Stereochemistry of some Reactions: S_N2', S_E2', and $E2$ Additions to Polyenes

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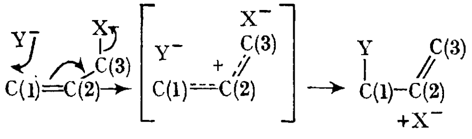
FUKUI and Fujimoto have recently discussed[1] the stereochemistry of S_N2' reactions, "non-cycloadditions" on polyenes and 1,2-eliminations. We suggest a more qualitative alternative, which does not involve a cyclic intermediate. The method used is analogous to the treatment of sigmatropic reactions by Woodward and Hoffmann.[2]

We postulate that in S_N2' reactions:

(1) the transition state may be formulated as an allylic cation interacting with two anions X and Y;

(2) the most important interactions are those existing between the lowest vacant molecular orbital (LV) of the allylic system and the highest occupied orbitals (HO) of X and Y, and they will determine the steric course of the reaction.

The LV of the allyl cation is the second molecular orbital. In the transition state, the atomic orbitals (AO) of carbon atoms C-1 and C-3 are intermediate in structure between p orbitals and sp^3 orbitals, so that the $2s$ atomic orbitals must be taken into consideration. Let us give arbitrarily the (+) sign to the $2s$ atomic orbital of carbon C-1.



As C-1, C-2, and C-3 are linked by σ-bonds, it follows that the $2s$ AO of C-2 and C-1 also have the (+) sign.[3] Mixing of the $2s$ and $2p$ AO results in the structure (I) for the LV of the allyl cation in the transition state. Two cases are then considered:

(a) The Y–C-1 bond forming and the X–C-3 bond breaking are synchronous. In the transition state, X and Y are simultaneously 'bonded' to the allylic system. The direction of the hybrid AO at C-1 shows that Y must enter the molecule *anti* to X [structure (II)]

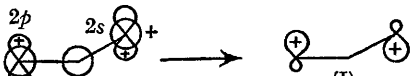
(b) The reaction is still concerted but the breaking of the X–C-3 bond happens before the forming of the Y–C-1 bond. In the transition state, the interaction of the allylic system is bonding with Y and antibonding with X [structure (III)]. The reaction then proceeds *via* the "suprafacial" route (Y entering *syn* to X)

The nucleophilic reagent Y might be expected to be more able to approach the C-1 atom in case (b) (where the breaking of the X–C-3 bond creates a partial positive charge at C-1) than in case (a) (where no such favourable electric effect exists). In fact, Stork and White[4] have shown that S_N2' reactions proceed *via* the *syn* route.

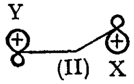
In S_E2' reactions the transition state is formulated as an allyl anion, interacting with two cations X and Y. The interactions between the second (highest occupied) MO of the allylic system and the vacant orbitals of X and Y will determine the stereochemistry. The same argument as above shows that the reaction will be *anti* when synchronous and *syn* when nonsynchronous.

The stereochemistry of S_E2' reactions is not yet known with certainty. However, Felkin and Roussi[5] have found that epoxide ring opening by allylic Grignard reagents does not proceed *via* cyclic transition states. This reaction might well be synchronous, as Nordlander and Roberts[6] have shown that Grignard allylic reagents in ether exist essentially in covalent forms.

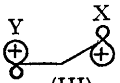
In an addition to a polyene, the final product contains one more bond (σ and π) than the starting polyene, so the symmetry of the LV of the π system is considered here.



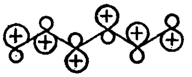
(I)

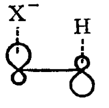


(II)

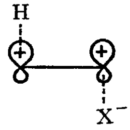


(III)


(IV)



(V)



(VI)

For example, the LV of hexatriene is the fourth. Mixing of the *p* and *s* orbitals gives the structure (IV). Symmetry arguments favour then 1,2-*anti*, 1,4-*syn*, and 1,6-*anti* additions. The same conclusions have been derived by Fukui[3] in a more rigorous manner. The *syn* stereochemistry predicted for 1,4-additions agrees with the experimental results obtained by Winstein, Hammond, and their respective co-workers.[7]

For *E*2 reactions three cases are considered:

(1) Synchronous eliminations—If eliminations and additions are considered as reverse processes, then symmetry arguments show that 1,2-*anti*, 1,4-*syn*, 1,6-*anti* . . . bimolecular eliminations are favoured. This would be a possible explanation of the superiority in 1,4-*syn* conjugate elimination over the corresponding *anti* process.[8]

(2) *E1cB*-like eliminations—For *E1cB* reactions, the transition state is formulated as an olefin interacting with X^-, the most important interaction being that between the HO of X^- and the LV of the olefin. For bimolecular reactions which are *EicB*-like, the transition state must be similar. The very crude assumption is then made that the stereochemistry is determined by the interactions of the second MO of the olefin with H^+ (antibonding) and X^- (bonding). The reaction is then predicted to be *syn* [structure (V)].

(3) *E*1-like eliminations—The important interactions are assumed to be those existing between the first MO of the olefin with H^+ (bonding) and X^- (antibonding). It follows [structure(VI)] that the reaction will be *anti*.

Our predictions for *E1cB*-like and *E*1-like reactions agree with the experimental results of Sicher and Zavada.[9] The selection rules deduced here only apply to the cases where orbital symmetry is the only important effect.

The study of S_N2' and S_E2' reactions was suggested by Dr H. Felkin. The author is indebted to Professors M. Fetizon, L. Salem, and J. Sicher for stimulating discussions and helpful comments and to a referee for pointing out an error.

(*Received, February 23rd, 1968; Com.* 216.)

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