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A THEORETICAL ACCOUNT FOR STEREOSELECTIVE E2 REACTIONS

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ONE of the conspicuous, stereoselective phenomena in organic reactions is the E2 beta-elimination, in which the leaving nucleophilic group prefers to be in the position <u>trans</u> to the proton being extracted by the attacking base[1]. To the best of our knowledge no satisfactory explanation has been given.

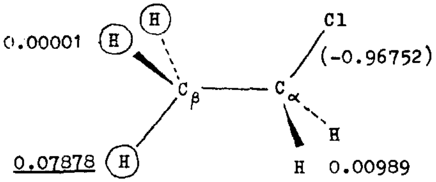
The object of the present communication is to present an MO (molecular orbital)-theoretical account for this sort of stereoselection. It is believed that the first step of this reaction is the approach of a base to β-carbon. Would the problem, as to which of β-hydrogen atoms should predominantly be abstracted, be solved in terms of the "orienting effect" of the leaving nucleophilic group, just as the case of displacement reactions in substituted aromatic hydrocarbons?

In this connection it is recollected that the reactivity of each hydrogen atom of a paraffinic molecule toward the radical attack was interpreted by an MO-theoretical index called the frontier electron density[2]. The parallelism between the reactivity of hydrogen atoms and their frontier electron density was found to be strikingly good.

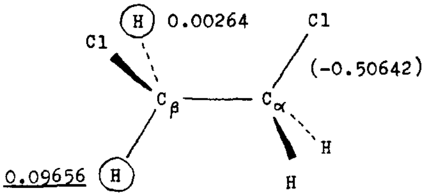
In order to test the availability of the frontier electron theory for the present problem, the electron density (square of the coefficient of hydrogen 1s atomic orbital) of the lowest vacant MO (LV) (the frontier orbital for the nucleophilic attack) at each hydrogen atom is calculated by the extended Hückel method[3]. For the convenience of calculation the leaving nucleophilic group is most simply typified by a chlorine atom.

Fig. 1. The frontier electron density of hydrogens in chloroparaffins.

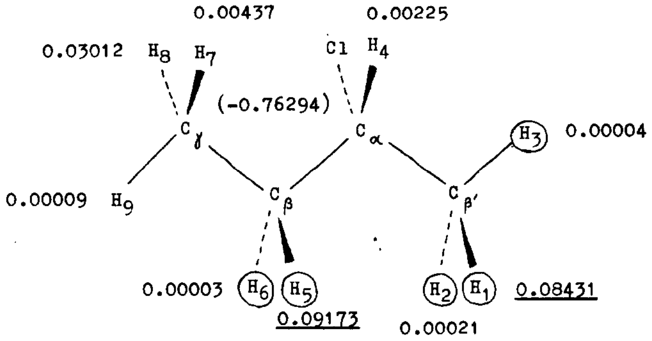
1) Ethyl chloride (trans).



2) 1,2-Dichloroethane (skew).



3) 2-Chlorobutane.

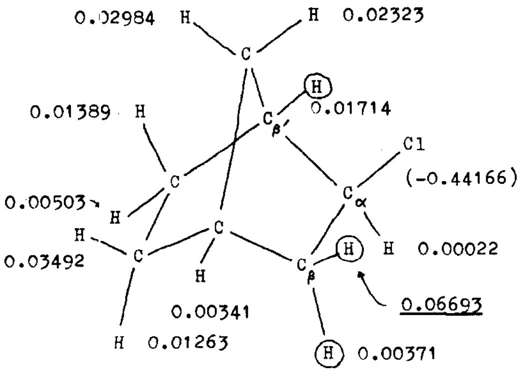


As is shown in the figure the <u>trans</u> β-hydrogen has an eminently larger value of the frontier electron density than the others in each of ethyl chloride, 1,2-dichloroethane, and 2-chlorobutane. The values indicated in parenthesis stand for the partial bond order of LV (the overlap population[4] in LV) between the chlorine atom and α-carbon, exhibiting large negative values. This implies that an electron occupying LV would contribute much to the antibonding character of this bond. This seems to be significant in view of the common idea of "concerted" mechanism that in most of E2 reactions the electron at the leaving β-hydrogen might be gradually drifted through the interaction with the attacking base into the C_α-halogen bond to repel that halogen atom.

The frontier electron density at α- and γ-hydrogens are seen to be considerably smaller than that of β-hydrogens. Also, it is of interest to compare β- and β′-hydrogens in 2-chlorobutane. Averaging of the frontier electron density on an appropriate basis with respect to all possible conformations would result in a larger value for the secondary hydrogen than the primary one in favour of the Saytzeff rule. The sterically-controlling effect of the chlorine atom is transmitted along the "antiperiplanar" path ($Cl-C_{\alpha}-C_{\beta}-H_5-C_{\beta}-C_{\gamma}-H_8$····, and $Cl-C_{\alpha}-C_{\beta'}-H_1$····). This seems to be *an important rule for the principle of steric control of the* nucleophilic group attached to n-alkanes.

Another more attracting case in the β-elimination in contrast with the trans-relationship in noncyclic compounds is the E2 reaction of 2-exo-bromonorbornane. Kwart et al. recently demonstrated the predominance of cis-elimination[5]. As is indicated in Fig. 2 the β-hydrogen at the position exo possesses a much larger frontier electron density than endo hydrogen, leading to the possible preference of cis-elimination in this bicyclic system.

Fig. 2. The frontier electron density of hydrogens in 2-exo-chloronorbornane.



Such a discussion may be illuminating in exploring the nature of this type of steric control.

The calculations were carried out on an IBM 7090 computer

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