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The Ionic Diels-Alder Reaction of the Allyl Cation and Butadiene: Theoretical Investigation of the Mechanism[#]

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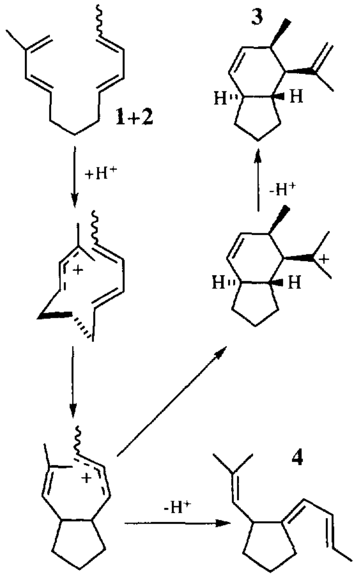
Abstract. The mechanism of the reaction of butadiene with allyl cation was explored using ab initio RHF and MP2 calculations and the 6-31G* basis set. Only stepwise mechanisms are found.

The Diels-Alder reaction is normally a concerted $[_{\pi}4+_{\pi}2]$ cycloaddition leading to six- membered rings. The reaction has been widely studied,[1-2] and the mechanistic aspects of this reaction have been much discussed and debated.[3] The possibility of 6 π-electron cycloadditions with allyl cations to form seven-membered rings (a (4+3) cycloaddition of the $_{\pi}4+_{\pi}2$ variety) was predicted some years ago by Woodward and Hoffmann.[4] Examples of this process have been observed,[2] but five- and six-membered rings and products of electrophilic substitution are also obtained.[5] It is uncertain whether the additions of butadiene to allyl cations are concerted reactions or whether they are stepwise and take place through intermediates.

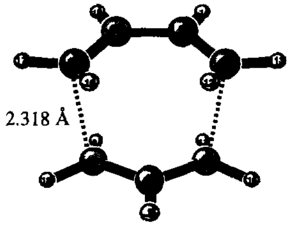


The reaction has been increasingly used in synthesis.[2] For example, it provides a straightforward route to the sesquiterpene artemisinin.[6]

A comprehensive mechanistic study of the reaction of allyl cations with 1,3-dienes was carried out by Hoffmann.[4] Gassman investigated extensively the scope of the "ionic Diels-Alder reaction"[7] and reported a mechanistic study on this cycloaddition.[8] A stepwise mechanism was proposed for the reaction of **1** and **2**; and treatment of either gave **3** (45%) and **4** (39%).[9] Gassman noted; "the allyl cation represents one extreme in the spectrum of polarities for a dienophile, and in consequence it seems reasonable that in that case the Diels-Alder reaction has reached the point where it is so asynchronous as to be stepwise".[7] We report a theoretical study of the potential energy surface for the reaction between butadiene and the allyl cation, using ab initio molecular orbital calculations[10] at different levels of theory.

[#] Dedicated to Paul Gassman, 1936-1993, who proposed and inspired this research.

An exploration of the potential energy surface at the RHF/6-31G* level was undertaken. Initially we restricted the geometry to C_S symmetry.[11] A minimum for an ion molecule complex was located at R=2.620 Å. This lies 14.4 kcal/mol below the reactants. A frequency analysis gave one imaginary frequency corresponding to reduction of C_S symmetry.



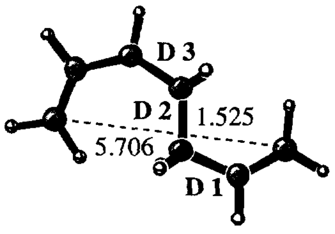
SP 1

A stationary point on the theoretical potential energy surface was located along the C_S reaction coordinate (R), corresponding to a bond forming distance of 2.318 Å (**SP 1**). This is a second order saddle point, since a vibrational frequency analysis gave two imaginary values (321i and 220i cm^{-1}) corresponding to the reaction coordinate and a second coordinate along which the symmetry is broken, respectively.

Further exploration of the theoretical potential energy surface led to the location of an energy minimum (**I 1**), where R1=1.525 Å and R2=5.706 Å. The energetics of all these processes are summarized in Table I.

Rotation about the dihedral angle **D1**=C1-C2-C3-C4 gave **TS 1**, with R1=1.530 Å and R2=5.654 Å. This transition structure is 0.9 kcal/mol less stable than **I 1**.

