J. Org. Chem. **2002,** *67,* 3841−3846 **3841**

Theoretical Studies on Cycloaddition Reactions between 2-Azoniaallene Cations and Olefins

Si-Ya Yang,[†,‡] Cheng-Ke Sun,[†,‡] and De-Cai Fang*[,†]

Department of Chemistry, Beijing Normal University, Beijing 100875, China, and Department of Chemistry, Qujing Normal College, Qujing 655000, China

dcfang@bnu.edu.cn

Received February 1, 2002

The mechanisms of cycloaddition reactions between 2-azoniaallene cations and olefins have been explored at the B3LYP/6-31G* level. It is found that the positive charge in 2-azoniaallene makes the reaction more complicated. For the reactions between olefins with Cl groups or CH_3 groups and 2-azoniaallene, the typical carboniums have been located along the reaction path. In addition, for the reactions between 1,1-dimethylethene and 1,3-dichrolo-2-azoniaallene, different paths and products have been rationalized and verified.

Introduction

The cycloaddition reactions between cumulenes and double bond compounds are very important routes for the synthesis of cycloadducts. In the past couple decades, [2 + 2] cycloaddition reactions of ketenes, ketenimines, allenes, and keteniminium cations have been extensively studied theoretically[1−4] and experimentally.[5,6] In our previous paper,[4] it was realized that the mechanism of cycloaddition reaction involving keteniminium cation is quite complicated, and thus it presents a great challenge for theoretical chemists. The 2-azoniaallene cation, a class of heterocumulenes, greatly interested chemists since the first 2-azoniaallene salts were prepared in 1969 by Samuel and Wade.[7] During the past couple of decades, Würthwein et al. developed a series of experimental and theoretical investigation for the synthesis,[8] structure property,[9−11] and chemical reactivity[12−15] of 2-azoniaallene salts. However, in comparison with the widespread use of keteniminium cations (or salts) in organic synthesis,[6] the cycloaddition reactions of 2-azoniaallene salts have received relatively little attention.[16−18] In 1994, the reaction of 1,3-dichloro-2-azoniaallene salt with olefins was first reported by Hitzler et al.[17] In 1995, [2 + 2] and [2 + 4] cycloaddition reactions of 2-azoniaallene salts with isocyanates were studied by Ismail et al.[18]

The theoretical study on the titled reaction mechanism, to our knowledge, is still untouched. Therefore, the mechanism studied for $H_2C{=}N^+{=}CH_2 + H_2C{=}CH_2$ (**1a** + **2a**) is presented here. The substituent and solvent effects of the titled reactions have also been investigated. The reactions considered are shown in Scheme 1.

---

* To whom correspondence should be addressed. Fax: (+86)10-62200567. Phone: (+86)10-62208508.

[†] Beijing Normal University.

[‡] Qujing Normal College.

(1) See, for example: (a) Sordo, J. A.; González, J.; Sordo, T. L. *J. Am. Chem. Soc.* **1992**, *114*, 6249. (b) Assfeld, X.; Sordo, J. A.; González, J.; Ruiz-López, M. F.; Sordo, T. L. *J. Mol. Struct.: THEOCHEM* **1993**, *287*, 19. (c) López, R.; Sordo, T. L.; Sordo, J. A.; González, J. *J. Org. Chem.* **1993**, *58*, 7036. (d) López, R.; Suárez, D.; Ruiz-LÓpez, M. F.; Sordo, J. A.; Sordo, T. L. *J. Chem. Soc., Chem. Commun.* **1995**, 1677. (e) López, R.; Ruiz-López, M. F.; Rindaldi, D.; Sordo, J. A.; Sordo, T. L. *J. Phys. Chem.* **1996**, *100*, 10600.

(2) See, for example: (a) Cossio, F. P.; Ugalde, J. M.; López, X.; Lecea, B.; Palomo, C. *J. Am. Chem. Soc.* **1993**, *115*, 995. (b) Cossio, F. P.; Arrieta, A.; Lecea, B.; Ugalde, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 2085. (c) Lecea, B.; Arrasta, I.; Arrieta, A.; Roa, G.; López, X.; Arriortua, M. I.; Ugalde, J. M.; Cossio, F. P. *J. Org. Chem.* **1996**, *61*, 3070. (d) Fang, D.-C.; Fu, X.-Y. *Int. J. Quantum Chem.* **1994**, *50*, 93. (f) Fang, D.-C.; Fu, X.-Y. *Int. J. Quantum Chem.* **1996**, *57*, 1107.

(3) See, for example: (a) Fabian, W. M. F.; Janoschek, R. *J. Am. Chem. Soc.* **1997**, *119*, 3253. (b) Fang, D.-C.; Fu, X.-Y. *Chem. Phys. Lett.* **1996**, *259*, 265. (c) Fabian, W. M. F.; Kollenz, G. *J. Org. Chem.* **1997**, *62*, 8497. (d) Alajarin, M.; Vidal, A.; Tovar, F.; Arrieta, A.; Lecea, B.; Cossio, F. P. *Chem.−Eur. J.* **1999**, *5*, 1106. (e) Wu, P.; He, S. R. *J. Beijing Norm. Univ., Nat. Sci.* **1999**, *35*, 90. (f) Fang, D.-C.; Li, H.-M. *J. Mol. Struct.* **2000**, *528*, 111. (g) Fabian, W. M. F.; Kollenz, G. *J. Phys. Chem.* **1994**, *7*, 1. (h) Arrieta, A.; Cossio, F. P. *J. Org. Chem.* **1999**, *64*, 1831.

