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A THEORETICAL ACCOUNT FOR THE STEREOSELECTIVE FREE-RADICAL HALOGENATION IN NORBORNANE

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IT has lately been shown that the frontier electron density supplies an excellent reactivity index for the stereochemical orientation problems in S_H2 reactions.[1] The purpose of this communication is to present a theoretical account for the stereoselection in homolytic halogenation reactions based upon the frontier electron theory, which was already employed for the elucidation of the reactivity of paraffinic hydrocarbons toward free radicals.[2]

Kooyman et al. showed that the free-radical chlorination of norbornane gave two main products, 2-exo-chloronorbornane and 2-endo-chloronorbornane with the predominance of the former.[3] The frontier electron density at each hydrogen atom for homolytic abstraction[4] which was calculated by the extended Hückel method[5] is indicated in Figure 1.

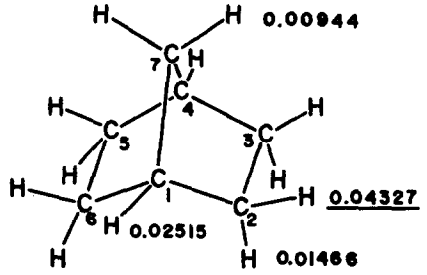

Figure 1. The frontier electron density of hydrogens in norbornane.

Thus, we can expect that the exo-hydrogen at carbon 2 (3, 5 or 6) would be removed by a radical more readily than any others. The chlorination of norbornane may take place in two stages, i.e. the abstraction of the exo-hydrogen by the first attacking radical followed by the approach of a halogen donor molecule to the 2-norbornyl intermediate produced by the first attack. One of the present authors recently gave a theoretical account for the stereoselection in noncycloadditions,[6] indicating the direction of extension of the frontier orbital at the reaction site would control the spatial direction of approach of the reagent. It is one of interesting problems in organic chemistry whether the trivalent carbon in a radical takes a strictly sp^2-planar configuration or a somewhat deformed one. The result of calculation with respect to 2-norbornyl radical is shown in Figure 2.

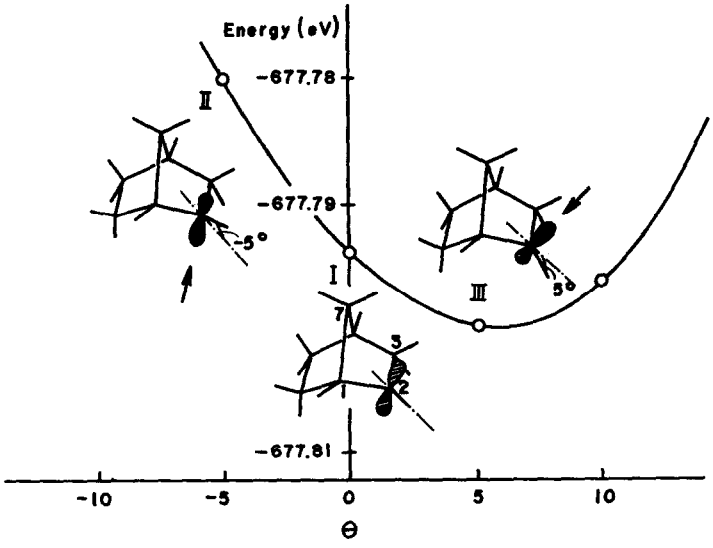

Figure 2. An energy diagram of 2-norbornyl.

(Θ : the angle between the C-H axis and the $C_1C_2C_3$-plane)

In the configuration I, the hydrogen atom bonded to carbon 2 is located on the plane determined by the carbon atoms 1, 2 and 3, while in II and III the 2s atomic orbital (AO) of carbon 2 enters into mixing with 2p AO in the unpaired electron orbital, so that the hydrogen attached to carbon 2 gets upwards and downwards out of the plane respectively. It is seen that stable configurations lie on the side of III, in which this half-occupied molecular orbital possesses its maximum extension to the exo-direction at carbon 2. This result makes one guess that the exo-approach of the halogen donor would be favourable. The difference in energy between configurations II and III, although rather small in these isolated systems, will be enlarged when the halogen donor approaches from the direction of the extension of the half-occupied orbital accompanied with the change in the degree of hybridization to form a tighter sigma overlapping.

The discussion disclosed above suggests the prevalence of the exo-hydrogen abstraction of carbon 2 by the first attacking radical followed by the exo-approach of a halogen donor molecule in the second stage. This course will obviously lead to the predominant occurrence of 2-exo-chloronorbornane. But the fact that the major product is the exo-compound gives no evidence that the exo-abstraction is actually preferred to the endo-abstraction since the radical produced by the endo-abstraction would also give the exo-chloro compound preferentially. This point would become clear by the experiment with e.g. 2-exo-deuterionorbornane.

It has been reported that 7-chloronorbornane is found in the product although in small content.[3] The theoretical index in Figure 1 is not likely to favour the occurrence of the direct abstraction of 7-hydrogens. We are disposed to suggest a route to 7-chloronorbornane through the migration of 7-hydrogen to the 2-exo position. Notwithstanding the favourable sterical situation the actual yield of the 7-chloro compound is rather poor.

This fact might be attributed to the weak antibonding character between 1s AO of the 7-hydrogen and the 2s and 2p AO's of carbon 2.

The deformation of radicals from the sp^2 planar structure is observed in the calculation by the extended Hückel method with respect to e.g. chloroethyl and 2-chlorocyclohexyl in favour of the homolytic trans addition of chlorine to ethylene and cyclohexene, and such a deformation seems to be a general feature of radicals. This point will be discussed in a separate paper in near future.

The calculations were carried out on an IBM 7090 computer under the permission of UNICON Committee whom the authors wish to acknowledge.

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4. In case of norbornane, there exists a vacant molecular orbital (MO) whose energy is very close to that of the lowest vacant MO. Accordingly, a modification is needed for calculating the frontier electron density so as to take the contribution of that MO into account on the basis of the technique early employed by the present authors in discussing the reactivity in conjugated systems; cf. K. Fukui, T. Yonezawa, C. Nagata, and H. Shingu, J. Chem. Phys., 22, 1433 (1954).
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