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A THEORETICAL INVESTIGATION OF CYCLOHEXANONE REDUCTION.

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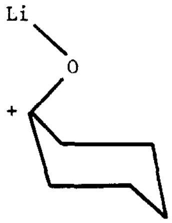
In spite of extensive investigation of the reduction of cyclohexanone [1] few quantum chemical interpretations of the preferential axial approach have been reported. In this paper we shall attempt to show how a theoretical approach can explain this stereoselectivity.

The use of electrostatic potentials in the study of cyclohexanone reduction.

Bonaccorsi and al [2] have proposed a treatment which calculates the potential due to the nuclear and electronic charges. The energy of interaction of a charge q (-q) with this potential is qV (-qV). A plot of the isopotentials obtained in this way represents directly the interaction energy with a charge + 1 or - 1. At large distances the polarization and charge transfer are small and the variation of energy with the angle of attack becomes essentially that of electrostatic interaction between the substrate and an approching species. Such maps are given in Fig. 1 and 2. Fig. 1 shows that the shape of the electrostatic potential around the carbonyl group is slightly dissymetric. Considering axial and equatorial directions of carbon carbonyl group, it can be seen that axial direction is close to zero potential value, while equatorial direction runs through negative potential values disfavouring a nucleophilic approach. We have also considered the possibility that as a first stage in the reaction, the oxygen atom moves out of the CO plane. This would produce a tetrahedral carbon with one position unoccupied. Bending the oxygen atom leads to the formation of an attractivepotential for nucleophilic agents in the fourth tetrahedral direction of the carbon carbonyl group. (Fig. 2 -A, B). The shape of electrostatic potential shows that the most favored approach channel for nucleophilic agents is directed towards the axial direction ; the 5 kcal contour lies 5 Å from carbon 1 for an axial vacant tetrahedral direction (fig. 2A), while this same contour lies 3.8 Å from carbon 1 for an equatorial vacant direction (Fig. 2B).

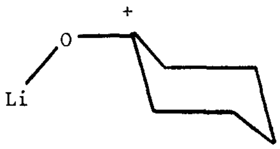
Energy results.

We have calculated the variation of the total energy for two different approaches of the hydride ion toward cyclohexanone, along equatorial and axial directions when the oxygen atom is bent out of the C = O plane. It was suggested that nucleophilic attack on cyclohexanone is preceded by the complexation of a lithium cation with the oxygen atom [3]. For this reason we have considered the approach of the hydride ion from complexes I (curves 1) and II (curves 2) (Fig. 3).



I

E = - 1886.12 eV



II

E = - 1887.63 eV

(Solvation energy included)

We have taken into account polarization only and polarization plus charge-transfer. Standard geometries are used. We have used a CNDO method in which solvation energy is introduced by a modification of the Hartree-Fock operator [4]. For our calculations we have chosen a value of 4.3 for the dielectric constant (diethyl ether). The energy obtained with polarization alone and the further energy gain due to charge-transfer appear larger for the axial approach (curves 2) than for the equatorial approach (curves 1) Complex II is calculated to be the most stable.

Fig. 1

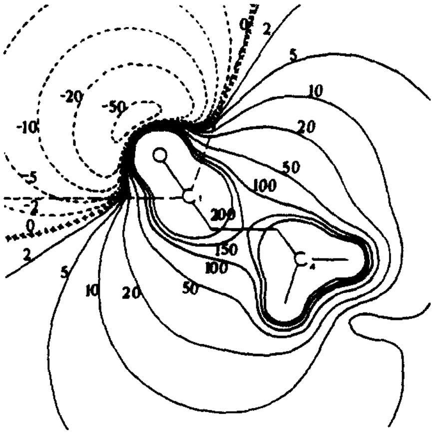


Fig. 2A

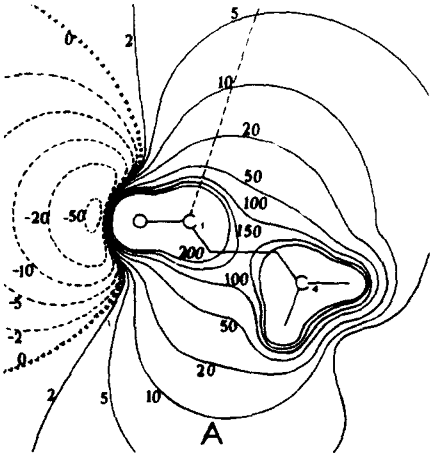


Fig. 2B

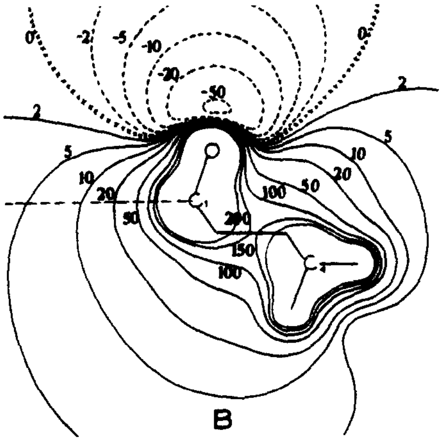


Fig. 3

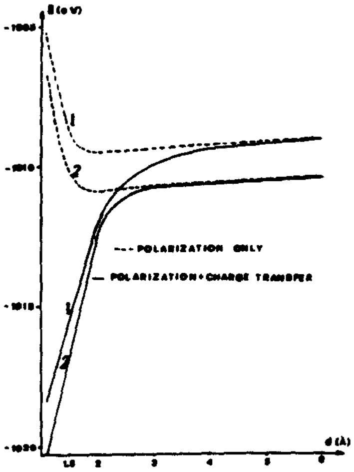


Fig. 1 and 2 - Electrostatic potentials (in kcal/mole) in the symmetry plane containing OC_1C_4 (negative potentials - dotted lines).

Fig. 3 - Energies (eV) for hydride ion approach towards ions I (curves 1) and II (curves 2) along equatorial and axial directions (d = distance in Angströms).

The conclusion that we wish to be drawn from this study is that the calculation of both the polarization effect, and the charge transfer effect is in agreement with the electrostatic model which indicates that axial attack should be favoured over equatorial. In order to establish the scope of the reported reaction work is in progress with other ketones, and with other nucleophiles.

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