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ORBITAL SYMMETRY CONSERVATION AND FRONTIER ORBITAL CONTROL IN THE REACTIONS OF ORGANIC RADICAL CATIONS

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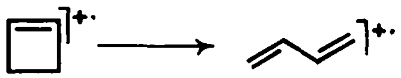
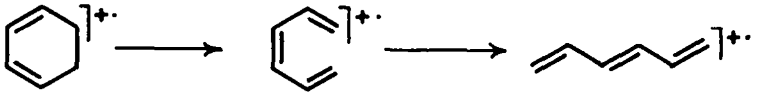
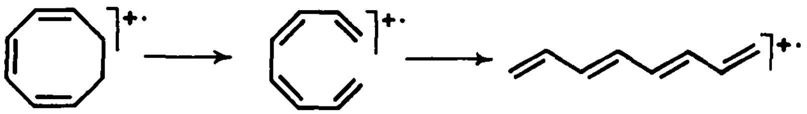
Abstract: Electrocyclic ring-openings, cycloreversions, cycloadditions, and sigmatropic rearrangements of organic radical cations are discussed in terms of a simple qualitative theory, based on orbital symmetry conservation or frontier orbital interactions. Special emphasis is placed on the photochemical reactions of the radical cations, numerous examples of which have recently been discovered experimentally. The theoretical models are in good general accord with the apparent facility with which radical cation rearrangements and fragmentations have been observed to take place, and provide some detailed predictions, especially with respect to stereochemistry, for further experimental testing.

Organic radical cations are best known in connection with mass-spectrometry, but several methods for generating them in low-temperature matrices have also been developed, thus allowing a thorough investigation of their photochemistry to be made. These methods include γ-irradiation of Freon matrices,[1,2] X-irradiation of Freon or Ar matrices,[1,3] simultaneous vacuum-u.v. irradiation and Ar-matrix deposition,[4] and two-photon ionization in Ar matrices.[4,5] As a result of recent studies, it is becoming apparent that radical cations can undergo a variety of very facile photochemical rearrangements and fragmentations. Some of the processes that have been observed or postulated are shown in Table 1, where the selection is intended to illustrate what is typical. A glance at this Table will reveal examples of radical cation analogues of electrocyclic ring-openings, sigmatropic shifts, and cycloreversions, such as are familiar in the chemistry of uncharged molecules. Hence there is at least a superficial resemblance between the reactions of singlet or triplet neutral species and those of doublet radical cations, and this resemblance prompts the question whether orbital symmetry or frontier orbital interactions play a part in determining the allowed pathways and stereochemistry of the radical cation reactions. Considerations of this type have already been discussed for the specific class of electrocyclic radical cation rearrangements.[7,16-18] During deliberations over recent experimental findings, however, it became apparent that some more general theoretical guidance as to the likely and unlikely reaction pathways would be helpful, particularly with regard to the photochemical transformations. What follows, therefore, is a simple extension of orbital control models to cover processes of the type exemplified in Table 1. In writing this paper, we have a threefold purpose: (i) to provide an elementary qualitative theoretical model of radical cation pericyclic reactions, (ii) to encourage further experiments aimed at testing the predictions of the theory, and (iii) to promote interest amongst organic chemists in this promising area, which hitherto has been largely the province of physical chemists and spectroscopists.

TABLE 1. Postulated and observed photoprocesses of radical cations.

1.		(Ref. 6)
2.		(Refs. 7 and 8)
3.		(Refs. 9 and 10)
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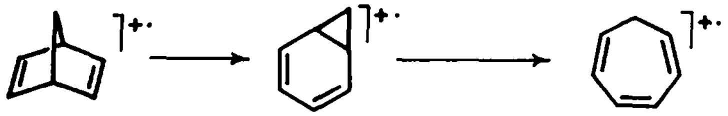
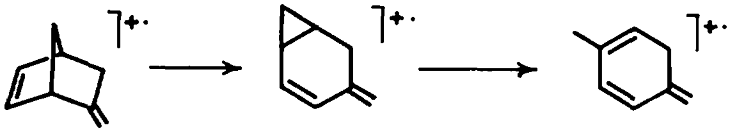
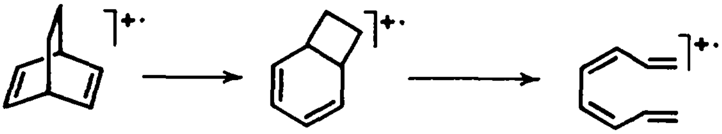
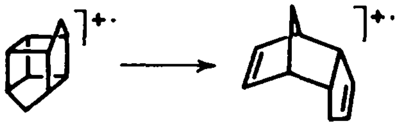
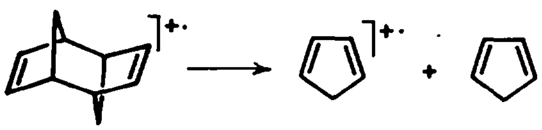
5.		(Ref. 12)
6.		(Ref. 13)
7.		(Ref. 9)
8.		(Ref. 14)
9.		(Ref. 15)

GENERAL CONSIDERATIONS

Descriptions of the orbital control of reaction paths — based on symmetry conservation,[19] frontier orbital interactions,[20] or orbital phase continuity[21] — are now part of the general currency of mechanistic organic chemistry. We have adopted the standard nomenclature and symbols of these well known treatments. In the Figures, for instance, molecular orbitals are depicted schematically as combinations of atomic orbitals solely to indicate their symmetry or phase properties; and, as is now conventional, a change from a shaded to an unshaded region denotes a change of phase in the wave-function.

Within the context of MO theory, the special feature of radical cations is that they each have a singly occupied molecular orbital (SOMO). For example, a ground state cation is derived by removal of one electron from the highest occupied orbital (HOMO) of the ground-state neutral parent molecule. As a consequence of their possessing a singly occupied orbital, radical cations generally have two relatively low-lying electronic excited states: one attained by promotion of an electron within the valence orbitals, i.e. from the highest energy doubly occupied orbital to the SOMO, the other by promotion of the electron in the SOMO to the lowest unoccupied orbital (LUMO). Although a fully adequate description of these excited states requires the inclusion of considerable configuration-interaction,[3b,7] the simple classification of the states as (π,π), (σ,π), or (σ,σ) on the one hand, and as (π,π^*) or (σ,σ^*) on the other, has an approximate validity, and will be adopted throughout this paper. It will be seen later that the existence of these two states is likely to remove some of the restrictions on photochemical reaction paths which might otherwise exist.

