and would preferably proceed with stereochemical inversion at the displacement site. All three reaction systems (mass spectrometric, thermolytic, and photolytic) should exhibit similar reactivity for internal radical displacement reactions when the radical site[36] is generated by an initial homolytic cleavage.

Reaction probabilities for β cleavage in thermal and photochemical reactions should be directly related to probability of class I β cleavage in the mass spectrometer (eq 8 will apply in all three cases). Photochemical α-cleavage reactions from $n \rightarrow \pi^*$ states should be directly related to the similar class I reactions in a mass spectrometer (eq 11 should apply in both cases). The related thermal reactions will be highly dependent on the $n \rightarrow \pi^*$ excitation energy of the initial system, and should not be directly related to the mass spectral reactivity.

The relationship between mass spectra and thermal and photochemical fragmentation of molecules is obviously complex. The PMO method together with an analysis of the reactive states of ions offers a simple semiquantitative procedure for interpreting mass spectra and predicting relationships between mass spectral, thermal, and photochemical reactions. Two additional factors should be considered prior to application of these procedures to specific cases. (1) The internal excitation energy for ions that give rise to class I reactions will generally be larger than the excitation energies accessible in thermal and photochemical experiments. This means that highly selective thermal and photoprocesses will very often not have analogs in mass spectra, and many of the high-energy (low probability) processes in mass spectra will not have analogs in thermal and photochemical reactions. In this regard field ionization mass spectra[37] should offer a direct basis for correlation of mass spectra with thermal and photochemical processes. Ion energy distribution on field ionization is much narrower than in electron-impact studies, and the field ionization time scale is substantially different than that for electron-impact mass spectra.[38] Because of the high potentials in the FI source, ion drawout is much faster than for EI sources and the majority of the normal fragment ions in FI mass spectra are formed in less than 10^{-9} sec after ionization. Most of these "field-induced" dissociations are simple cleavage reactions and should be considered as class III reactions. The numerous and often very intense metastable transitions in FI mass spectra represent reactions that very probably occur from the electronic ground state of the reacting ion. (2) It is always possible, and in many cases likely, that a given class I reaction in the mass spectrometer occurs from a rearranged molecule ion that is not accessible at modestly high thermal or photochemical energies. For these reactions the analogy will also break down.

The following paper[39] illustrates the application of these procedures to several selected electrocyclic reactions.

Acknowledgments. The National Institutes of Health has generously supported our work.

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(37) H. D. Becky and H. Hey, *Org. Mass Spectrom.*, 1, 47 (1968).

(38) H. D. Becky, H. Knöppel, G. Metzinger, and P. Schultze, *Advan. Mass Spectrom., Proc. Conf. Univ. London*, 3, (1964).

(39) R. C. Dougherty, *J. Amer. Chem. Soc.*, 90, 5788 (1968).

Application of the Perturbation Molecular Orbital Method to the Interpretation of Organic Mass Spectra. The Hexahelicine Rearrangement and Other Electrocyclic Mass Spectrometric Reactions

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Abstract: This paper will explore the application of first-order perturbation theory (the PMO method)[1] to the interpretation of several mass spectrometric reactions using the analysis of reactive states of ions previously developed.[1] Our purpose is to illustrate the broad utility of the PMO approach in dealing with electrocyclic reactions. In the previous paper we developed the basis for classification of mass spectral reactions according to the electronic state of the reacting ion. Class I reactions predominantly occur from low-lying (fully bonding) electronic states of the parent. Class II reactions occur from excited electronic states. Observation of a prominent metastable ion for a reaction of an odd-electron parent indicates that the half-life of the parent is sufficiently long to place the reaction in class I. Class II reactions include those reactions of odd-electron parents for which metastable ions are not observed, and most of the reactions of doubly charged ions. The hexahelicene rearrangement, the retro-Diels–Alder reaction, and the McLafferty rearrangement are considered in these terms.

Once we have classified mass spectral reactions according to their electronic type,[1] application of modern theories of reactivity[2] to these reactions is a straightforward problem. Frontier orbital arguments and orbital symmetry selection rules[2b] can be applied

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(1) R. C. Dougherty, *J. Amer. Chem. Soc.*, 90, 5780 (1968).