(4) Ding, W.-J., Fang, D.-C. *J. Org. Chem.* **2001**, *66*, 6673.

(5) See, for example: (a) Bellus, D.; Ernst, B. *Angew. Chem.* **1988**, *100*, 820. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 797. (b) Snider, B. B. *Chem. Rev.* **1988**, *88*, 793. (c) Georg, G. I.; Ravikumar, V. T. In *The Organic Chemistry of β-Lactams*; Georg, G. I., Ed.; VCH: New York, 1993.

(6) For some keteniminium cation systems, see: (a) Ghosez, L. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 852. (b) Falmagne, J.-B.; Escudero, J.; Taleb-Sahraoui, S.; Ghosez, L. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 879. (c) Genicot, C.; Gobeaux, B.; Ghosez, L. *Tetrahedron Lett.* **1991**, *32*, 3827. (d) 23) Irie, O.; Shishido, K. *Chem. Lett.* **1995**, 53. (e) Barbaro, G.; Battaglia, A.; Btuno, C.; Giorgianni, P.; Guerrini, A. *J. Org. Chem.* **1996**, *61*, 8480. (f) Shim, P.-J.; Kim, H.-D. *Tetrahedron Lett.* **1998**, *39*, 9517. (g) Adam, J.-M.; Ghosez, L.; Houk, K. N. *Angew. Chem., Int. Ed.* **1999**, *38*, 2728.

(7) Samuel, B.; Wade, K. *J. Chem. Soc. A* **1969**, 1742−1745.

(8) (a) Barton, D. H. R.; Bracho, R. D.; Gunatilaka, A. A. L.; Widdowson, D. A. *J. Chem. Soc, Perkin Trans. 1* **1975**, 579. (b) Reetz, M. T.; Stephan, W.; Maier, W. F. *Synth. Commun.* **1980**, *10*, 867. (c) Würthwein, E.-U.; Wilhelm, E.; Seitz, B. *Tetrahedron Lett.* **1983**, *24*, 581. (d) Al-Talib, M.; Jochims, J. C. *Chem. Ber.* **1984**, *117*, 3222. (e) Frey, H.; Mehlhorn, A.; Rühlmann, K. *Synthesis* **1987**, 2945. (f) Hamed, A.; Jochims, J. C.; Przybylski, M. *Synthesis* **1989**, 400. (g) Moustafa, A. H.; Wirschun, W.; Freyhardt, C. C.; Jochims, J. C. *J. Prakt. Chem./Chem.-Ztg.* **1997**, *339*, 615.

(9) Al-Talib, M.; Jibril, I.; Würthwein, E.-U.; Jochims, J. C.; Huttner, G. *Chem. Ber.* **1984**, *117*, 3365.

(10) Wüthwein, E.-U. *J. Org. Chem.* **1984**, *49*, 2972.

(11) Böttger, G.; Geisler, A.; Fröhlich, E.; Würthwein, E.-U. *J. Org. Chem.* **1997**, *62*, 6408.

(12) Al-Talib, M.; Jibril, I.; Jochims, J. C.; Huttner, G. *Tetrahedron* **1985**, *3*, 527 and reference therein.

(13) Albrecht, E.; Mattay, J.; Steenken, S. *J. Am. Chem. Soc.* **1997**, *48*, 11608.

(14) Weidner, R.; Würthwein E.-U. *Chem. Ber.* **1989**, *122*, 1095.

(15) Kupfer, R.; Meier, S.; Würthwein, E.-U. *Chem. Ber.* **1992**, *125*, 2487.

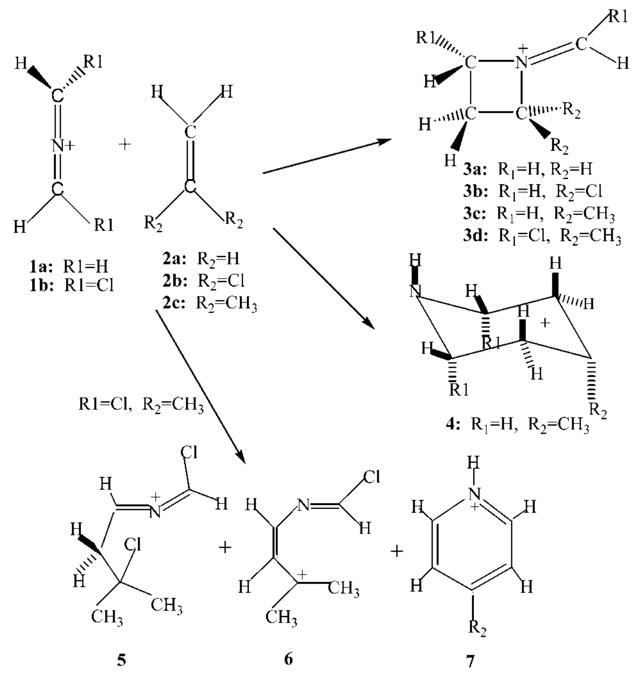
(16) Geisler, A.; Würthwein, E.-U. *Tetrahedron Lett.* **1994**, *35*, 77.