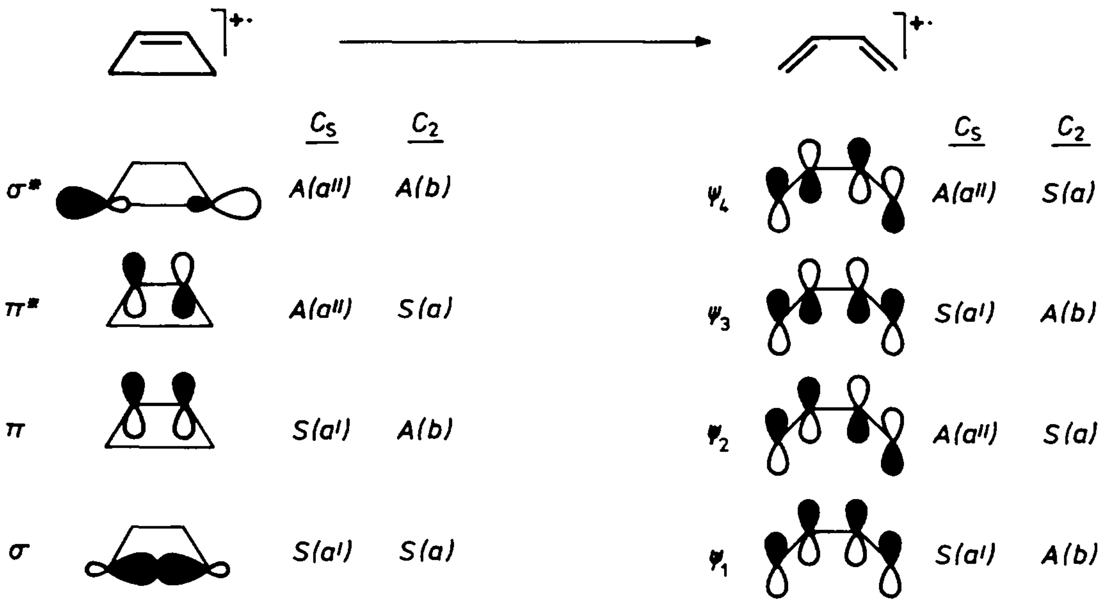
ELECTROCYCLIC REACTIONS

Orbital symmetry treatments of the prototype electrocyclic ring-openings of neutral cyclobutene, cyclohexa-1,3-diene, and higher cyclic polyenes were first proposed by Woodward and Hoffmann[22] and by Longuet-Higgins and Abrahamson.[23] Since then, similar treatments of electrocyclic processes in radical cations have been published by several groups,[7,16-18] with special emphasis on ground state correlations. Examples of photochemical electrocyclic processes in radical cations are found in Table 1 (Reactions 1-3, 5, and 7). The schemes we outline below do not differ essentially from the simpler versions of those previously advanced, and are included both for completeness and to emphasize the excited state correlations.

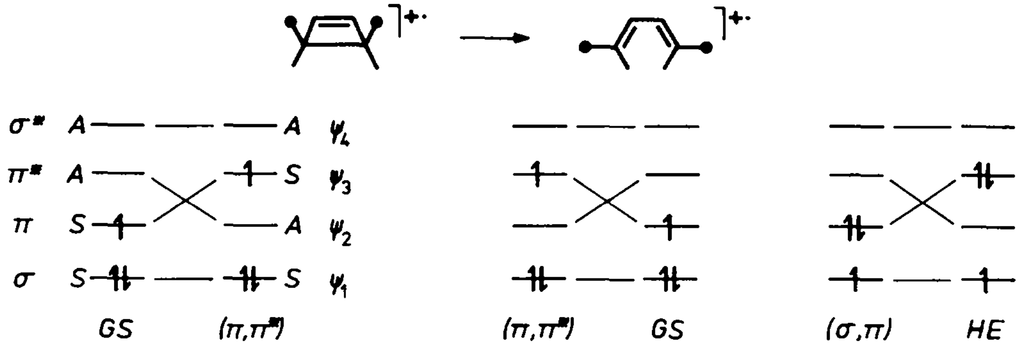
[Cyclobutene]$^{+\cdot}$ $\rightleftarrows$ [buta-1,3-diene]$^{+\cdot}$

Figure 1 shows the important orbital correlations for the ring-opening of [cyclobutene]$^{+\cdot}$ to [buta-1,3-diene]$^{+\cdot}$. The top section depicts, for both reactant and product, the molecular orbitals most directly involved in the reaction. For the reactant, they are the orbitals associated with the C-C bond that is broken (σ and σ^*), and also the π and π^* orbitals, while for the product, they are the set of four π orbitals (ψ_1 - ψ_4). Each of these orbitals is classified by symmetry labels (S: symmetrical; A: antisymmetrical) relating to (i) disrotatory opening, where $\underline{C}_s$ (mirror) symmetry is maintained, and (ii) conrotatory opening, where $\underline{C}_2$ (two-fold axial) symmetry is maintained. Alternative symmetry labels appropriate to the two point groups ($\underline{C}_s$:$\underline{a}'$,$\underline{a}''$; $\underline{C}_2$:$\underline{a}$,$\underline{b}$) are also included. In the lower part of Figure 1, orbital correlations for both disrotatory and conrotatory openings are elaborated for each of the ground (GS), (π,π^*), and (σ,π) states of [cyclobutene]$^{+\cdot}$. The correlations rely on the assumption that reactant orbitals will transform into product orbitals which have the same symmetry with respect to the symmetry element that is maintained during the transformation. These correlations indicate that, for the disrotatory opening, the (π,π^*) state of

FIGURE 1. Orbital correlations for the electrocyclic opening of $[\text{cyclobutene}]^{+\cdot}$



(i) Disrotatory opening — C_s (mirror) symmetry maintained.



(ii) Conrotatory opening — C_2 (two-fold axial) symmetry maintained.

