Tetrahedron Letters No.33, pp. 3673-3678, 1968. Pergamon Press. Printed in Great Britain.

The Electrocyclic Transformation of Cyclopropyl to Allyl Anion, an all valence SCF MO treatment

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(Received in UK 30 April 1968; accepted for publication 22 May 1968)

1. Introduction.

The original proposals[1,2,3] concerning the stereochemistry of the electrocyclic transformation of cyclopropyl to allyl system have stimulated a considerable amount of research in the case of the cationic species.[4,5] By contrast transformations involving the radical and anion have been relatively neglected. Recently Kutzelnigg[6] has presented the results of more complete EHT calculations for the cationic species. However for charged species EHT is theoretically unsound.[7] We have therefore recently investigated in considerable detail the ground state and excited state transformations of cyclopropyl to allyl cation using a modified CNDO II SCF MO method.[8] In continuance of this work we present results obtained by this method for the ground state and lower excited states for the transformation of cyclopropyl to allyl anion. In a later communication we shall present similar results for the transformation involving the radical. The latter is particularly interesting since our preliminary calculations suggest that the ground state reaction should proceed in a disrotatory manner analogous to the cationic case. This is in direct contrast to the predictions of Woodward and Hoffman.[1]

2. Method of Calculation.

The method of calculation has been fully described elsewhere and the parameters used here were identical to those employed in the treatment of the excited states of cyclopropane.[9] Configuration interaction between all singly excited states involving the four lowest unoccupied and four highest occupied orbitals has been included for each calculation. The reaction co-ordinate was taken to be the same as in the cationic case, previously described,[8] a continuous transformation being assumed between the cyclopropyl and allyl system. For a concerted process there are three distinct modes for the transformation of cyclopropyl to allyl system; disrotatory modes 1 and 2 and conrotatory mode 1. This is shown in fig. 1.

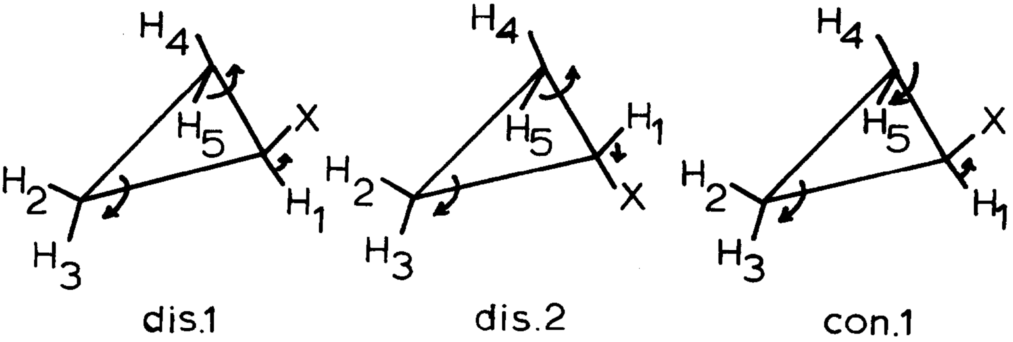


Fig. 1.

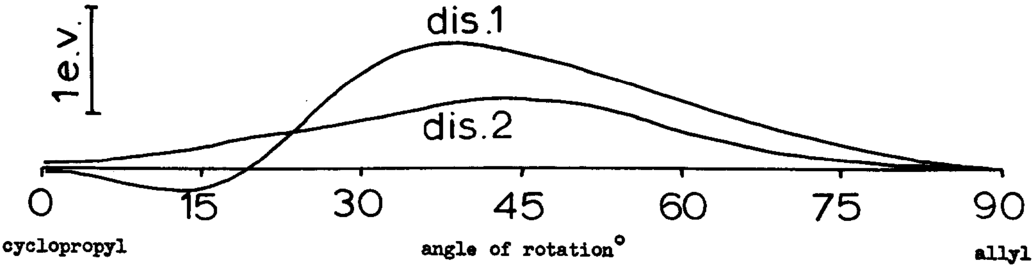
If however a cyclopropyl anion is formed prior to rearrangement, the local potential minimum has H-1 bent out of the plane of the ring so that there are still two distinct disrotatory modes (cf. the cationic case).[8] Since the effect of the leaving group is not specifically taken into account a direct comparison between the energetics for a concerted or non-concerted process cannot be made, however for a given process the relative energies for each mode of transformation should be reasonable. For each mode we have carried out calculations corresponding to 15° intervals in the rotation of the H_2-C_2-H_3 (H_3-C_3-H_4) planes with respect to the plane of the ring.

3. Results and Discussion.

(a) Ground state reactions.