(2) (a) M. J. S. Dewar, *Tetrahedron Suppl.*, 8, 75 (1966); (b) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1, 17 (1968).

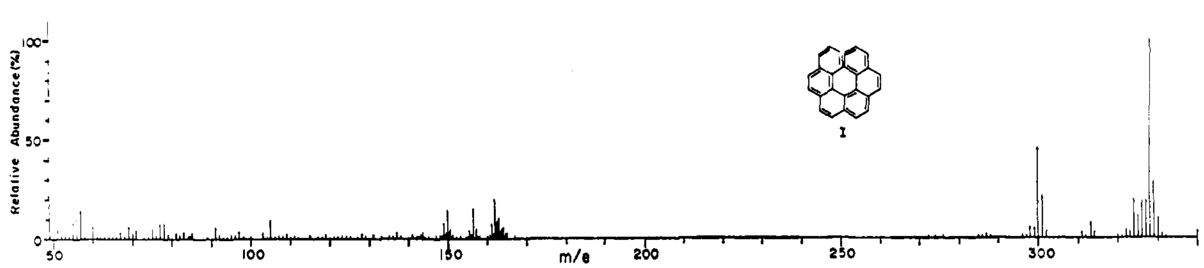
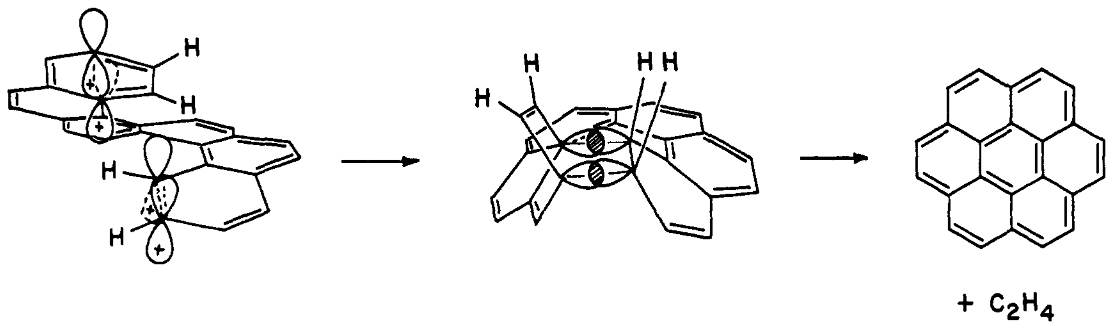


Figure 1. Mass spectrum of hexahelicene.

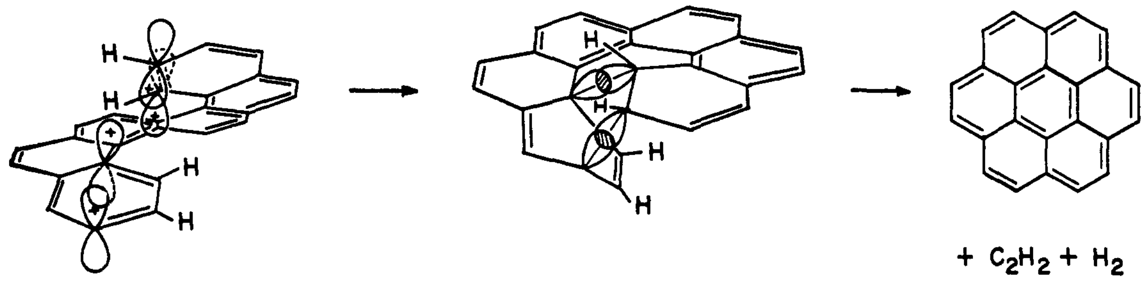
to those reactions that involve symmetric electronic states; however, the number of cases that satisfy this requirement is limited. Dewar's rules for electrocyclic reactions[2a] can be applied to any example without consideration of electronic symmetry. Class I reactions should follow the rule for thermal electrocyclic processes.[1]

Thermal Electrocyclic Reactions Take Place *via* Aromatic Transition States.[2a] Application of this rule with consideration of orbital phase relationships gives the same results as orbital symmetry arguments in symmetric cases, and the procedure may be applied to any electrocyclic reaction.

to the normal features one expects in the mass spectra of polynuclear aromatic hydrocarbons,[4] the hexahelicene mass spectrum has a very intense peak (*m/e* 300) for loss of C_2H_4 from the molecule ion (*m/e* 328) and a number of ions which are clearly daughters of the *m/e* 300 species. The relative intensities in the mass spectrum of hexahelicene are completely compatible with the formulation of the structure of the *m/e* 300 ion as being that of the coronene molecule ion (the 70-eV coronene mass spectrum[5] may be subtracted from the hexahelicene mass spectrum with no negative residuals). Any other formulation would require postulation of extensive rearrangement.