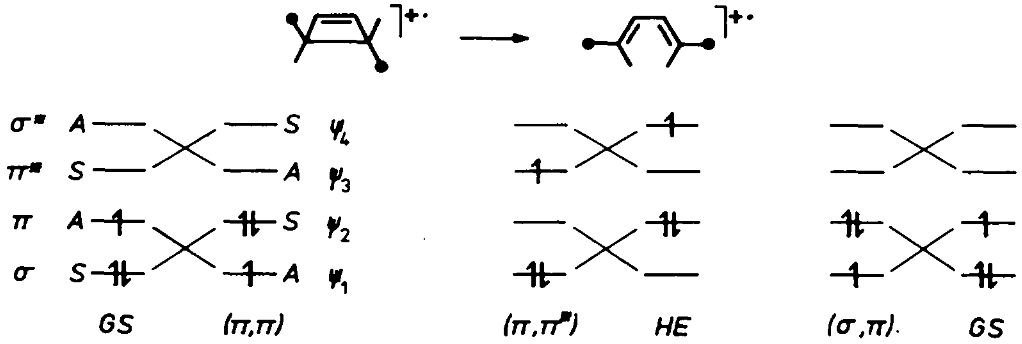
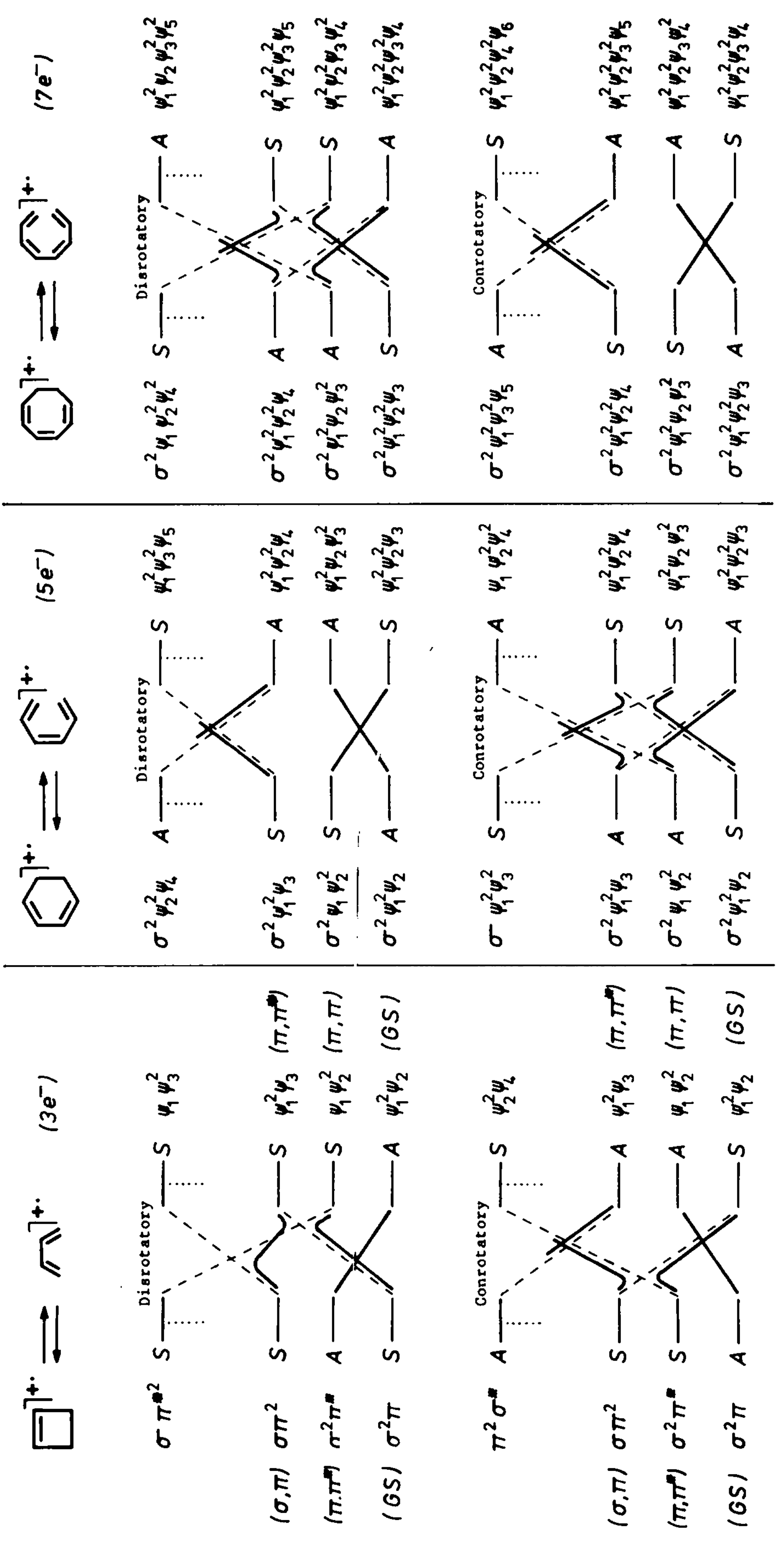


FIGURE 2. State correlations for radical cation electrocyclic processes involving 3, 5, and 7 electrons.



[cyclobutene]$^{+\cdot}$ should transform directly into the ground state of [buta-1,3-diene]$^{+\cdot}$ and the (σ,π) state only into a highly excited (HE) state; while for the conrotatory opening, it is the (σ,π) state which correlates directly with the product ground state. In this model, therefore, both modes of ring-opening are photochemically allowed, the preferred pathway depending on the particular excited state involved. Moreover, neither disrotatory nor conrotatory opening is associated with a ground state-ground state correlation, corresponding to a favourable thermal reaction.

The relationships shown in Figure 1, (i) and (ii), are displayed more compactly as state correlation diagrams in the left-hand portion of Figure 2. Broken lines show correlations, derived directly from Figure 1, that would obtain in the absence of configuration-interaction, but more realistic correlations (solid lines) observe a non-crossing rule for states of the same symmetry.[23] As first explained for the cyclopropyl and allyl radicals,[23] state correlation diagrams constructed on this basis give a qualitative indication of energy barriers in the various pathways. It can thus be seen that the (σ,π) state of [cyclobutene]$^{+\cdot}$, which has the electronic configuraton $\sigma\pi^2$, is likely to open predominantly by conrotation, dropping down to the lowest symmetrical state in the process. The alternative disrotatory pathway has an appreciable energy barrier to be surmounted. The (π,π^*) state, in contrast, should open mainly in a disrotatory manner. The ground state of [cyclobutene]$^{+\cdot}$ correlates either with the (π,π^*) state of the product (disrotation) or with the lower energy (π,π) state (conrotation). The ring-opening from the ground state will thus involve a substantial energy barrier whichever path is followed, but this barrier is likely to be lower for the conrotatory pathway, which should therefore be favoured. By similar reasoning, the ring-closure of [buta-1,3-diene]$^{+\cdot}$, although energetically unfavourable and thus unlikely to occur in reality, would be expected to proceed by disrotation from the ground and (π,π^*) states, and by conrotation from the (π,π) state.

