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TRANSITION STRUCTURES FOR THE REACTION OF DIFLUOROCARBENE WITH PROPENE

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Summary: Two ab initio transition structures for the reaction of difluorocarbene with propene have been located with gradient techniques and the 3-21G basis set. The activation energy is 1.3 kcal/mol lower than for the reaction with ethylene. Two transition structures with the fluorines approaching syn or anti to the methyl group are identical in energy.

We have recently reported ab initio gradient transition structures for the reactions of difluorocarbene and dichlorocarbene with ethylene.[1] We have now studied the reaction of difluorocarbene with propene, and report how alkyl substitution on the alkene alters the activation energy and geometry of the transition structure. Of additional interest was the influence of the methyl group on the direction of approach of the carbene to the double bond, a point for which no direct experimental evidence can be obtained, since only a single product can be formed. Related MNDO studies of reactions of alkylidenecarbenes with unsymmetrical alkenes have also addressed this point.[2]

Transition structures were computed using gradient techniques[3] and the 3-21G basis set.[4] Two modes of difluorocarbene attack on propene were examined. One has the two fluorines syn to the substituted terminus while the the other has the fluorines oriented anti. In the following discussion, the syn and anti nomenclature will be used to describe the transition structures(TS). The transition structures for the CF_2-propene cycloaddition are depicted in the Figure along with the 3-21G CF_2-ethylene transition structure,[1] included here for comparison. The Figure also includes the bond lengths in the transition structures. The numbers below each structure are the activation energies according to the 3-21G calculations. The bond angles, dihedral angles, and other bond lengths are summarized in the Table.

The anti TS occurs earlier than the syn, as assessed by comparisons of the CC bond lengths for the two transition structures. The forming CC bonds in the syn TS are 0.067Å and 0.004Å shorter than those in the anti, and the olefinic CC bond in the syn TS is 0.01Å longer than that in the anti. For comparison, the CF_2-ethylene TS is intermediate between the syn and anti transition structures. This is apparent from the lengths of the olefinic CC bonds and the intermediate length of the shorter CC forming bond when compared to those in the syn and anti CF_2-propene transition structures.

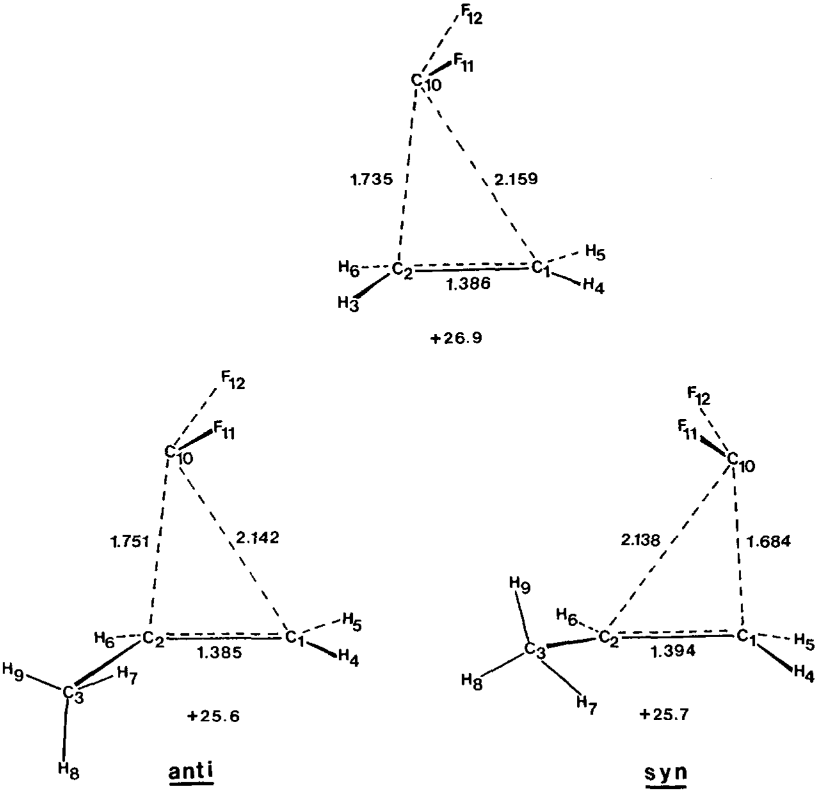

Figure 1. Transition structures for CF_2-ethylene, anti, and syn CF_2-propene reactions.