(1)



(2)

In the previous paper we used the PMO method to analyze the aromaticity of two systems that are important in mass spectroscopy. Six-orbital, five-electron states that are isoelectronic with the benzene radical cation will be marginally aromatic. Five-orbital, five-electron states that are homonuclear will be nonaromatic. Five-orbital, five-electron systems that are heteroatomic will, in general, be aromatic.

We will apply these considerations to the interpretation of the mass spectrum of hexahelicene, the retro-Diels–Adler reaction, and the McLafferty rearrangement.

The Hexahelicene Rearrangement. The mass spectrum of hexahelicene[3] (Figure 1) offers a unique opportunity for the application of the PMO method to the analysis of a mass spectrometric reaction. In addition

There is an intense metastable ion at *m/e* 274.5 which corresponds to the *m/e* 328 → *m/e* 300 transition. Observation of a metastable ion for a reaction from a molecule ion places the reaction in class I,[1] that is, the reaction probably occurred from a low-lying (fully bonding) doublet state of the parent. We can directly apply the PMO method[1] and Dewar's rule for thermal electrocyclic reactions to this process.

There are two ways in which hexahelicene could smoothly rearrange to coronene plus small molecules.

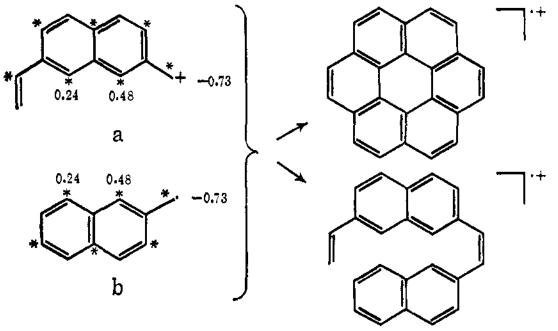
Reaction path 1 requires that the molecule twist through a symmetrical conformation. A substantial amount of strain is introduced in this process; how-

(3) M. S. Newman and D. Lednicer, *J. Amer. Chem. Soc.*, **78**, 4756 (1956).

(4) (a) H. Budzikiewicz, D. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day Inc., San Francisco, Calif., 1967; (b) P. Natalis and J. L. Franklin, *J. Phys. Chem.*, **69**, 2935 (1965); (c) R. A. W. Johnstone and B. J. Millard, *Z. Naturforsch.*, **21a**, 604 (1966).

(5) R. C. Dougherty, unpublished results.

ever, the same process is known to occur in the racemization of resolved hexahelicene samples at temperatures slightly above the melting point.[6] Reaction path 2 simply requires bond formation to give a *trans*-fused internal adduct. The transition state for path 1 will be isoelectronic with the coronene π-electron system; all of the interacting orbitals have the same phase relationships throughout the transformation. The aromaticity of the coronene molecule ion can be examined in the PMO formalism by considering the change in π energy on union to two naphthyl residues (a and b in eq 3 and 4). The NBMO coefficients were obtained with pencil and paper by the Longuett-Higgins procedure[1,2a] and are shown in the figure. The change in π energy on union of an odd-alternate radical and an odd-alternate cation is given by[1]



(3)

(4)

$$\Delta E_{\pi \mathrm{RS}\cdot +} = \sum_{r,s}^{\substack{\text{bonded}\\ \text{atoms}}} \{a_{or}b_{os} - {}^2/_5(1 + a_{or}^2 + b_{os}^2 - 3a_{or}^2b_{os}^2)\}\beta$$

where a_{or} and b_{os} are the NBMO coefficients at atoms r and s. The difference in the ΔE_π of union for path 3 and path 4 is strongly negative (a positive coefficient times β). This clearly indicates that the coronene molecule ion π system is aromatic with respect to its open-chain, conjugated, bisnaphthyl analog.