Since it is the relative energies of the three paths which are of interest, the theoretical results are best represented in the form of energy difference diagrams. Fig. 2 shows the energy differences plotted as a function of angle of rotation for disrotatory modes 1 and 2 compared with the lowest energy mode conrotatory 1. The results using EHT are essentially the same although the charge distributions for individual species differ considerably from the SCF results as was found for the cationic case.[8] This is shown for the favoured mode conrotatory 1 in Table 1.

Fig. 2.



Energy differences for Disrotatory Modes 1 and 2 compared with lowest energy mode, conrotatory 1.

Table 1

SCF and EHT MO atomic charge distributions as a function of angle of rotation for conrotatory mode 1

Angle of Rotation	Method	H-1	H-2	H-3	H-4	H-5	C-1	C-2	C-3
0	SCF	−0·0612	−0·0594	−0·0655	−0·0594	−0·0655	−0·5184	−0·0853	−0·0853
	EHT	+0·0139	+0·0231	+0·0122	+0·0231	+0·0122	−0·9492	−0·0677	−0·0677
15	SCF	−0·0586	−0·0381	−0·0662	−0·0505	−0·0467	−0·4694	−0·1413	−0·1294
	EHT	+0·0172	+0·0416	+0·0130	+0·0345	+0·0290	−0·8698	−0·1451	−0·1199
30	SCF	−0·0485	−0·0395	−0·0578	−0·0331	−0·0509	−0·3900	−0·2193	−0·1610
	EHT	+0·0290	+0·0357	+0·0171	+0·0487	+0·0214	−0·7152	−0·2796	−0·1560
45	SCF	−0·0424	−0·0685	−0·0209	−0·0066	−0·0748	−0·1329	−0·3904	−0·2635
	EHT	+0·0460	+0·0010	+0·0461	+0·0625	−0·0038	−0·2610	−0·5707	0·3191
60	SCF	−0·0465	−0·0635	+0·0061	+0·0078	−0·0651	+0·0537	−0·4859	−0·4065
	EHT	+0·0511	+0·0100	+0·0660	+0·0660	+0·0106	+0·0190	−0·6883	−0·5353
75	SCF	−0·0506	−0·0482	+0·0086	+0·0081	−0·0486	+0·1184	−0·5041	−0·4837
	EHT	+0·0458	+0·0295	+0·0519	+0·0606	+0·0297	+0·0854	−0·6761	−0·6368
90	SCF	−0·0597	−0·0334	+0·0029	−0·0334	+0·0029	σ−0·0285 π+0·1725	+0·0747 −0·5863	+0·0747 −0·5863
	EHT	+0·0300	0·0447	+0·520	+0·0450	+0·0520	σ+0·0195 π+0·0690	−0·1217 −0·5345	−0·1217 −0·5345

By comparison with our results[8] for the latter, the energy differences between the various modes is slightly lower for the negatively charged species.

(b) Excited state reactions.

Longuet Higgins and Abrahamson[2] have given a qualitative discussion of the excited state transformation of cyclopropyl to allyl anion in terms of state correlation diagrams. However they assumed that the species involved remains planar about C_1-H_1 with respect to the ring throughout the transformation. Our calculations indicate that this is not the case and an initial pyramidal arrangement about C_1-H_1 is a local minimum for the cyclopropyl anion in the ground state and for the excited states which we have investigated. Table 2 shows the three lowest energy excited states and oscillator strengths calculated for the cyclopropyl anion and the corresponding states of allyl anion.

