248. The Electrocyclic Cyclopropyl-Allyl Rearrangement

Preliminary communication[1])

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Summary. MINDO-2 SCF calculations indicate that ring-opening of cyclopropyl radical (I) to allyl radical (II) is more favourable *via* a disrotatory reaction path, the calculated activation energy being ~30 kcal/mole. (For conrotatory opening the activation energy was found to be ~44 kcal/mole.) The two critical motions of the nuclei during the transformation are found to be strongly decoupled, *i.e.* rupture of the CH_2—CH_2 bond precedes rotation of the CH_2 groups. As predicted by qualitative theories both ring-opening modes are unfavourable since they involve a change in electronic ground-state symmetry between I and II. The preferred ring-opening mode is discussed qualitatively in terms of *Evans'* principle.

The stereochemistry of the ring opening of the cyclopropyl cation or anion has been the subject of several experimental and theoretical investigations [1] [2]. In this communication we report a theoretical study of the electrocyclic transformation of cyclopropyl radical (I) to allyl radical (II) using the MINDO/2 SCF procedure [2] [3] [4]. This method has proved to yield heats of formation, geometries and force constants with reasonable accuracy for a great number of closed- and open-shell hydrocarbons. For the present calculation we have employed the half-electron method [2] [3] [5]. In contrast with previous work of this kind, the half-electron correction was included in each iteration cycle. As reaction coordinate we have chosen the CH_2–CH–CH_2 angle φ. For each value of φ the total molecular energy was minimized with respect to all geometrical parameters except the C–H bond-lengths, and the H–C–H angle, assumed to be 1.09 Å and 120°, respectively. The energy minimization was carried out using the SIMPLEX algorithm [6]. The initial geometry and bond-order matrix for each SIMPLEX step were taken as those of the preceding step.

The results indicate that ring opening of I to II should be more favorable *via* a disrotatory reaction path, the calculated activation energy for this process being ~ 30 kcal/mole. (The activation energy for conrotatory opening was calculated to be ~44 kcal/mole.) This supports the early suggestion of *Clark & Smale* [7], based on preliminary *ab-initio* calculations without minimization of the energy with respect to the geometry. However, our prediction is in contrast to the results obtained by *Longuet-Higgins & Abrahamson* [8] on the basis of a state correlation diagram and by *Woodward & Hoffmann* [9] on the basis of extended *Hückel* calculations, both of which suggested that the conrotatory mode is slightly preferred.

However, *Longuet-Higgins & Abrahamson* [8] pointed out that both ring-opening modes are unfavorable since in each case the ground state of I is correlated with an excited state of II. This prediction is supported by our calculations. Thus the energy

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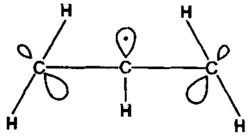
[1]) A full paper will be published elsewhere.

rises steadily with increase in φ from the ground state of I, but the reaction does not proceed at all, the planes containing the CH_2 groups remaining essentially perpendicular to the plane of the carbon atoms. The same behaviour is observed for the reverse process, *i.e.* the ring closure of planar II. Again the energy rises, but the CH_2 groups fail to rotate. The crossing of the two energy profiles corresponding to ring opening and closure occurs at $\varphi \sim 87°$ at an energy about 30 kcal/mole higher than that of ground state I. With φ kept constant at 87°, rotating the CH_2-groups from perpendicular to planar indicates that:

a) A disrotatory motion occurs practically free of activation energy. During the process the methine proton moves progressively out of the carbon plane by up to 0.70 Å and finally becomes coplanar again[2]). The direction of motion is indicated below in a front-view picture.



b) The conrotatory motion needs an additional activation energy of ~14 kcal/mole. At the transition state the CH_2 groups are rotated ~50° from perpendicular and the methine proton is 0.28 Å out of coplanarity.

Although the complete energy surface for this reaction has not yet been obtained [12] the following conclusions emerge from these calculations:

1. Ring-opening of I is not an "easy" process [8], judging from the special features of the reaction paths described above. Indeed, this reaction with unsubstituted I has not yet been observed [13], which seems surprising, given that relief of ring strain and the appreciable gain of resonance energy in allyl (II) would make the process exothermic. Only recently, ring-opening of a heavily-substituted derivative of I has been achieved [14]. Specially, our results indicate that rupture of the $-CH_2-CH_2-$ bond precedes rotation of the CH_2 groups. A similar non-linearity of the two critical motions has also been noticed recently by *Hsu, Buenker & Peyerimhoff* [15] in the ring-opening of cyclobutene. It is clear that results of calculations in which all geometrical parameters are assumed to vary simultaneously and monotonically should be taken with caution.

2. Ring-opening of I should take place *via* a disrotatory motion of the CH_2 groups. The motion of the methine proton during this process (see a) indicates that of the two *a priori* possible disrotatory modes the same motion will be favoured as in the case of $C_3H_5^+$ [16], provided that abstraction of the leaving group and ring-opening occur in a concerted manner. Unfortunately, no conclusions concerning the stereochemistry of this transformation can be drawn from the experiments cited above [14].

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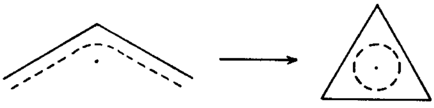
[2]) Our calculations predict the methine proton in ground state $C_3H_5^{\cdot}$ to be coplanar with the C_3-ring. The ESR.-work of *Fessenden & Schuler* [10] indicates that this might not be so, $C_3H_5^{\cdot}$ being a rapidly inverting species. *Walborsky & Chen* [11] have found that generation of 1-methyl-2,2-diphenyl-cyclopropyl radical and subsequent reaction of it with a substrate yields racemic cyclopropyl derivatives except when performed in a solvent cage, where partial retention of configuration is observed. However, these results suggest also that the barrier to inversion is rather small.

It has been pointed out already that no definite prediction can be deduced from orbital correlation diagrams for the steric course of this reaction [8]. In trying to apply *Evans'* principle [2], one is left with the question whether cyclopropenyl radical (III), which is isoconjugate with the transition state for this reaction, is aromatic, non-aromatic, or anti-aromatic. III, a [4n + 3] neutral perimeter (n = 0), can be formally generated by intramolecular union [2] of the terminal carbon atoms of allyl (II). This process involves no first-order energy change since the bond order between centers of like parity in alternant hydrocarbons vanishes. However, there will be a stabilizing second-order energy change, since bond self-polarizabilities are positive in sign. These arguments – also valid for [4n + 1] neutral perimeters – suggest that III should be slightly aromatic³) and hence that the transition state for I → II should be of *Hückel* type [2], which would demand a disrotatory pathway, in agreement with the MINDO/2 results presented in this paper.



II III

While this work was in progress, Professor *M. J. S. Dewar* informed me that he had arrived at qualitatively similar conclusions concerning the stereochemistry of the $C_3H_5^{\bullet}$ ring-opening, using a modified MINDO/2 version.

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³) A recent determination of the heat of formation of tropenyl radical has yielded an empirical resonance energy for this [4n + 3] system (n = 1) of ~30 kcal/mole [17]; *i.e.* only slightly less than that of benzene (~36 kcal/mole [18]).