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THE [1,2] VS. [2,3] SIGMATROPIC REARRANGEMENTS IN α-ALLYLOXYCARBENE[1]

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The [2,3] sigmatropic rearrangement has been predicted by MO theoretical calculations (MINDO/3) to be preferred to the [1,2] shift in α-allyloxycarbene giving 3-buten-1-al. The activation energy for the former process is governed by the non-neighboring two center terms, indicating that the reaction can be replaced by the [1,2] shift under increased steric demand as observed in an γ,γ-dimethylallyloxycarbene.

We have recently reported that a wide range of allyl and benzyl groups undergoes rearrangement from the oxygen to the carbenic center in the aryl-α-alkoxycarbenes generated by the photolysis of 1-alkoxytriptycenes.[2] When 1-(γ,γ-dimethylallyloxy)triptycene was irradiated in an inert solvent, the main product was aryl ketone 1 in which no allylic "inversion" had taken place, showing the occurrence of [1,2] shift rather than [2,3] shift at least in the γ,γ-dimethylallyloxycarbene 2.[2] The result offers a striking contrast with allylthiocarbenes 3 which rearrange without exception in a [2,3] fashion.[3]

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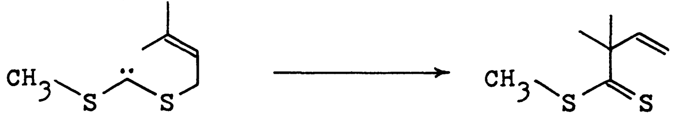

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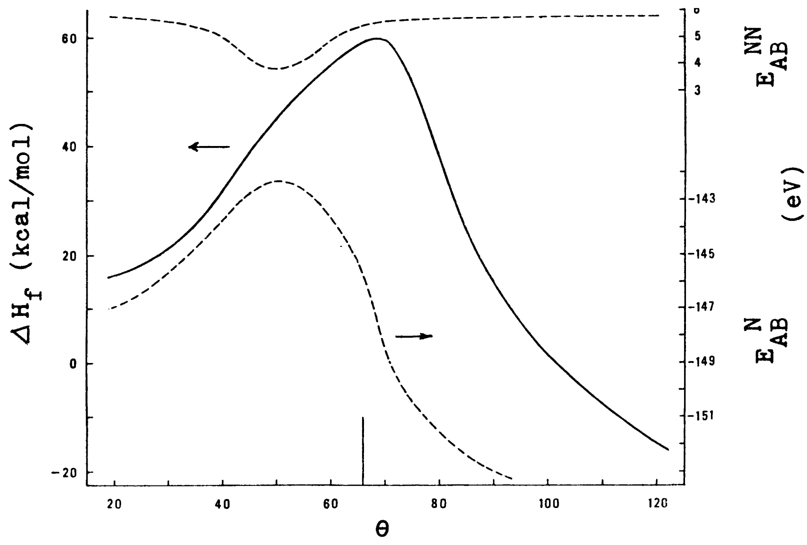
It is usually the case that [2,3] shifts are favored over [1,2] shifts in a number of intramolecular electrophilic migrations.[4] The former is an allowed reaction and the latter is forbidden in terms of the orbital symmetry rule for the concerted reactions.5) It was therefore deemed of special interest to scrutinize theoretically the pathway by which the migration of an allyloxycarbene takes place.

The MINDO/3 calculations were carried out for the elucidation of the reaction surfaces interrelating α-allyloxycarbene in the singlet electronic state and ground state 3-buten-1-al by means of a HITAC 8800/8700 computer. The MINDO/3 program written by Bingham, Dewar and Lo 6) and obtained from QCPE 7) was used to calculate the minimum energy bond lengths and angles. The reaction coordinates were defined by angle (θ) $\angle O\ddot{C}C$ for the [1,2] shift as shown in Fig. 1. The theoretical structure for the starting carbene molecule was obtained by minimizing total energy with respect to θ at around 20°. The reaction is represented by gradual increase in θ in steps of 10° in general and more closely near the transition state. At each step of fixed θ, the energy of the molecule was minimized with respect to all the other degree of freedom. At θ = *ca.* 130°, we arrive at another energy minimum corresponding to the end product. For the [2,3] shift, distance r between the terminal carbon of the allyl moiety and the carbenic carbon was taken as a measure of the progress of the rearrangement (see Fig. 2). By starting at r = 4.49 Å which is the equilibrium distance between the two carbon atoms of interest in the ground state α-allyloxycarbene, we complete the [2,3] migration when r = 1.49 Å.