(17) Hitzler, M. G.; Freyhardt, C. C.; Jochims, J. C. *Synthesis* **1994**, 509.

(18) Ismail, A.-H.; Hamed, A.; Hitzler, M. G.; Troll, C.; Jochims, J. C. *Synthesis* **1995**, 820.

10.1021/jo025575o CCC: $22.00

Scheme 1. Reaction System



Methods of Calculation

All the calculations included in this work have been performed with the Gaussian 98w program.[19] The geometries of the reactants, products, intermediates, and transition states have been fully optimized at the B3LYP/6-31G* level. All stationary points have been further confirmed by the computations of force constants analytically and characterized by the number of imaginary vibrational frequencies. Bader's theory of AIM[20,21] has been used to study the bonding character and charge distribution for stationary points in the reaction **1a** + **2a**.

The AIM98PC package,[22] a PC version of AIMPAC,[23] has been employed for the electron density topological analysis using the electron densities obtained in the B3LYP/6-31G* calculation.

Results and Discussion

The Model Reaction: $H_2C{=}N^+{=}CH_2 + H_2C{=}CH_2$. The geometries of the reactants (**1a** and **2a**), intermediate (**INT1**), transition states (**TS1** and **TS1a**), and product (**3a**) are optimized at the B3LYP/6-31G* level. The numbering systems of above the stationary points are shown in Scheme 2, and the optimized parameters are listed in Table S1 of the Supporting Information.

Scheme 2

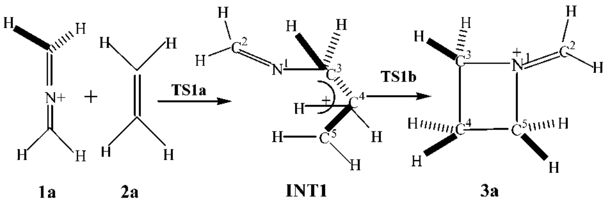
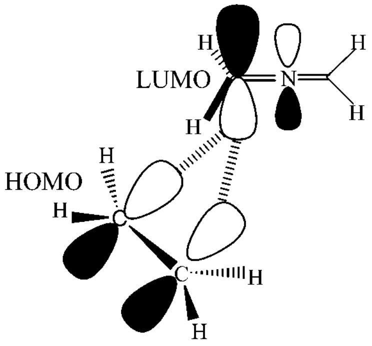


Chart 1



The structural parameters reveal that one reactant, 2-azoniaallene cation (**1a**), is a linear molecular with its skeleton atoms on the same plane. Two methylene planes are perpendicular to each other. The obtained bond length and angle are in reasonable agreement with those Böttger et al.[7] reported in 1997 at the B3LYP/6-31+G* level. In the product (see Scheme 2 and Table S1), the ring atoms and the methylene group attached to N_1 are on the same plane, while the hydrogen atoms are distributed zygomorphically.

When the reactant molecules **1a** and **2a** approach, the electron-rich ethylene first attacks terminal C_3 in 2-azoniaallene ion, which is electron deficient, forming an intermediate (**INT1**) via **TS1**. It can be seen, from Table S1 of the Supporting Information, that **TS1** is a sort of three-membered ring structure (the distances of C_3-C_4 and C_3-C_5 to be formed are 1.87 and 1.87 Å, respectively). In **TS1**, one positive charge on the central nitrogen atom (in the reactant) is mainly transferred to C_3, C_4, and C_5 to form a carbonium (the net charges on C_3, C_4, and C_5 of each CH_2 group are 0.300, 0.325, and 0.325, respectively). The bond length of C_3-N_1 changed to 1.42 Å in **TS1** from 1.25 Å in reactant **1a**. **INT1** is close to **TS1** in geometric parameters (see Table S1). The bond lengths C_3-C_4 and C_3-C_5 in **INT1** are changed to 1.81 and 1.90 Å, and the dihedral angle $C_4-C_3-N_1-C_2$ is reduced to 125.0° in **INT1** from 157.2° in **TS1**. Analyzing the frontier orbital interaction, only the interaction between the LUMO in **1a** and HOMO in **2a** could favor the formation of **TS1** and **INT1** (see Chart 1), in which one Pz orbital of C_3 overlaps both Pz orbitals in ethylene. Because **INT1** is unstable (8.6 kcal/mol higher than **1a** + **2a**), it is very easy to form a four-membered product, **3a**, via **TS1a** (only 4.5 kcal/mol as shown in Figure 1). **TS1a** has a gauche conformation (dihedral angle $C_5-C_4-C_3-N_1 = 57.4°$; see Table S1). In **TS1a**, the C_4-C_3 bond length is 1.71 Å, but the distance of C5 to N1 is still 2.64 Å.