Further rotation around **D1**, **D2** and **D3**, gave the transition structures and intermediates shown below. The energetics and geometrical features of these structures are shown in Table I. These may be considered as intermediates and transition states involved in conformational changes of **I 1**, or in cyclization (**TS 3**).



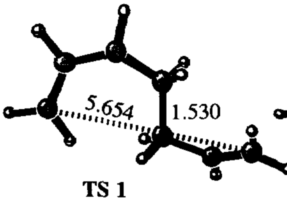
I 1

Table I. Calculated energies* of the transition structures and intermediates with respect to reactants (kcal/mol). Reaction coordinate values (Å) and dihedral angles (degrees) are also given.

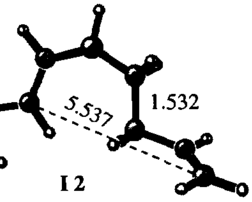
Structure	RHF/6-31G*	MP2/6-31G*// RHF/6-31G*	R1	R2	D 1	D 2	D 3
SP 1	-13.8	-43.3	2.318	2.318	89.4	-82.9	77.1
I 1	-30.6	-38.3	1.525	5.706	0.0	180.0	0.0
TS 1	-29.7	-37.5	1.530	5.654	46.3	176.6	3.3
I 2	-32.2	-39.6	1.532	5.537	115.0	178.5	0.5
I 3	-36.4	-43.3	1.549	5.084	116.8	-59.8	133.2
TS 2	-36.2	-43.9	1.566	4.311	116.9	-73.2	109.3
I 4	-36.4	-45.8	1.579	3.634	113.1	-82.8	92.3
TS 3	-34.3	-53.4	1.580	2.519	103.2	-76.2	65.9
P 1	-44.5	-61.1	1.603	1.603		-72.0	
P 2	-41.4	-53.2					
P 3	-61.5	-73.4					

Total energies of butadiene plus allyl cation are -271.10667 (RHF/6-31G) and -271.95842 (MP2/6-31G*//RHF/6-31G*)

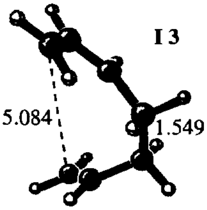
However, MP2/6-31G* single point calculations on the RHF/6-31G* optimized geometries (Table I), indicate that only intermediate **I 1** (with an energy of -38.3 kcal/mol) and transition structure **TS 1** (whose energy is -37.5 kcal/mol), are likely to be true stationary points along the potential energy surface for this reaction. The MP2 results predict that from **TS 1** to product is all energetically downhill. Only the small rotational barrier separates the intermediates from highly exothermic cyclization.



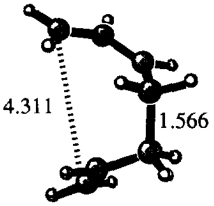
TS 1



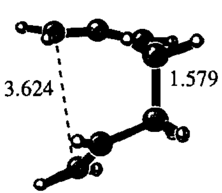
I 2



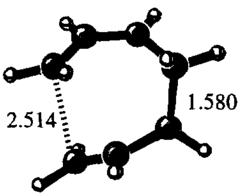
I 3



TS 2

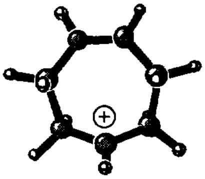


I 4

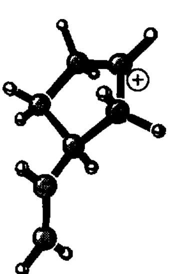


TS 3

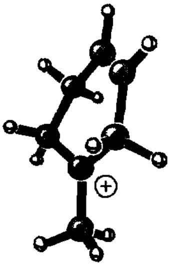
Two possible products for the cycloaddition reaction between butadiene and the allyl cation were calculated, the seven-membered ring **P 1** and the higher energy five-membered ring **P 2**. The six-membered ring Diels-Alder adduct is not an energy minimum and undergoes a spontaneous hydrogen shift to give **P 3.**



P 1



P 2



P 3

As predicted by Gassman, this reaction represents an extreme of activation such that the stepwise process is now favored over the concerted. Whether substitution or solvent effects can modify this conclusion will require further investigations.[12]

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