Reaction path 2 shows one set of carbon orbitals on hexahelicene with inverted phase from the electronic ground state. The phase inversion in path 2 is necessary for formation of the new σ bonds, and it makes the transition state "antiaromatic."[2a]

Class I electrocyclic reactions in the mass spectrometer should follow the same course as thermal processes,[1] and Dewar's rule clearly predicts that reaction path 1 should dominate the reactivity because of the aromaticity of the coronene molecule ion. In path 1, the molecule is geometrically disposed for elimination of ethylene as a molecule by simple bond shift. In path 2, coronene can be obtained only by loss of acetylene and hydrogen as discrete units. The latter reaction would not necessarily be concerted.

An experimental distinction between paths 1 and 2 can be obtained by critically examining all of the metastable processes for reactions in the *m/e* 300, *m/e* 328 region.

By use of an electronic scanning circuit for the accelerating voltage power supply on the MS-902 mass spectrometer,[7] it is possible to scan the accelerating voltage while maintaining constant electrostatic and magnetic analyzer fields. It has previously been shown that this general technique can be used to characterize precisely metastable ions which are formed in the field-free region between the source and the electrostatic analyzer of a double-focusing mass spectrometer.[8,9] Using this system the only observed metastable transition for formation of the *m/e* 300 ion in the hexahelicene mass spectrum was *m/e* 328 → *m/e* 300. We observed no metastable ions for the *m/e* 326 → *m/e* 300 transition under conditions which have allowed detection of metastables from initial ions of much lower relative intensity than the hexahelicene *m/e* 326 ion.[5] This evidence suggests that the mass spectrometric reaction proceeds primarily by path 1, as predicted by the PMO method.

We have measured the internal energy release for the *m/e* 328 → *m/e* 300 reaction using Ottinger's method.[8] At 4-kV accelerating voltage the difference in energy half-width for *m/e* 300 ions formed in the source and between the source and electrostatic sector corresponded to an internal energy release of 0.15 ± 0.05 eV. By combining this value with calculated π-electron energies[10] for the reactant and products, a rough maximum may be set for the strain energy of hexahelicene as 0.4 eV. The true strain energy of hexahelicene must be considerably smaller than this, possibly by two orders of magnitude, as the measured energy release directly represents the difference in bond energy between the intermediate and products in reaction 1.

Since the loss of C_2H_4 from hexahelicene is a class I reaction, the PMO method predicts that the same reaction should occur on thermolysis of hexahelicene. Hot wire pyrolysis in flow systems provides the best analogy for mass spectral reactions, as thermal bimolecular processes are minimized in the flow system; however, sealed tube experiments offer many advantages in terms of simplicity. We have examined the thermolysis of hexahelicene in a sealed evacuated (10^{-6} torr at 25°) tube at 485°. After 2 hr the only product above the reaction mixture that was volatile at 0° was shown by mass measurement to be ethylene. If acetylene was present, it was at least two orders of magnitude less abundant than ethylene. Traces of coronene were identified in the solid product by low-voltage mass spectrometry and comparison on silica thin layer chromatography. The major solids obtained from this experiment consisted of recovered starting material (~85%), dimers of hexahelicene (*m/e* 656) (~10%), and high molecular weight tars. The Diels-Alder dimer of hexahelicene may be a photoprecursor of the dodecahelicene system or a similar polycondensed and twisted aromatic hydrocarbon. We are presently examining the dimer structure.

7-Methylhexahelicene[11] behaves very similarly to hexahelicene in the mass spectrometer. Its mass spectrum is complicated by the possibility of rearrangement and elimination reactions involving the methyl side chain; otherwise the normal and metastable spectra are consistent in detail with the picture presented above.

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(6) M. S. Newman, R. S. Darlak, and L. Tsai, *J. Amer. Chem. Soc.*, **89**, 6191 (1967), and papers cited therein.

(7) C. R. Weisenberger and R. C. Dougherty, unpublished results; details are available on request.

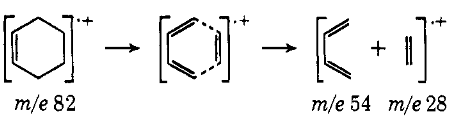
(8) Ch. Ottinger, *Phys. Lett.*, 17, 269 (1965).