Two transition states and one intermediate have been located and validated by our IRC calculation.[24] The **TS1**

---

(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(20) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 983.

(21) Bader, R. F. W. *Atoms in molecules, a Quantum Theory*; Clarendon Press: Oxford, 1990.

(22) Fang, D.-C.; Tang, T.-H. *AIM98PC. The modified PC version of AIMPAC*; Beijing Normal University, Beijing, 1998.

(23) Available from Professor R. F. W. Bader's laboratory, McMaster University, Hamilton, Ontario, Canada L8S 4M1.

(24) (a) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154. (b) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

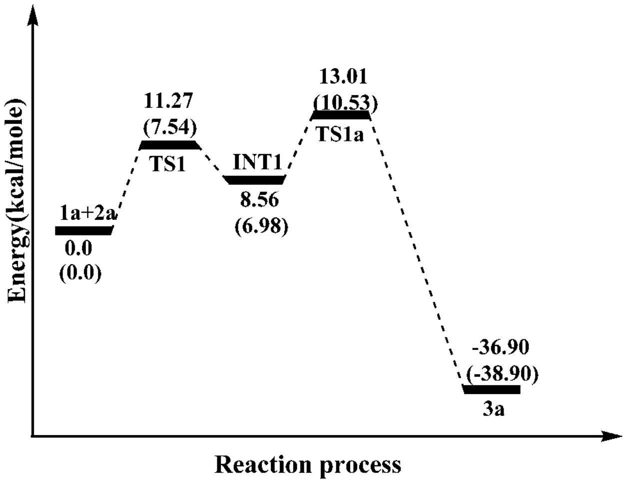
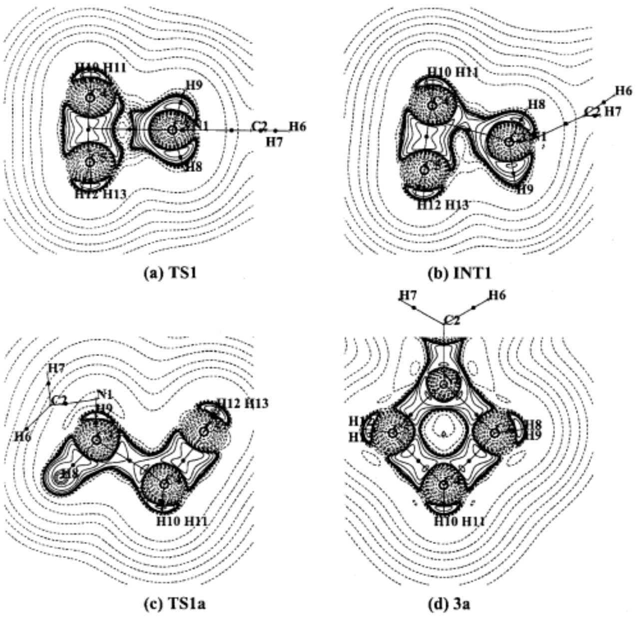


Figure 1. Schematic potential energy surface for the reaction **1a** + **2a** (the data in parentheses are for CH_2Cl_2 solvent; all energies are with zero-point energy correction).



(a) TS1 (b) INT1

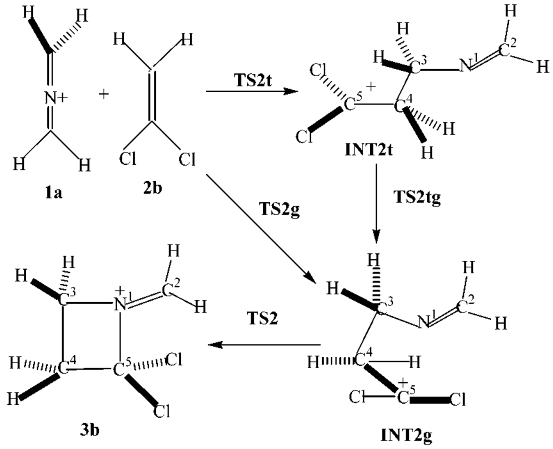
(c) TS1a (d) 3a

Figure 2. Molecular graphs and Laplacian distribution of the stationary points in the model reaction. In these figures, dashed lines denote positive values of $\nabla^2\rho_b$ and full lines stand for negative values of $\nabla^2\rho_b$. Bonded charge concentrations are indicated by solid squares. In addition, bond paths (heavy solid lines), bond critical points (solid circle), and ring critical points (triangles) are shown for $\rho(r)$.

and **TS1a** are further confirmed by the only one imaginary frequency (−90.96i and −143i, respectively). The relative energies for the stationary points are given in Figure 1, which shows that the barrier of the first step (from **1a** + **2a** to **INT1**) is 11.3 kcal/mol and that of the second step (from **INT1** to product) is only 4.5 kcal/mol (with zero-point energy correction).