In both CF_2-propene transition structures, the hydrogens attached to the allylic carbon are approximately staggered with respect to the forming CC bond For example, in the anti transition structure the dihedral angles $H_7C_3C_2C_{10}$, $H_8C_3C_2C_{10}$, $H_9C_3C_2C_{10}$ are 55° 175° and 295°, respectively, while in the syn TS these dihedral angles are 86° 207° and 327° respectively. While one of the allylic hydrogens of propene is eclipsed with the double bond in the ground state, this eclipsed hydrogen rotates and forms a torsion angle of 38° and 30° with respect to the partial double bond in the anti and syn TS, respectively. This alteration in conformation of allylic bonds upon proceeding from the reactants to the TS is a general phenomenon that we have discovered in other addition reactions as well.[5] In the TS, the FCF bisector of the attacking CF_2 is rotated ~3° with respect to the developing cyclopropane plane, in such a way that the fluorine syn to the methyl group is moved closer to the methyl substituent. This is contrary to what one would expect on the basis of steric effects, but may indicate slight electrostatic attraction of F and CH_3.

Table. Transition structures for the cycloadditions of difluorocarbene to ethylene and propene.

	CF_2-ethylene	anti-CF_2-propene	syn-CF_2-propene
bond lengths(Å)			
C1H4	1.069	1.071	1.073
C1H5	1.069	1.070	1.073
C2C3		1.512	1.495
C2H6	1.072	1.073	1.071
C3H7		1.082	1.084
C3H8		1.084	1.083
C3H9		1.081	1.088
C10F11	1.356	1.362	1.365
C10F12	1.356	1.357	1.365
bond angles(°)			
C1C2C10	86.8	85.3	51.9
C1C10C2	39.9	40.1	40.7
C1C2C3		120.8	122.8
C1C2H6	119.8	118.3	118.2
C1C10F11	97.5		117.9
C1C10F12	97.5		116.6
C2C1C10	53.4	54.6	87.5
C2C1H4	120.6	120.4	119.2
C2C1H5	120.6	120.9	119.0
C2C10F11	117.9	116.1	
C2C10F12	117.9	119.9	
C2C3H7		110.3	111.6
C2C3H8		109.3	110.6
C2C3H9		110.3	110.0
C3C2H6	114.8[a]	115.6	118.7
H4C1H5	118.8	118.7	114.7
F11C10F12	107.8	107.5	107.6
dihedral angles(°)			
C10C2C3H7		55.1	86.0
C10C2C3H8		174.9	207.0
C10C2C3H9		295.0	326.6
C1C2C10F11		68.2	-63.0[b]
C1C2C10F12		-63.7	67.2[c]
C3C2C1C10		104.7	88.3
H6C2C1C10		-102.4	-85.1
H4C1C2C10		88.8	107.0
H5C1C2C10		-89.6	-104.5

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[a] H3C2H6

[c] C2C1C10F11

[d] C2C1C10F12

The activation energy for the difluorocarbene cycloaddition to propene via the anti TS is 25.6 kcal/mol, a negligible 0.1 kcal/mol lower than the activation energy for the syn TS. We have shown earlier that the activation energy for the CF_2-ethylene reaction is overestimated by ~15 kcal/mol at the RHF 3-21G level, due to neglect of correlation energy.[1] The small difference between the activation energies for the two modes of CF_2 attack on propene suggests that unsymmetrical alkyl substitution on the olefin has no appreciable influence on which end of the double bond is approached preferentially by the attacking difluorocarbene. This is consistent with the idea that in carbene cycloaddition transition structures, the electrophilic vacant LUMO of the carbene interacts more or less at the center of the double bond.[6] Consequently, the enlargement of the C_1 coefficient of the propene HOMO, relative to the C_2 coefficient, does not have an effect on orientation. The LUMO of an unsymmetrically substituted alkene is polarized insignificantly by donors, so that the carbene HOMO - alkene LUMO interaction has no influence on orientation of approach. This conclusion is in contrast to that of Apeloig et al. for alkylidenecarbene cycloadditions to unsymmetrical alkenes, where MNDO predicts a large preference for attack in the syn mode.[2]

The activation energy for the CF_2-propene reaction is 1.3 kcal/mol lower than the activation energy for the CF_2-ethylene cycloaddition. This is a manifestation of the electrophilic nature of the carbene. That is, donor substitution on the olefin increases the HOMO energy, and consequently the nucleophilicity of the alkene. These calculations also show that substitution has essentially no effect on the position of the transition structure along the reaction coordinate. Whereas the transition structure shifts earlier along the reaction coordinate when activation energies are lowered, due to increased product stability or decreased reactant stability (Hammond postulate),[6] the average transition structure for the propene reaction is essentially the same as that for the ethylene reaction. In the case described here, the reaction exothermicity changes insignificantly, and substitution alters the energy, but not the extent of reaction progress, of the transition structure

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