(9) M. Barber, K. R. Jennings, and R. Rhodes, *Z. Naturforsch.*, **22a**, 15 (1967).

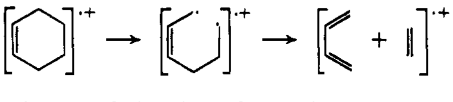
(10) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations," W. H. Freeman and Co., San Francisco, Calif., 1965.

(11) M. S. Newman and R. S. Darlak, submitted for publication.

The Retro-Diels–Alder Reaction. The concerted retro-Diels–Alder reaction must proceed through a six-orbital, five-electron transition state, which is isoelectronic with the π-electron system of the benzene molecule ion. In the absence of substituent interactions there should be little difference between paths 5a and 5b below, because the calculated π-electron stabilization of the benzene molecule ion with respect to the hexatriene molecule ion is small,[1] $\sim 0.04\beta$.



(5a)

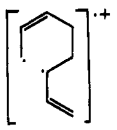


(5b)

Virtually all of the data from the mass spectrum of cyclohexene can be interpreted in terms of path 5a. The thermochemical predictions of relative ion abundances given by Budzikiewicz, *et al.*,[12] would apply equally to either concerted (electrocyclic) or stepwise processes; there is no need in this case to postulate a concerted reaction.

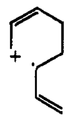
It is possible to make a clear theoretical distinction between the electrocyclic and stepwise RDA reactions in 4-vinylcyclohexene. In this case the intermediate in the electrocyclic process (reaction 5a) would be II, and the stepwise intermediate (reaction 5b) would be III.

II



III

There should be no first-order difference in the energy of the two ions IIIa and IIIb. The contributions of the



IIIa

IIIb

two butadiene fragments to the ion current at m/e 54 should be equal if the stepwise path 5b dominates the reaction.

The mass spectrum of deuterium-labeled 4-vinylcyclohexene has been reported.[13] The positive charge is preferentially retained by the butadiene group containing the vinyl group by a factor of up to 1.85:1. This means that path 5b can be excluded for this class I RDA reaction.

The suggestion that the selective charge retention is due to a *s-cis* transition state for the butadiene from the ring and a *s-trans* transition state (lower energy) for the butadiene containing the vinyl group[13] conflicts with the evidence that suggests that both butadienes are in the *s-cis* conformation in the thermal DA reaction.[14]

The selective charge retention in the RDA reaction of 4-vinylcyclohexene can be easily rationalized by a frontier orbital argument. The RDA reaction in 4-vinylcyclohexene gives a strong metastable ion, and should be a class I reaction. In this case we need only consider the bonding MO's in the molecule ion. Figure 2 indicates the atomic orbital phases for the bonding π orbitals in 4-vinylcyclohexene and butadiene.

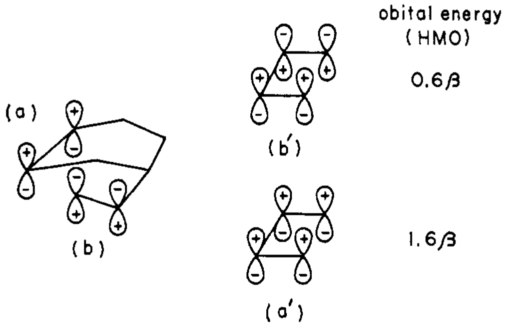


Figure 2.

If the unpaired electron is associated with the π orbital in the ring and this orbital smoothly transforms to one of the butadiene π orbitals, the charged butadiene must be formed in its first excited state. The ring π orbital cannot be smoothly transformed into the antisymmetric bonding orbital of butadiene (0.6β) because of the necessary phase inversion. If the unpaired electron is associated with the vinyl group, the charged butadiene may be formed in its electronic ground state because no phase inversion is required to correlate the vinyl π orbital with the highest occupied orbital of the butadiene molecule ion ground state. The difference in energy for formation of the butadiene molecule ion from the ring or the side-chain fragments should be the first excitation energy of the butadiene molecule ion, or approximately β in the HMO approximation. Configuration interaction should substantially decrease this energy difference which is larger than that required for only a factor of 2 in relative intensities. We are presently carrying out a complete orbital correlation for the RDA reaction of the 4-vinylcyclohexene molecule ion to test this hypothesis.[15]

The McLafferty Rearrangement. Other Five-Electron, Five-Orbital Rearrangements. The mass spectral analog of the Norrish type II photochemical cleavage of aldehydes and ketones[16] was first investigated by Nicholson[16a] and Martin and Pitts.[16b] Subsequent to these pioneering studies numerous examples of specific γ-hydrogen rearrangements have been reported and these reactions have been generically characterized as the "McLafferty rearrangement."[16c] Numerous mechanisms have been proposed for these reactions.[17] Our purpose here is to indicate how the PMO formalism can account for the large amount of data concerning these rearrangements.

