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THE STO-3G TRANSITION STRUCTURE OF THE DIELS-ALDER REACTION

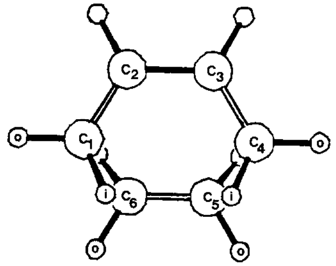
FRANK K. BROWN and K. N. HOUK*
Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260 U.S.A.

Summary: A transition structure with C_s symmetry for the Diels-Alder reaction of butadiene with ethylene has been obtained with the STO-3G basis set. Stereochemical consequences are discussed.

The Diels-Alder reaction of butadiene with ethylene has been studied by both ab initio[1,2] and a variety of semi-empirical[3-6] techniques, but the mechanistic conclusions of those studies have been contradictory and controversial.[7] Ab initio calculations with small basis sets, limited CI, and only partial geometry optimization, predict a synchronous concerted transition structure, which is lower in energy than that leading to a biradical.[1] Semi-empirical techniques using full optimizations and gradient techniques indicate that the concerted transition structure is very high in energy and has two negative eigenvalues, while a mechanism involving a stable biradical intermediate is favored.[5,6] McIver offered arguments suggesting that a C_s transition structure was impossible for this reaction,[3] while we and others proposed that deficiencies in the parameterization of semi-empirical techniques led to an unnatural preference for a diradical mechanism using these techniques.[4b,7] Although the two mechanisms probably occur with nearly equal activation energies for this prototype reaction,[8] Dewar has recently publicized the view, originally conceived by Woodward and Katz,[9] that the reaction is concerted, but with an asynchronous (unsymmetrical) transition structure.[6b,c]

The results reported here prove that a concerted synchronous transition structure exists at the ab initio minimal basis set level. While this result does not prove whether the concerted mechanism is, in reality, energetically favored over the diradical intermediate mechanism, the result does show that qualitative arguments about asynchronicity are not supported computationally. Since the biradical intermediate predicted by MNDO or MINDO/3 is now acknowledged to be an artifact of the method,[6] there is no reason to believe that the asynchronous transition sructure (actually two different ones which we are now to meld into one, presumably of intermediate geometry) is definitively proven.

The ab initio transition structure for the prototype Diels-Alder reaction between butadiene and ethylene was calculated using the STO-3G basis set[10,11] and gradient techniques[12] with optimization of all variables. An "authentic" transition structure was obtained, possessing one imaginary vibrational frequency, an activation energy of 36.0 kcal/mol (32.7 kcal/mol after zero point energy corrections) and an activation entropy of −30 e.u. The geometry is shown in Figure 1. As discussed by Komornicki et al.,[13] cycloaddition transition structures can be symmetrical, since the relative magnitudes of diagonal and off-diagonal force constants involving the two forming bonds are different from those anticipated by McIver.[3] Thus, qualitative arguments based upon two independent bond-making processes cannot be used to predict the symmetry,[3] or energetics,[6c] of processes involving strongly coupled bonding processes such as occur in aromatic transition states The details of geometry found here[14] reveal several remarkable features about this entity and facilitate understanding of various stereochemical phenomena observed for substituted examples.



BOND LENGTHS	
C1-C2	1.359
C2-C3	1.421
C5-C6	1.366
C1-C6	2.217
C1-Hi	1.079
C1-Ho	1.083
C2-H	1.083
C6-Hi	1.080
C6-Ho	1.080

BOND ANGLES	
C1-C2-C3	121.2
C1-C6-C5	109.3
C6-C1-C2	101.4
C2-C1-Hi	120.2
C2-C1-Ho	121.1
Hi-C1-Ho	114.3
C3-C2-H	117.8
C1-C2-H	119.3
C5-C6-Hi	120.3
C5-C6-Ho	120.2
Hi-C6-Ho	114.9
C1-C6-Hi	89.4
C1-C6-Ho	91.8
C6-C1-Hi	84.9
C6-C1-Ho	103.9

TORSIONAL ANGLES	
C1-C2-C3-C4	0.0
C1-C6-C5-C4	0.0
C2-C1-C6-C5	-50.9
C2-C1-C6-Hi	72.2
C2-C1-C6-Ho	-173.0
C5-C6-C1-Hi	69.8
Ho-C1-C2-H	7.7
C5-C6-C1-Ho	-176.3
Hi-C1-C2-H	-163.0
C3-C2-C1-Hi	32.1
C3-C2-C1-Ho	-172.6
C4-C3-C2-H	-165.1
C1-C6-C5-Hi	-104.1
C1-C6-C5-Ho	101.0

Figure 1. The STO-3G Diels-Alder transition structure

In Figure 2, we have summarized a number of notable features of geometry, which permit qualitative understanding of a variety of stereochemical phenomena. (1) The diene and ethylene units approach each other in a distinctly non-parallel-planes fashion (see A), as has been suggested previously.[15] However, the trajectories of bond formation (< C---C=C) are nearly tetrahedral on the alkene (109°) and somewhat smaller (101°) on butadiene.