We should not necessarily expect high stereospecificity in all these reactions. Upper excited states may readily undergo non-radiative decay to lower excited states or to the vibrationally excited electronic ground state. Distinctions amongst the various states will be blurred if this happens to a large extent. Additionally, the considerable excess vibrational energy, which may well be present in the excited states as a consequence of the initial electronic excitation of a cation, will reduce the subsequent kinetic effect of differences in the heights of energy barriers on the available reaction paths. High stereospecificity is most likely to be found where the lowest excited state of the reactant can correlate directly with the ground state of the product. In the ring-opening of [cyclobutene]$^{+\cdot}$, assuming the states are ordered correctly in Figure 2, this condition is met by the (π,π^*) state, which is expected, therefore, to undergo ring-opening stereospecifically in a disrotatory manner.

[Cyclohexa-1,3-diene]$^{+\cdot}$, [cycloocta-1,3,5-triene]$^{+\cdot}$, and higher cyclic polyene radical cations.

Orbital correlations similar to those described above for [cyclobutene]$^{+\cdot}$ may be worked out for the electrocyclic openings of [cyclohexa-1,3-diene]$^{+\cdot}$ and [cycloocta-1,3,5-triene]$^{+\cdot}$, and for the reverse reactions, the ring-closures of [hexa-1,3,5-triene]$^{+\cdot}$ and [octa-1,3,5,7-tetraene]$^{+\cdot}$, respectively. These lead to the state correlation diagrams shown in Figure 2 at centre and right, the first of which should be compared to that given by Shida *et al.*[7] In these diagrams, states are identified by their electronic configurations, making use of conventional labels (ψ_n) for the orbitals of conjugated π-systems. For each of the four cations shown, the lowest three states, in order of increasing energy, are the ground state, the (π,π) state, and the (π,π^*) state. From the diagrams it may be deduced that, for the six-carbon five-electron system, the ground and (π,π) states will undergo predominantly disrotatory transformations and the (π,π^*) state conrotatory transformations, while for the eight-carbon seven-electron system, the reverse will hold. This applies to both ring-opening and ring-closure. As suggested above, highest stereospecificity in these reactions is expected for those processes where the lowest excited state of the reactant correlates directly with the product ground state. This condition obtains in the disrotatory ring-opening of the (π,π) state ($\sigma^2\psi_1\psi_2^2$) of [cyclohexa-1,3-diene]$^{+\cdot}$ and its reverse reaction, and the conrotatory ring-opening of the (π,π) state ($\sigma^2\psi_1^2\psi_2\psi_3^2$) of [cycloocta-1,3,5-triene]$^{+\cdot}$ and its reverse reaction.

Obviously the treatment which we have elaborated for [cyclobutene]$^{+\cdot}$, [cyclohexa-1,3-diene]$^{+\cdot}$, and [cycloocta-1,3,5-triene]$^{+\cdot}$ may be readily extended to higher systems. Generalized predictions for the stereochemistry of the electrocyclic reactions of radical cations are presented in Table 2.

TABLE 2. Favoured electrocyclic modes for radical cations.

No.of Electrons	Ground State	Excited State (σ,π)	(π,π)	(π,π*)
3	conrotatory† disrotatory‖	conrotatory†	conrotatory‖	disrotatory
4n+1 (n=1,2,3...)	disrotatory	-	disrotatory	conrotatory
4n+3 (n=1,2,3...)	conrotatory	-	conrotatory	disrotatory

† Ring-opening only. ‖ Ring-closure only.

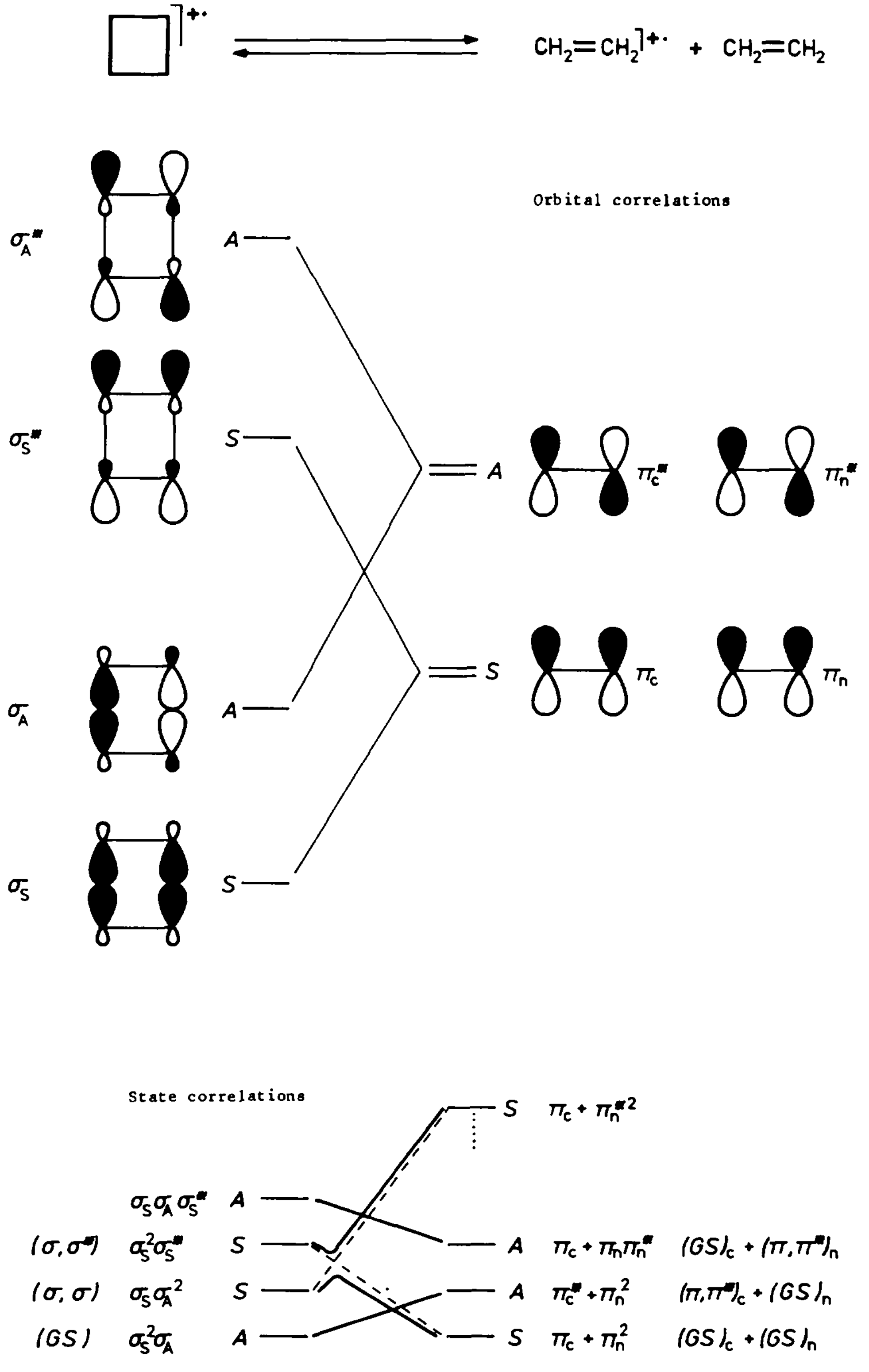
CYCLOREVERSIONS AND CYCLOADDITIONS

Symmetry rules for cycloadditions and cycloreversions of neutral molecules were first enunciated by Hoffmann and Woodward.[24] Adaptations of these rules to the analogous radical cation reactions are presented in the following sections. Examples of cycloreversions of radical cations are found in Table 1 (Reactions 8 and 9), but we know of no corresponding cycloadditions that have been reasonably well established.

