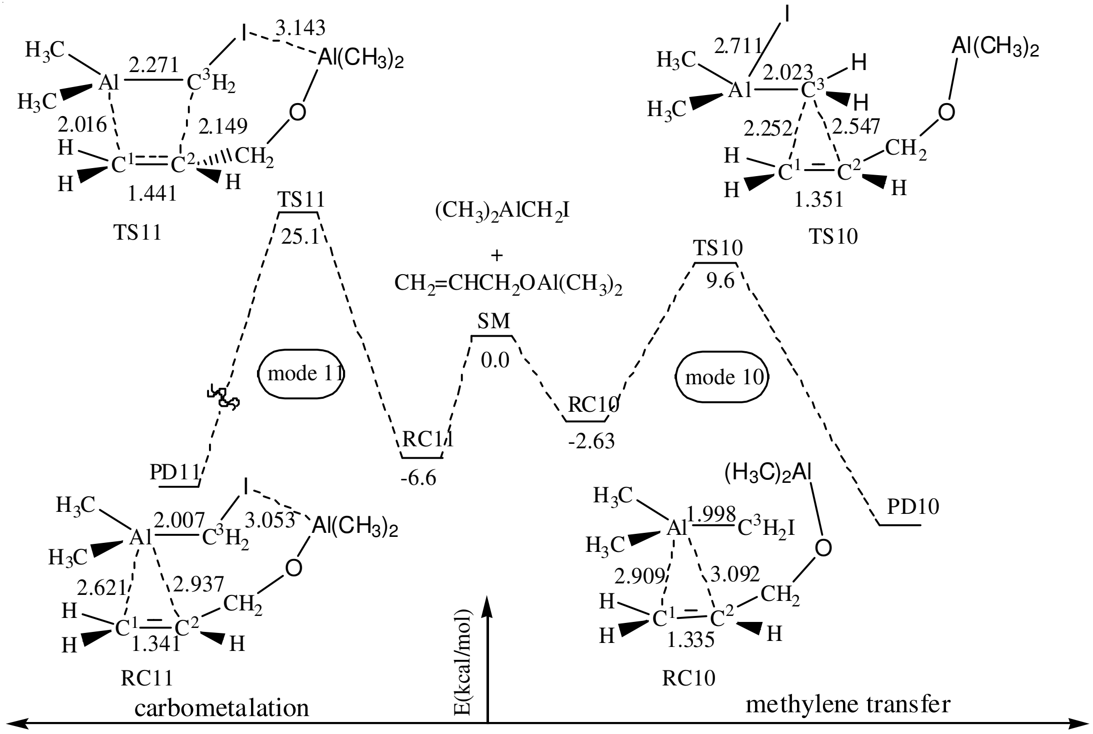


Fig. 6. Structures and energies of intermolecular cyclopropanation reaction of $(CH_3)_2AlCH_2I$ with monomeric(allyloxy)$Al(CH_3)_2$ via methylene transfer and carbometalation. Bond lengths are shown in angstroms.energies relative to the separated reactants are shown in kilocalories per mole

(allyloxy)$AlCH_3CH_2I$ promoted by $(CH_3)_2AlCH_2I$ molecule. Analogous to the cases of monomeric (allyloxy)$AlCH_3CH_2I$, the reaction barrier for methylene transfer reaction with model 8, model 10 is 10.9 kcal/mol, 9.6 kcal/mol, respectively and 29 kcal/mol, 25.1 kcal/mol for carbometalation reaction with the model 9, model 11, respectively. This indicates that the methylene transfer pathway is the optimal for the cyclopropanation reaction of both the monomeric (allyloxy)$AlCH_3CH_2I$ and monomeric (allyloxy)$Al(CH_3)_2$ with $(CH_3)_2AlCH_2I$ carbenoid and provides evidence that the reactivity of the monomeric (allyloxy)$Al(CH_3)_2$ is similar to the monomeric (allyloxy) $AlCH_3CH_2I$.

Conclusion

In this paper we have studied, using a DFT (B3LYP) approach, the potential energy surface for the reaction between allylic alcohol and $(CH_3)_2AlCH_2I$ which represents a model system for aluminum carbenoids promoted cyclopropanation reaction. Two reaction channels are investigated *i.e.*, methylene transfer and carbometalation. The energy barrier of the former (9.6-10.9 kcal/mol) is significantly smaller than that of the later (24.0-29.8 kcal/mol). The methylene transfer process is favored and the competition of insertion is negligible, which is in good agreement with result found experimentally. We have also demonstrated that the methylene transfer transition state corresponds to a three-centered structure similar to that originally suggested by Simmones[14a] and Moser[33]. The lowest barrier for the methylene transfer process is mainly due to the following: an increase of the small structure changes that occur in the $(CH_3)_2AlCH_2I$ carbenoid as the reactions go from the reactants to the transition states. Our result is consistent with and can help explain that Al carbenoid can undergo efficient cyclopropanation reactions with olefins at -40 °C.

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