The potential energy curve where heats of formation of the C_4H_6O system were plotted as a function of the reaction coordinate is given in Figs. 1 and 2 together with the dissected energy terms E_{AB}^{N} and E_{AB}^{NN}.8) We note the following characteristic features. Firstly, the activation energy for the rearrangement is 42.5 and 31.5 kcal/mol for the [1,2] and [2,3] shifts, respectively. The latter is decidedly lower than the former process, although the alternative result, namely the "retention" of the γ,γ-dimethylallyl group migration has been obtained experimentally.2) Secondly, the [1,2] sigmatropy is a typical "Wittig rearrangement" in that the migrating allyl group is pseudo-cation at the earlier stage of the reaction. The observed allyl and benzyl migration and resistance of simple alkyl and aryl groups to rearrangement are consistent with this idea of electrophilic rearrangement.2) Thirdly, it is apparent from the shape of the curves in Fig. 2 that the transition state is considerably reactant-like in the [2,3] shift; the transition state is reached when the original O-allyl bond still has the bond order of 0.85 and the new C-C bond is formed only to 0.2 unit. This is reasonable for an exothermic reaction requiring relatively small activation energy.[9] Thus the [2,3] shift is expected to be easily amenable to non-bonded interactions in the transition state which has a five-membered ring structure. It may well be that the transition state for the [2,3] rearrangement will be raised energetically by introduction of two methyl groups at the terminal position of the allyl group as in the γ,γ-dimethylallyloxycarbene, while that for the [1,2] shift is obviously rather indifferent to this effect. The two rearrangement paths can be better illustrated by the changes in the two center energy terms along the reaction coordinates. The potential energy curve is



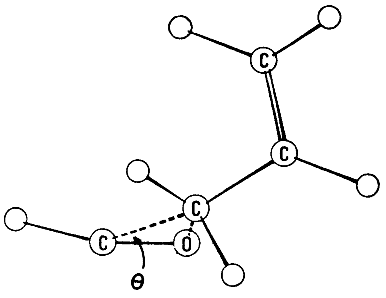
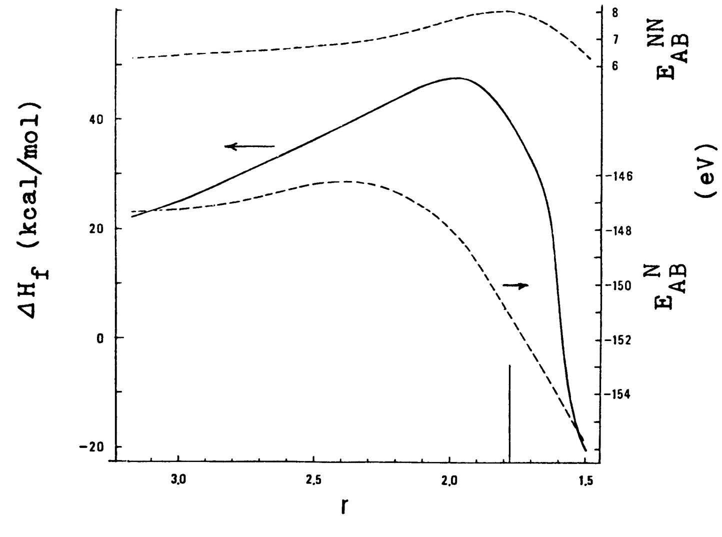


Fig. 1. Energy profile and the transition state structure for the [1,2] sigmatropy in α-allyloxycarbene.



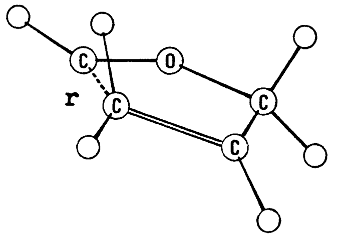


Fig. 2. Energy profile and the transition state structure for the [2,3] sigmatropy in α-allyloxycarbene. The vertical mark denotes 50 % reaction.

quite similar to the repulsive E_{AB}^{NN} term in the [2,3] migration (Fig. 2) and is practically governed by the E_{AB}^{N} term in the [1,2] rearrangement (Fig. 1).[8]

Last of all, we point out that selectivity for [2,3] shifts is extremely high in allylthiocarbenes and even the γ,γ-dimethylallyl group migrates in **3** *via* the [2,3] process.[3] One of the origin for this different behavior may be found in the longer C-S bond distances as compared to the corresponding C-O. This would possibly decrease the non-bonded repulsion in the cyclic transition state for the [2,3] migration. Furthermore, as the forming C=S bond is weaker than the C=O, these less exothermic reactions will have a late transition state. A maximum of the E_{AB}^{N} *vs*. reaction curve will be shifted to the product side, and contribution of the E_{AB}^{NN} term to the total energy of the transition state could be less important in the thiocarbene rearrangements.[10]

References and Notes

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7) QCPE Program No. 279.

8) E_{AB}^{N} and E_{AB}^{NN} denote the neighboring and non-neighboring two-center energy terms, respectively, where the A and B atoms in E_{AB}^{N} are a pair connected by the chemical bond and the pair of A and B in E_{AB}^{NN} are not directly bonded. For the sake of consistency during the course of the reactions, both atom pairs to be formed and to be cleaved by the reaction were always included in summing up the neighboring terms. E_{AB}^{N} corresponds to the strength of bond A-B and to ring strain if it is contained in the ring. E_{AB}^{NN} represents non-bonded repulsion.

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10) A similar reasoning may be applicable to higher selectivity of the [2,3] over [1,2] sigmatropic rearrangement of sulfur ylides and related anionic species as compared to the oxygen analogs.

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