The [2+2]$^{+\cdot}$ reaction: [cyclobutane]$^{+\cdot}$ $\rightleftarrows$ [ethylene]$^{+\cdot}$ + ethylene.

Figure 3 shows the relevant MO's and their correlations for the cycloreversion of [cyclobutane]$^{+\cdot}$, and the corresponding cis-cis [2+2]$^{+\cdot}$ cycloaddition of [ethylene]$^{+\cdot}$ and ethylene. Both processes are assumed to take place with retention of mirror symmetry with respect to a plane perpendicular to the ring and parallel to the two σ-bonds which are broken or formed; the labels S (symmetrical) and A (antisymmetrical) refer to this mirror plane. Subscripts c and n are used to denote cation and neutral molecule, respectively; thus π_c denotes the π orbital of [ethylene]$^{+\cdot}$ and π_n that of ethylene. In order to construct the state correlation diagram, it is necessary to note that, amongst the orbitals directly involved in the transformation, a doubly occupied orbital of [cyclobutane]$^{+\cdot}$ must correlate with a doubly occupied orbital of the neutral ethylene molecule, because the radical cation has only one electron in the π_c or π_c* orbitals. With this constraint, a unique set of state correlations is found, as shown in the lower part of Figure 3. The state correlations suggest that cycloreversion of [cyclobutane]$^{+\cdot}$ should occur more readily from the (σ,σ*) state than from the ground or (σ,σ) states. The reverse reaction, the [2+2]$^{+\cdot}$ cycloaddition, is especially favoured for ground state ethylene and the (π,π*) state of [ethylene]$^{+\cdot}$.

FIGURE 3. Orbital and state correlations for the cycloreversion of [cyclobutane]$^{+\cdot}$ into [ethylene]$^{+\cdot}$ and ethylene, and for the corresponding [2+2]$^{+\cdot}$ cycloaddition.



The same conclusion with regard to the $[2+2]^{+\cdot}$ cycloaddition may be reached more quickly by consideration of frontier orbital interactions. It should be noted that the (π,π^*) state of $[\text{ethylene}]^{+\cdot}$ has its LUMO — the vacant π-orbital — at lower energy than the SOMO. Figure 4 shows how frontier orbital interactions between the (π,π^*) state of $[\text{ethylene}]^{+\cdot}$ and the ground state neutral molecule favour the cis-cis cycloaddition. Frontier orbital interactions also favour a cis-trans $[2+2]^{+\cdot}$ cycloaddition between ground state ethylene and either ground state or the (σ,π) state of $[\text{ethylene}]^{+\cdot}$, although the geometric requirements of such a reaction are, of course, formidable (Figure 5).

FIGURE 4. Favourable frontier orbital interactions for the (π,π^*) state of $[\text{ethylene}]^{+\cdot}$ and the ground state of ethylene.

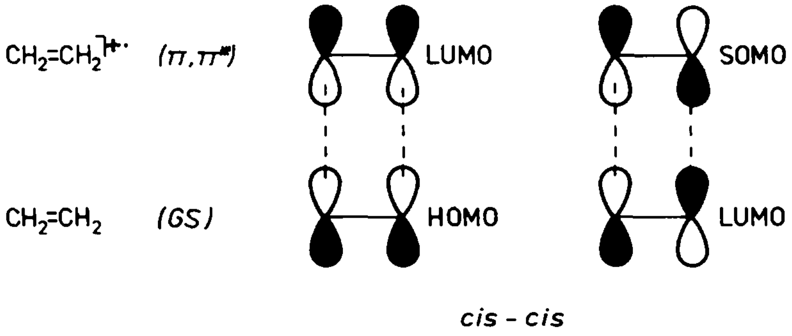


FIGURE 5. Favourable frontier orbital interactions for the ground state or (σ,π) state of $[\text{ethylene}]^{+\cdot}$ and the ground state of ethylene.