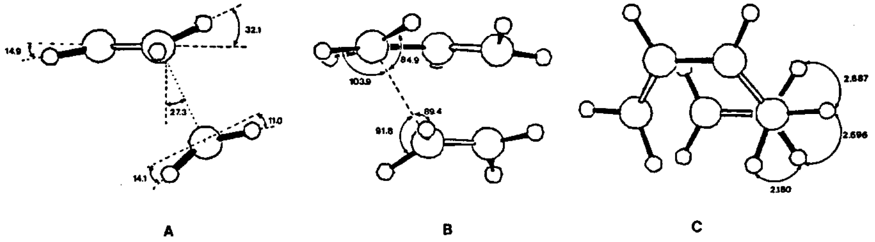


Figure 2. Three views of the STO-3G transition structure

(2) The diene terminal methylenes are pyramidal and rotated inward to facilitate overlap with the termini of ethylene (see B). (3) The hydrogens attached to C-2 and C-3 of butadiene are bent out of the C-1,C-2,C-3,C-4 plane by 14.9° (see A), even though these hydrogens are in-plane in both reactants and products! This occurs so as to maintain overlap of the p orbitals at C-1 and C-2 with the rotated terminal methylene orbitals of butadiene, as shown in B. (4) There is nearly perfect staggering about the forming CC bonds (see C), but the steric environment of *exo* and *endo* hydrogens on the ethylene group are different, as indicated by the H-H distances shown in Newman projection C. In particular, each *exo* hydrogen on the alkene is close to an "inside" hydrogen on butadiene.

The transition structure allows qualitative insights into many stereochemical phenomena found for the Diels-

Alder reaction. As noted, the exo-hydrogens on ethylene are in a more crowded region of space than the endo-hydrogens. This difference in crowding should be even larger in cyclopentadiene, for which experimental results indicate that methyl and other alkyl groups on the dienophile prefer the endo stereochemistry.[9,16] For example, cyclopentadiene and propene give a 77:23 ratio of endo and exo isomers at 200°.[16] Methyl acrylate and acrylonitrile react with lower endo selectivity, even at 50°![17] Clearly, steric effects have a pronounced influence on cyclopentadiene endo stereoselectivity.

The pyramidalization of C-2 and C-3 of butadiene is related to the bottom-stereoselectivity stereoselectivity observed in Diels-Alder cycloadditions of isodicyclopentadiene to a variety of dienophiles.[18] Side views of transition structures for these processes are illustrated in Figure 3.[19] Attack on the bottom of the diene occurs with pyramidalization at the norbornene ring in the favored endo direction,[20] while attack on the top will cause exo pyramidalization at the norbornene, a less favored process.

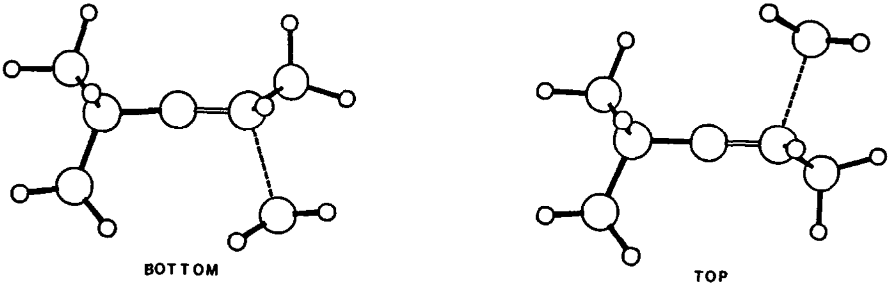


Figure 3. Transition structures for Diels-Alder attack on the bottom and top of isodicyclopentadiene

Applications to a variety of stereochemical phenomena will be forthcoming.

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(14) The geometry is different from that obtained in previous ab initio calculations. For example, computations performed before gradient techniques were available produce the following heavy-atom bond lengths. Salem (STO-3G + 3x3CI):[1] r_{12} = 1.40Å, r_{23} = 1.36Å; r_{56} = 1.40Å; r_{16} = 2.21Å. Leroy (STO-3G):[2b] r_{12} = 1.375Å, r_{23} = 1.410Å; r_{56} = 1.380Å; r_{16} = 2.240Å. Salem's calculations may give more accurate values of the listed quantities, due to inclusion of CI, but since full optimizations were not performed, other subtleties of geometry were not revealed.

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