For the reaction **1a** + **2a**, electron density analysis has been carried out. Laplacian distributions of the stationary points are illustrated in Figure 2, from which one can realize that there is a critical point between C_3 and the bond critical point of the C=C bond in **TS1**, which is in agreement with the orbital interaction shown in Chart 1. However, the bonding characters of **INT1** and **TS1a** are quite different from that of **TS1**, because the bond critical point from C_3 to the middle point of C_4-C_5 in **TS1** is shifted to that of C_3 to C_4. The electron densities ρ_b for the C_3–C_4 bonds are 0.125 (**INT1**), 0.151 (**TS1a**), and 0.240 (**3a**), respectively, but a second bond (N_1-C_5) is mainly formed after **TS1a**.

Scheme 3



The solvent effect of the model reaction has been investigated with the PCM model[25] and CH_2Cl_2 as the solvent, which had been used in experimental investigations. It is found that the structure of all stationary points in the solution phase is in excellent agreement with those in the gas phase (see Table S1 of the Supporting Information). The mechanism does not change as the CH_2Cl_2 solvent is introduced, but the barriers for the first and second steps are lower than those in the gas phase (see Figure 1). This indicates that the reaction can take place in solution more easily.

Substituent Effects on the Carbon in Ethene. In this section, the substituent effect on the carbon in ethylene (see Scheme 1) has been discussed. In our studies, only two Cl or CH_3 groups are attached to one carbon atom in ethylene for convenience, in which when the substituted ethylene adds to 2-azoniaallene ion, it could form the ortho- or para-product. Only the preferential ortho-product is considered here.

First we considered the Cl-substituted case, i.e., the **1a** + **2b** reaction. The numbering systems for all possible stationary points are shown in Scheme 3, and the optimized parameters are listed in Table S2. The 1,1-dichloroethene can approach 2-azoniaallene ion by a trans or gauche mode. Scheme 3 shows that the **1a** + **2b** reaction proceeding in the gauche mode undergoes a two-step process to form **3b** via two transition states (**TS2g** and **TS2**) and an intermediate (**INT2g**). However, in the trans mode, the reaction first forms **INT2t** via **TS2t**, then the rotation of **INT2t** along the C_3-C_4 bond forms **INT2g** via **TS2tg**, and the last step is the same as the gauche one. Compared with the reaction **1a** + **2a**, the mechanism for the present reaction is somewhat different. From the Mulliken populations of **INT2t** and **INT2g**, one can realize that most of the positive charge on N in 2-azo-

---

(25) (a) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117. (b) Miertus, S.; Tomasi, J. *Chem. Phys.* **1982**, *65*, 239. (c) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Chem. Phys. Lett.* **1996**, *255*, 32. (d) Cances, M. T.; Mennucci, V.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032. (e) Barone, V.; cossi, M.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3210. (f) Cossi, M.; Barone, V.; Mennucci, B.; Tomasi, J. *Chem. Phys. Lett.* **1998**, *286*, 253. (g) Barone, V.; Cossi, M.; Tomasi, J. *J. Comput. Chem.* **1998**, *19*, 404. (h) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *109*, 249. (i) Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1998**, *109*, 2.

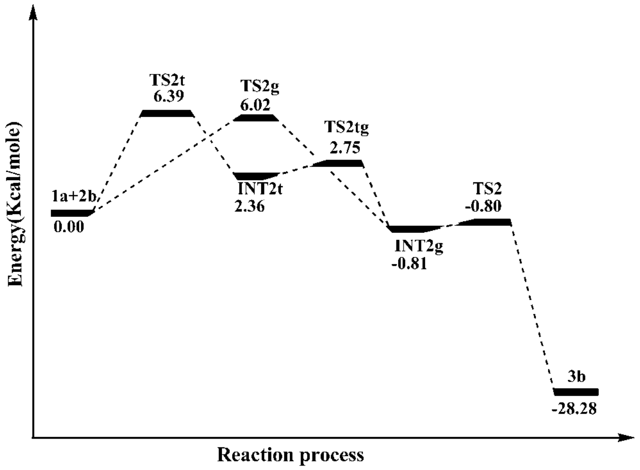


Figure 3. Schematic potential energy surface for the reaction **1a** + **2b** (with ZPE correction).

niaallene is transferred to the $C(Cl)_2$ group in such intermediates; i.e., the **INT2t** and **INT2g** are typical carboniums due to Cl atoms making the carbonium stable. The schematic description of the possible energy surface for this reaction is shown in Figure 3, from which it can be seen that the **INT2g** is more stable than **INT2t**. Because the bond lengths of C_3-C_4 in **INT2t** (1.60 Å) and **INT2g** (1.61 Å) are longer than the normal C−C bond length, the energy barrier from **INT2t** to **INT2g** is very low (0.39 kcal/mol), and thus the trans and gauche modes are in competition.