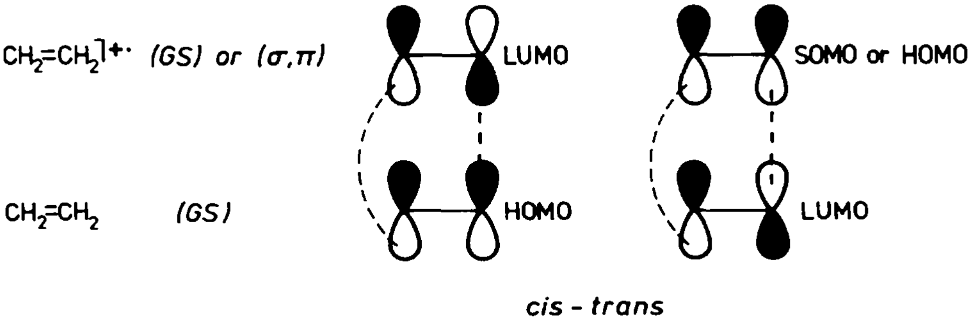
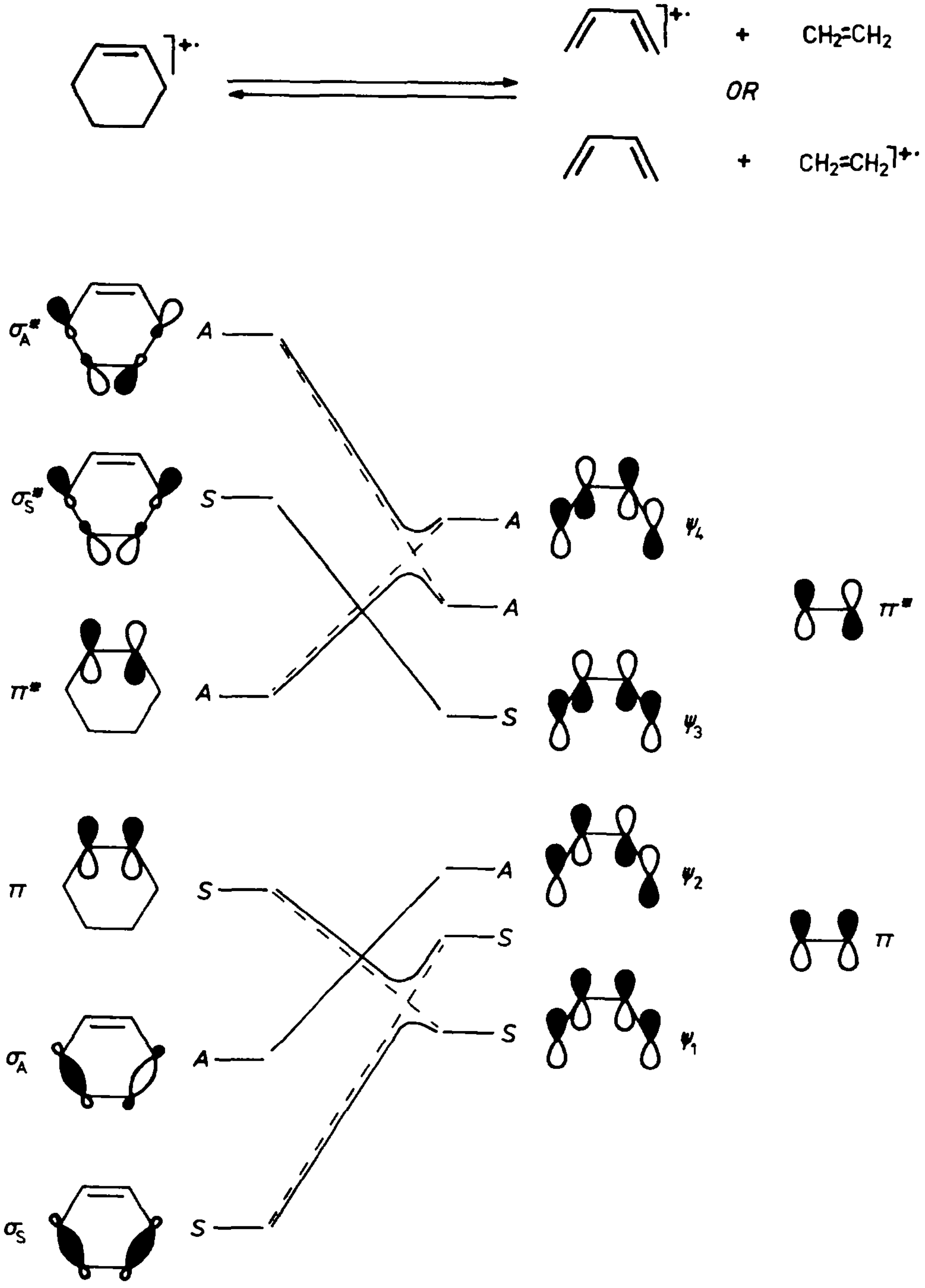


FIGURE 6. Orbital correlations for the cycloreversion of [cyclohexene]$^{+\cdot}$ and the corresponding $[2+4]^{+\cdot}$ cycloadditions.

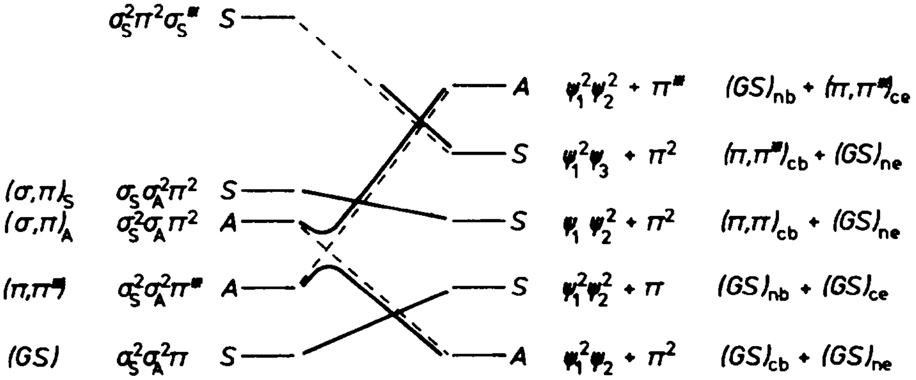


[2+4]$^{+\cdot}$ cycloreversions and cycloadditions.

Analysis of the cycloreversion of [cyclohexene]$^{+\cdot}$ and the corresponding cycloadditions is considerably more complicated than that of the [2+2]$^{+\cdot}$ reactions. Not only are there more orbitals involved, but two distinct reactions may take place in either direction. Thus [cyclohexene]$^{+\cdot}$ may decompose either into [butadiene]$^{+\cdot}$ and ethylene or into [ethylene]$^{+\cdot}$ and butadiene; and this possibility increases the number of plausible reaction pathways. Figure 6 shows orbital correlations for the cis-cis reaction, in which mirror symmetry is retained throughout. Broken lines denote correlations that are suggested by the forms of the orbitals, but avoided crossings of orbitals with the same symmetry give rise to the correlations shown as solid lines. From the orbital correlations of Figure 6, we can construct the state correlation diagram shown in Figure 7. On the right-hand side of this diagram, subscripts are used to identify neutral butadiene (nb), cationic butadiene (cb), neutral ethylene (ne), and cationic ethylene (ce). The relative ordering of the states on this side of the diagram may not be immediately obvious, but is based on vertical ionization potentials derived from the photoelectron spectra of ethylene and buta-1,3-diene.[25] The relevant values are 10.5 eV for the π orbital of ethylene, and 9.0 and 11.5 eV for ψ_2 and ψ_1, respectively, of butadiene. It is clear that, for the ground state species, [butadiene]$^{+\cdot}$ and neutral ethylene are a lower energy pair than [ethylene]$^{+\cdot}$ and neutral butadiene, since the first ionization potential of butadiene is 1.5 eV lower than that of ethylene. Moreover, this difference of 1.5 eV compares with the larger difference of 2.5 eV between ψ_2 and ψ_1 of butadiene. These data suggest, therefore, that the ordering of states adopted for the right-hand side of Figure 7 is the most likely. On the left-hand side of the Figure, the ordering of the states of [cyclohexene]$^{+\cdot}$ is more straightforward, except that it should be noted that two (σ,π) states are possible: symmetric (S) and antisymmetric (A). These probably lie very close in energy, with the antisymmetric state being the lower of the two.