Table 2

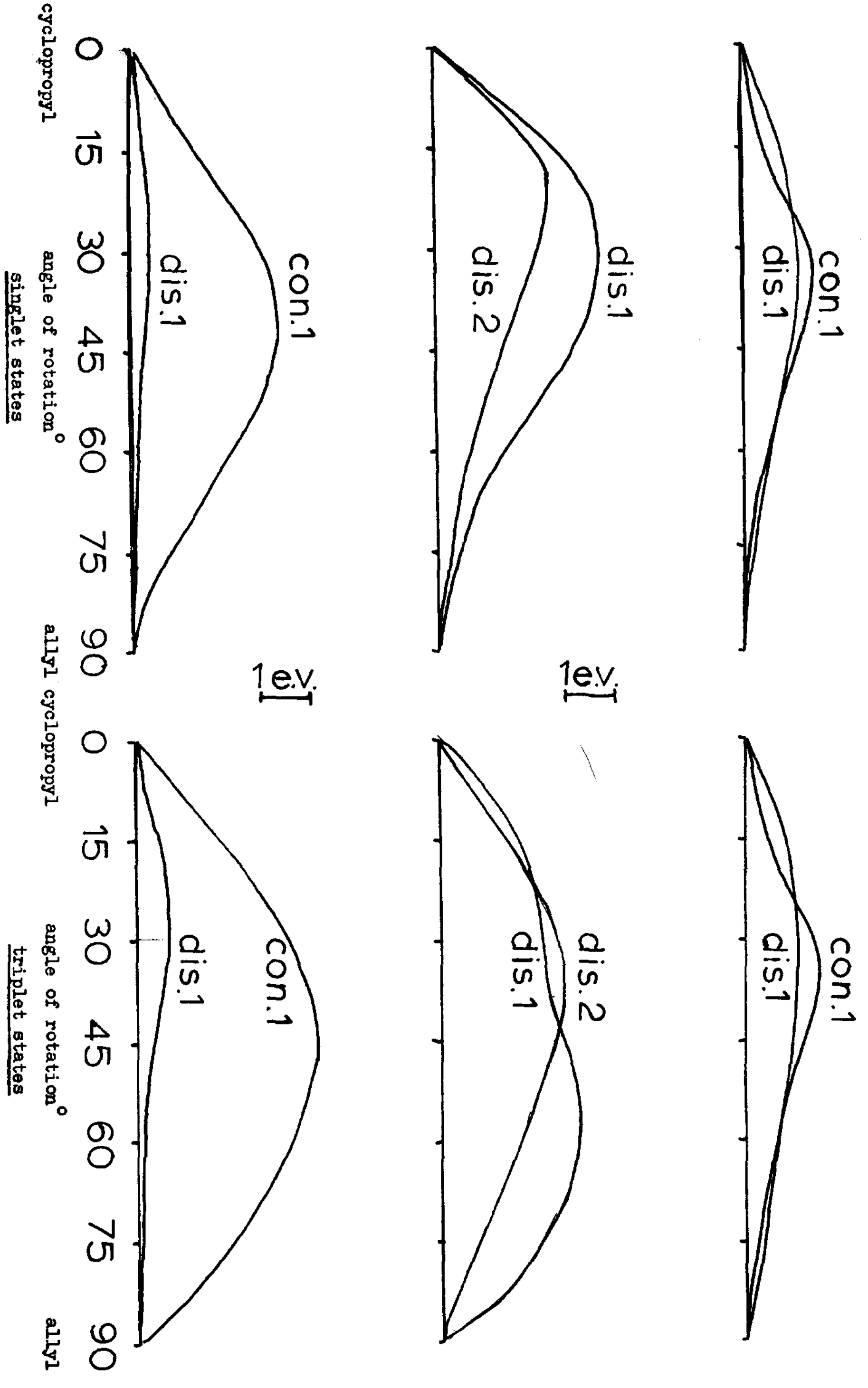
Calculated excited states of cyclopropyl anion and allyl anion.

		Cyclopropyl anion (H-1 pyramidal arrangement)				Allyl anion			
		C_s				C_{2v}			
		Singlet	f	Triplet		Singlet	f	Triplet	
I	A"	4·458	0·017	4·233	B_2	4·223	0·226	2·511	$(\pi^* \leftarrow \pi)$
II	A"	5·358	0·002	5·267	A_2	4·298	0	4·298	$(\sigma^* \leftarrow \pi)$
III	A'	5·778	0·014	5·694	B_1	5·135	0	5·135	$(\sigma^* \leftarrow \pi)$

There is little experimental evidence to compare with theory for the anionic species, but the interpretation of the electronic spectra of cyclopropane[9] and allyl cation,[8] previously discussed suggests that the results are reasonable. The location of the first $(\pi^* \leftarrow \pi)$ transition in allyl anion is similar to that predicted using a PPP SCF MO treatment.[10] Fig. 3 shows the energy difference diagrams for the three lowest energy singlet states and the corresponding triplet states.

The overall predictions concerning the mode of ring opening are essentially the same for both singlet and triplet states. For the first excited singlet and triplet states the favoured mode is clearly disrotatory, the energy for disrotatory mode 2 being slightly the lower. This would indicate that photochemical cyclization of allyl anion via the $(\pi^* \leftarrow \pi)$ transition should occur in a disrotatory fashion. The second and third excited state transformations of cyclopropyl to allyl anion are

Fig. 3.



Energy differences between the various modes of transformation of cyclopropyl to allyl anion as a function of angle of rotation.

predicted to be stereochemically clear cut and proceed via conrotatory and disrotatory 2 modes respectively. Transitions to the corresponding states in a monosubstituted cyclopropane precursor are all symmetry allowed, however unless the substituent contains a conjugating chromophore these states will almost certainly have energies corresponding to absorption in the vacuum ultraviolet region of the spectrum. From the published U.V. spectra[11] there is little doubt that there is considerable electronic interaction between the cyclopropyl and phenyl groups in phenyl cyclopropanes, and it seems likely that with the appropriately substituted phenyl cyclopropane at least some of the excited state transformation to the allylic system should be possible, in the U.V. region of the spectrum.

Acknowledgement.

One of us (G.S.) thanks the Science Research Council for the award of a Research Studentship.

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(References 4 and 5 contain a rather complete list of previous work on the cyclopropyl-allyl cation transformation).

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