For the reaction between 1,1-dimethylethene and 2-azoniaallene (**1a** + **2c**), the mechanism is different from that of **1a** + **2a** or **1a** + **2b**. Two possible reaction products (**3c** and **4**) have been suggested and verified, as shown in Scheme 4. The geometries of all possible stationary points, as listed in Table S3, have been located, along with the numbering systems shown in Scheme 4. The approach of **1a** and **2c** also has two modes (trans and gauche) as in the reaction **1a** + **2b**, but the energy surface is quite different from the previous one. Two ion−molecule complexes, denoted **COM3t** and **COM3g** in Scheme 4, have been located, in which **COM3t** is a trans complex ($C_5-C_4-C_3-N_1$ = 178.8°) and **COM3g** is a gauche one ($C_5-C_4-C_3-N_1$ = −79.6°). The bond length of C_4-C_3 in **COM3t** is 2.45 Å, which is 0.09 Å shorter than that of **COM3g**, but **COM3t** is 0.7 kcal/mol more stable than **COM3g**. As reactant molecules approach further, the complexes could be transformed to intermediates **INT3g** and **INT3t** via **TS3g** and **TS3t**; the rotation of **INT3t** along the C_3-C_4 bond forms **INT3g** via **TS3tg**. The bond length of C_4-C_3 in **INT3t** and **INT3g** is decreased to 1.60 Å, almost a single bond. After **INT3g**, there are two ways to go. One is to form **3c**, the same as the reaction **1a** + **2a** or **1a** + **2b**; the other is to form a six-membered ring product (**4**). As for the formation of product **4**, the step from **INT3g** to **INT3** is a hydrogen-transfer process, i.e., ene-reaction process (H_{15} from C_{12} to N_1 via **TS3)**, in which the distances of N_1-H_{15} and $C_{12}-H_{15}$ (see Table S3) are 2.05 and 1.14 Å (**INT3g**), 1.89 and 1.16 Å (**TS3**), and 1.03 and 2.44 Å (**INT3**), respectively. In **INT3**, the positive charge is shifted back to the original 2-azoniaallene portion from the $C(CH_3)_2$ group in **INT3g** or **INT3t**, and a $C_{12}-C_5$ double bond is formed. The cyclization reaction of **INT3** proceeds via **TS3b**, which breaks the double bonds C_{12}-C_5 and N_1-C_2 and finally leads to the formation of the product **4**. The product **4** is a carbonium with ring structure and is a more stable chair configuration (see Scheme 4). The mechanism of reaction of product **4** is analogous with the experimental result by Hitzler et al.[17] One can realize from Figure 4 that all the possible complexes, intermediates, and transition states are well below the reactant asymptote. **INT3g** is 6 kcal/mol lower than **INT3t**, but the energy barrier for the transformation from **INT3t** to **INT3g** is only 0.9 kcal/mol, which means that these two reaction paths are comparable. In addition, the energy barrier of the H-shift process (from **INT3g** to **INT3**) is about 5 kcal/mol, but the energy barrier of electrocyclization requires only 0.5 kcal/mol,

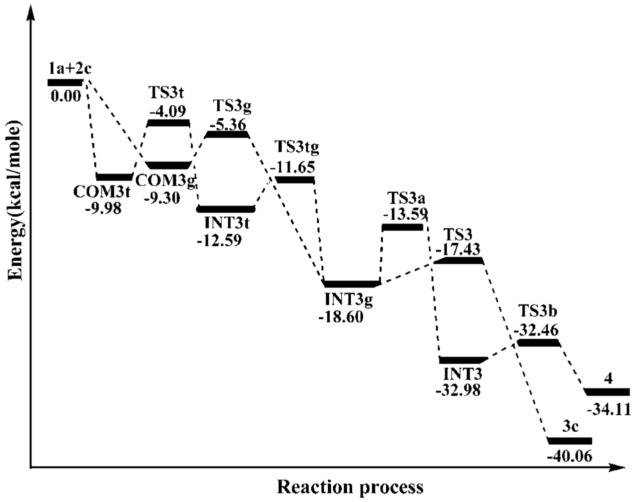
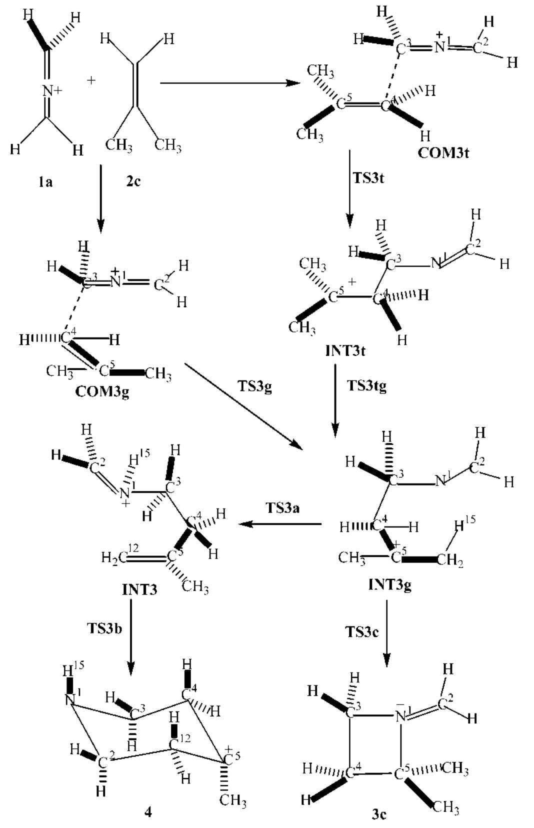
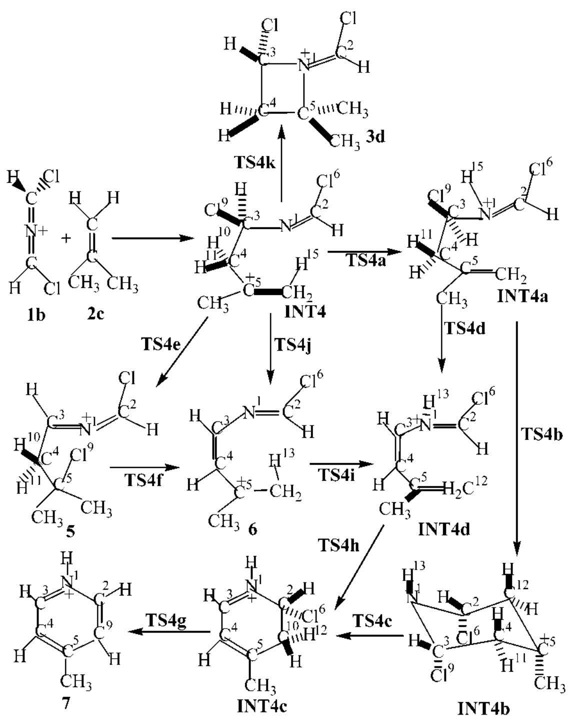