Interpretation of the state correlation diagram as discussed above leads to the conclusion that the $(\sigma,\pi)_A$ state of [cyclohexene]$^{+\cdot}$ should readily undergo cycloreversion to ground state [butadiene]$^{+\cdot}$ and ethylene, and that the cis-cis [2+4]$^{+\cdot}$ cycloaddition of butadiene and [ethylene]$^{+\cdot}$ is especially favourable. Other processes all have higher energy barriers to overcome.

FIGURE 7. State correlations for the cycloreversion of [cyclohexene]$^{+\cdot}$ and the corresponding [2+4]$^{+\cdot}$ cycloadditions.



Similar state correlations may be constructed for <u>cis-trans</u> and <u>trans-trans</u> cycloadditions and cycloreversions. As shown above for the $[2+2]^{+\cdot}$ cycloaddition, however, the consideration of frontier orbital interactions in the $[2+4]^{+\cdot}$ cycloadditions yields the same stereochemical predictions in a much simpler manner. The penalty for the simplification is that some of the detail is lost, for example the interesting difference between the ground state reaction of $[\text{ethylene}]^{+\cdot}$ and butadiene and that of $[\text{butadiene}]^{+\cdot}$ and ethylene. Predictions for the stereochemistry of $[2+4]^{+\cdot}$ cycloadditions and cycloreversions, based on frontier orbital interactions, are included in Table 3.

General cycloreversions and cycloadditions.

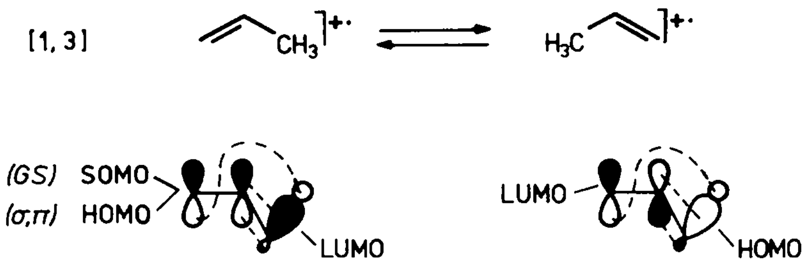
The preferred stereochemical outcomes of $[m+n]^{+\cdot}$ cycloadditions and the corresponding cycloreversions, as predicted by orbital symmetry models or frontier orbital interactions, are set out in Table 3. Some of the orbitally preferred routes — <u>cis-trans</u> or <u>trans-trans</u> additions or cycloreversions in small rings — are geometrically unfavourable, of course. Some processes, on the other hand — where the lowest excited states correlate directly in a <u>cis-cis</u> manner with ground state products — will be especially favourable. It is amongst this latter group of reactions that a high degree of stereospecificity is most likely to be found. Finally, it is worth pointing out that, with these reactions, there is a distinct similarity between the predictions for both neutral molecules and radical cations. There are, however, no direct ground state-ground state correlations for the cations, except for charge-transfer pairs such as butadiene and $[\text{ethylene}]^{+\cdot}$ (Figure 7), and this is likely to lead to reduced stereospecificity in the ground state reactions of these species.

<u>TABLE 3</u>. Orbitally preferred stereochemistry of $[m+n]^{+\cdot}$ cycloadditions and the corresponding cycloreversions. The cycloadditions are between two ground state reactants or between one excited state and one ground state.

No.of Electrons = m+n-1	Ground State	Excited State				
		(σ,σ)	(σ,σ^*)	(σ,π)	(π,π)	(π,π^*)
3	cis-trans	cis-trans†	cis-cis† or trans-trans	cis-trans‖	-	cis-cis‖ or trans-trans
5	cis-cis or trans-trans	-	-	cis-cis† or trans-trans	cis-cis‖ or trans-trans	cis-trans
4n+3 (n=1,2..)	cis-trans	-	-	-	cis-trans	cis-cis or trans-trans
4n+5 (n=1,2..)	cis-cis or trans-trans	-	-	-	cis-cis or trans-trans	cis-trans

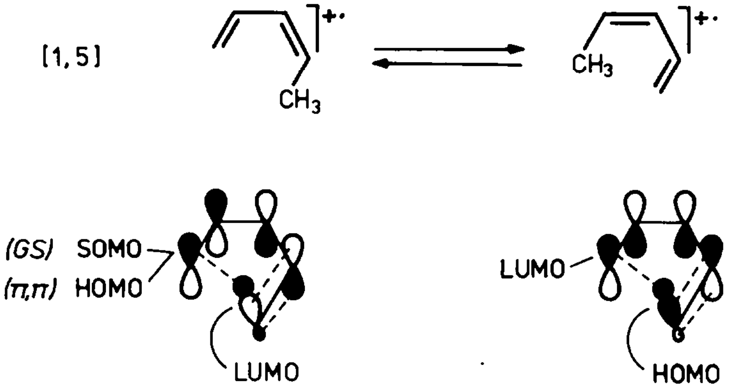
† Cycloreversion only. ‖ Cycloaddition only.

FIGURE 8. Favourable frontier orbital interactions for radical cation sigmatropic H-shifts of order [1,3] and [1,5].

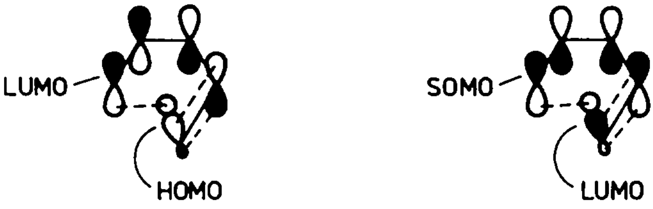


Ground and (σ,π) states — antarafacial

(π,π^*) state — suprafacial



Ground and (π,π) states — suprafacial



(π,π^*) state — antarafacial

SIGMATROPIC SHIFTS

The orbital control of sigmatropic shifts in neutral molecules was dealt with first by Woodward and Hoffmann.[26] Because of low symmetry in the reacting systems, orbital and state correlations based on conservation of symmetry are inapplicable to sigmatropic shifts. The most straightforward models make use of frontier orbital interactions or orbital phase continuity to indicate the lowest energy pathways. In the following treatment of sigmatropic shifts in radical cations, we have adopted the former approach. Examples of sigmatropic shifts in radical cations are found in Table 1 (Reactions 4-7).

Radical cation sigmatropic shifts of order [1,3] and [1,5].