Figure 4. Schematic description of the potential energy surface for the reaction **1a** + **2c** (with ZPE at B3LYP/6-31G* level).

Scheme 4



Scheme 5



which indicates that the ene-reaction step is the rate-controlling one and the electrocyclization process finishes with extreme ease. From the viewpoint of kinetics and thermodynamics, the formation of product **3c** is slightly more favorable than that of product **4**.

It should be kept in mind that the hydrogen atom in one CH_3 group, attached to the terminal carbon of the ethylene portion, will be transferred from C to N (ene-reaction process), which makes the difference between Cl-substituted and CH_3-substituted reactions. In addition, because the electron-releasing CH_3 group has both notable donation and a hyperconjugation effect, it will make the ethylene portion richer in electrons and disperse the positive charge on C_5 in the intermediates. However, the Cl group, despite its hyperconjugation effect, is an electron-attracting one, which reduces the electron density of the C−C double bond and disfavors the reaction.

Substituent Effects on Carbon in 2-Azoniaallene Cation and Olefin. According to the experimental suggestion, by Hitzler et al.,[17] in the reaction of 1,3-dichloro-2-azoniaallene salts with olefins, the reaction mechanism of 1,3-dichloro-2-azoniaallene cation with 1,1-dimethylmethene (see Scheme 1, **1b** + **2c**) has been investigated to elucidate the substituent effects. In view of the reaction probabilities, the reaction pathways are outlined in Scheme 5. Compared with the reaction **1a** + **2c**, the first step of the reaction **1b** + **2c** is to form a more stable intermediate (**INT4**) without a barrier. After **INT4**, there are four ways to go: (1) **INT4** → **INT4a** → **INT4b** → **INT4c** → **7**, (2) **INT4** → **5** → **6** → **INT4d** → **INT4c** → **7**, (3) **INT4** → **6** → **INT4d** → **INT4c** → **7**, (4) **INT4** → **4d**.

All the possible transition states and intermediates have been located at the B3LYP/6-31G* level, whose geometries and energies are all tabulated in Tables S4 and S5, respectively. For path 1, first step (**INT4** → **INT4a)** is a hydrogen-transfer process (H_{15} from C_{12} to N_1) via a six-membered ring (**TS4a**) ($H_{15}-C_{12} = 1.32$ Å, $H_{15}-N_1 = 1.48$ Å), and a chair six-membered ring intermediate (**INT4b)** is formed via **TS4b** through a cyclization reaction. The above process is similar to the reaction **1a** + **2c**. At the last two steps (from **INT4b** to **INT4c** via **TS4c** and from **INT4c** to **7** via **TS4g**), one HCl molecule is eliminated each. The elimination of the first HCl molecule is quite easy (the energy barrier is 8.4 kcal/mol in Figure 5), but to remove the second HCl needs about a 30.0 kcal/mol energy barrier, the highest barrier in this path. Because the last product, pyridinium (**7**) + HCl, is 23.7 kcal/mol lower than **INT4c**, the reaction process is still possible despite a higher energy barrier. In this path, there is also a side chain reaction, which is the elimination of HCl from **INT4a** to form **INT4d**. It needs to overcome the energy barrier of 53.4 kcal/mol, so such a path is almost impossible. For path 2, the first step (**INT4** → **5**) is a Cl-transfer process from C_3 to C_5 via a four-membered ring (**TS4e) (**$Cl_9-C_3 = 1.97$ Å, $Cl_9-C_5 = 2.30$ Å), and it is quite easy to form the product **5** (with 7.8 kcal/mol of energy barrier), which is quite stable due to a subsequently high barrier (36.6 kcal/mol) for the elimination of HCl molecule. Therefore, our calculation result is in good agreement with the experimental fact that product **5**, a new type of 2-azoniaallene cation, was obtained; i.e., the reaction along this path might stop here. For path 3, the first step (**INT4** → **6)** is to remove one HCl molecule and to form another product (**6**), a 1,1-dimethyl-4-azapentadiene cation, which requires a 26.5 kcal/mol energy barrier, about 10 kcal/mol lower than that from **5** to **6**. The product **6** was also isolated by Hitzler et al.,[17] which is in agreement with our calculation. When the reaction continues (**6** → **INT4d**, using reflux in the experiment[17]), an ene reaction could take place via **TS4i** ($H_{13}-N_1 = 1.35$ Å, $C_{10}-H_{13} = 1.39$ Å), which is 12.3 kcal/mol higher than the ene reaction (**INT4** → **INT4a)** in path 1; i.e., H-shift on carbonium **6** is more difficult than that on carbonium **INT4**. After **INT4d** a stable six-membered ring (**INT4c)** is produced by an electrocyclization. The last step is the same as path 1. Path 4 is a simple process with the production of **3d** via **TS4k**, which has only a 1.3 kcal/

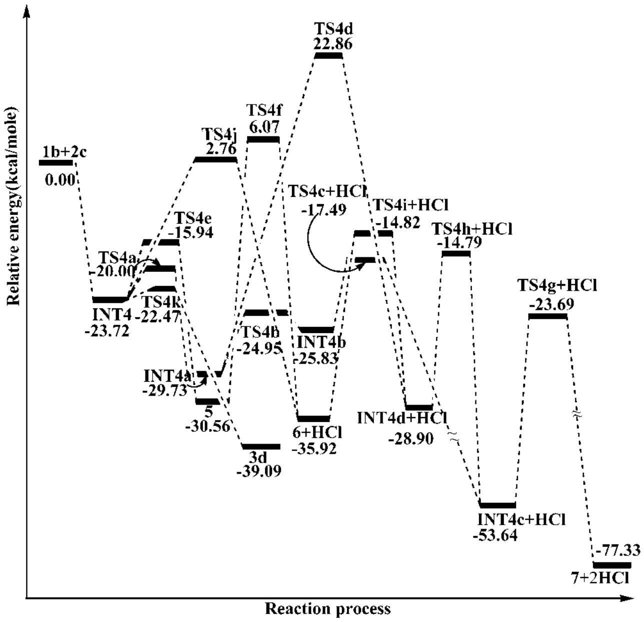


Figure 5. Schematic potential energy profile for the reaction **1b** + **2c** (with ZPE correction).

mol energy barrier. Hitzler et al.[17] did not observe a four-membered ring product in their experiments, which is due to the fact that phenyl or substituted phenyl groups on 1,3-dichloro-2-azoniaallene will bring a great steric hindrance and hinder the approach of C_5 to N_1 (see Scheme 5).

While **5** and **6** could be isolated, intermediates **INT4d** and **INT4c** are only plausible as suggested by Hitzler et al. In our calculation (see Figure 5), the formation of **INT4d** is not favorable compared to the formation of **INT4c**. **INT4c** will lead to the more stable product pyridinium (**7**). However, the **INT4b**, similar to product **4** in the reaction **1a** + **2c**, is not stable in the present reaction. Although some model reactions are employed in our present calculations, we believe that our results rationalize all possible reaction products.

Summary

The reaction **1a** + **2a**, namely, the model reaction, is the [2 + 2] cycloaddition reaction of an unsynchronous mechanism. For the reaction of 1,1-dichloroethene with 2-azoniaallene, a four-membered ring product is formed via a carbonium intermediate.

When the reaction of 1,1-dimethylethene with 2-azoniaallene takes place, two reaction products (**3c** and **4**) have been verified; the reaction path for product **3c** is slightly more favorable than that for product **4**. Moreover, the reaction between electron-deficient 2-azoniaallene and olefin with electron-releasing subsituents is preferential.

For the system of 1,3-dichloro-2-azoniaallene and 1,1-dimethylethene, the reaction paths are quite complicated. Four possible products are rationalized in the present calculations.

Acknowledgment. This project was supported by the National Natural Science Foundation of China (Grant No. 20073006). Y.S.-Y. and S.C.-K. also thank the Natural Science Foundation of Qujing Normal College (Grant No. 0113908).

Supporting Information Available: **Z** matrixes, energetics (total energies and ZPE) of all the stationary points (Tables S1–S5), along with the numbering systems (Figures S1–S4). This material is available free of charge via the Internet at http://pubs.acs.org.

JO025575O