The early stages of a sigmatropic shift may be considered as an interaction between two separate moieties in the molecule· (i) the original π-system, and (ii) the σ-bond which is to be broken. Figure 8 shows HOMO- or SOMO-LUMO interactions for [1,3] and [1,5] hydrogen-shifts in the ground states and lowest two excited states of $[\text{propene}]^{+\cdot}$ and $[\text{penta-1,3-diene}]^{+\cdot}$, respectively. As noted above, the most striking features of the (π,π*) states of the radical cations are low energy LUMO's, which lie below the SOMO's. In the frontier orbital model of the early stages of the reaction, positive overlap between the appropriate orbitals of the π-system and the C-H σ-bond indicates the beginning of a lower energy pathway than where overlap is negative. From Figure 8, it is clear that orbital preferences for the [1,3] H-shift are the geometrically unfavourable antarafacial pathway in the ground and (σ,π) states, and the suprafacial route for the (π,π*) state. These preferences are reversed, mutatis mutandis, for the [1,5] H-shift. suprafacial for the ground and (π,π) states, and anatarafacial for the (π,π*) state.

If the migrating group is capable of inversion, i.e. if is is able to migrate in an antarafacial manner with respect to its own configuration, as is possible with methyl or methylene groups, for example, the possible reaction pathways are doubled in number and become those which are included in Table 4.

TABLE 4. Orbitally preferred stereochemistry of radical cation sigmatropic shifts of order [i,j].

i + j	Ground State	Excited State (σ,π)	(π,π)	(π,π*)
4	supra-antara	supra-antara	-	supra-supra or antara-antara
4n+2 (n=1,2..)	supra-supra or antara-antara	-	supra-supra or antara-antara	supra-antara
4n+4 (n=1,2..)	supra-antara	-	supra-antara	supra-supra or antara-antara

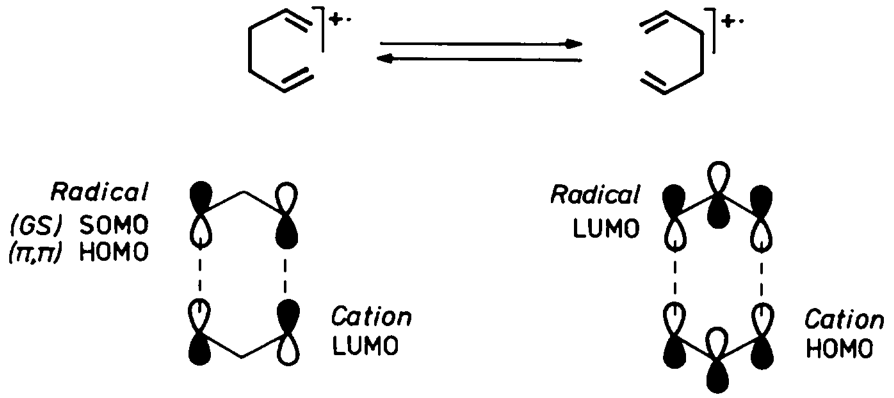
Radical cation sigmatropic shifts of order [3,3].

The prototype radical cation Cope rearrangement may be treated as the interaction between an allyl radical and an allyl cation. The HOMO- and SOMO-LUMO interactions in this system are depicted in Figure 9. The ground and (π,π) states of $[\text{hexa-1,5-diene}]^{+\cdot}$ should rearrange in the suprafacial-suprafacial (or the geometrically unlikely antarafacial-antarafacial) manner, while the (π,π^*) state should rearrange only in the less favourable suprafacial-antarafacial manner. In the latter state, therefore, the molecule is more likely to drop down to the (π,π) state.

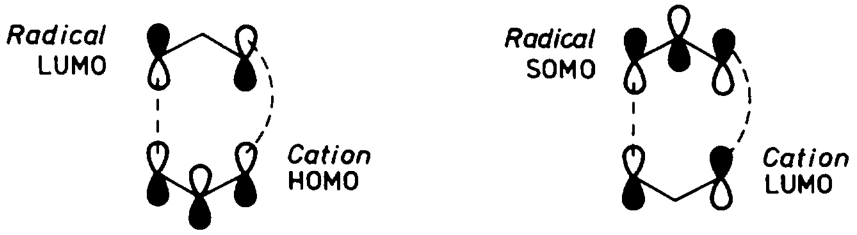
The general radical cation [i,j] sigmatropic shift.

Extension of the preceding discussion to higher systems leads to the generalized rules given in Table 4. As with cycloadditions and cycloreversions, some of the orbitally favoured pathways are geometrically unfavourable and unlikely to be followed. Perhaps the most significant feature of Table 4 is that a suprafacial-suprafacial shift is always possible photochemically, from one or other of the lowest two excited states.

FIGURE 9. Favourable frontier orbital interactions for the radical cation sigmatropic shift of order [3,3].



Ground and (π,π) states — suprafacial-suprafacial



(π,π^*) state — suprafacial-antarafacial

CONCLUSIONS

In the foregoing sections, we have presented a simple qualitative theory of organic radical cation electrocyclic reactions, cycloadditions, cycloreversions, and sigmatropic rearrangements. The theory is based throughout on orbital symmetry conservation or frontier orbital interaction models, which are well established for the analogous reactions of neutral molecules. Organic radical cations have doublet ground states which are derived, in MO theory, by removal of an electron from the HOMO of the parent neutral molecule, thus leaving a singly occupied orbital (SOMO). As a result of this electronic configuration, the radical cations possess two relatively low-lying doublet excited states, which may be attained by promotion of an electron from the highest doubly occupied orbital to the SOMO, or from the SOMO to the LUMO. The existence of the doublet ground state and two relatively low-lying excited states leads to significant differences in the theoretical predictions for radical cations and neutral molecules. Foremost amongst these is that there are few restrictions on the stereochemistry of the photochemical reactions of radical cations, since the lowest two excited states generally have different orbital-phase or symmetry properties, and different pathways will be favoured for each of them. Moreover, in the electrocyclic, cycloaddition, and cycloreversion reactions of radical cations, direct correlations between the reactant excited state and product ground state are a recurring feature. Such correlations are possible because of the unpaired electron, and are not found in the analogous excited state reactions of neutral molecules. These indications from the qualitative theory, together with the fact that radical cations are higher in energy and more loosely bound than their neutral parents, form a general rationalization of the very facile and extensive photochemical rearrangements that radical cations can undergo.

Whether consistent patterns of stereospecificity can be found in these reactions, whether different pathways can occur for the lowest two excited states, and, indeed, whether the reactions are concerted or stepwise all remain to be demonstrated experimentally. In the meantime, there is every sign that the photochemistry of organic radical cations is a rich field for investigation.

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