The "localized electron" mechanism for the γ-hydrogen rearrangement in alkenes[17a] involves stepwise hydrogen atom transfer and cleavage (reaction 6).

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(12) H. Budzikiewicz, J. I. Brauman, and C. Djerassi, *Tetrahedron*, **21**, 1855 (1965).

(13) E. P. Smith and E. R. Thornton, *J. Amer. Chem. Soc.*, **89**, 5079 (1967).

(14) B. Eisler and A. Wassermann, *J. Chem. Soc.*, 979 (1953).

(15) J. G. Watt and R. C. Dougherty, submitted for publication.

(16) (a) A. J. C. Nicholson, *Trans. Faraday Soc.*, **50**, 1067 (1954); (b) T. W. Martin and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **77**, 5465 (1955); (c) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1966.

(17) (a) F. W. McLafferty, *Chem. Commun.*, 78 (1966); (b) F. W. McLafferty, *Anal. Chem.*, **31**, 82 (1959).

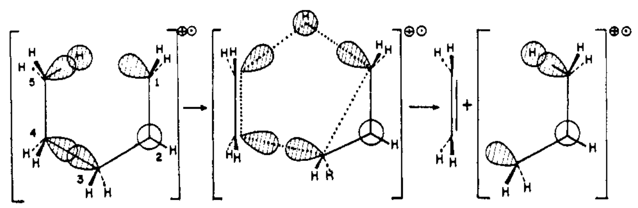
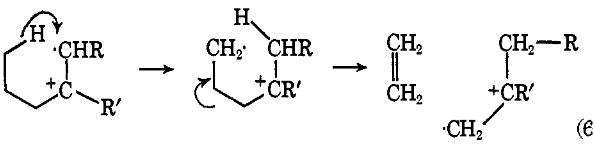
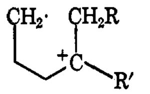


Figure 3.

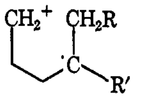


(6)

The preference for hydrogen atom (radical) transfer *vs.* hydride transfer should be controlled by the difference in energy between IVa and IVb. The PMO energies for the two-electron (hydride) and three-electron (radical) allyllike transitions should be the same. There should be no first-order energy difference between IVa and IVb, which makes it difficult to account for differences in reactivity on this basis.



IVa

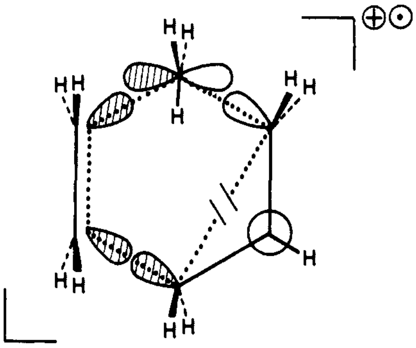


IVb

These γ-hydrogen rearrangements can alternatively be examined as electrocyclic processes. When the PMO approach is applied to these processes all of the major observations are easily accounted for. Figure 3 shows the orbital phase relationships for the γ-hydrogen rearrangement in the pentene molecule ion. We have previously shown that heteronuclear five-electron, five-orbital cyclic conjugated systems should be aromatic.[1] Application of Dewar's rule for thermal electrocyclic reactions suggests that the rearrangement should follow the path shown in Figure 3. Maximum 1,3 overlap is possible only if the double bond (in olefins) is twisted. Valence electron MO calculations[15] indicate that the twisted conformation (shown in Figure 3) in addition to allowing for homoconjugation is also the lowest energy conformation. In systems with nonbonding electrons on atom 1 the normal conformations allow for this homoconjugation.

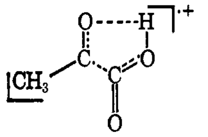
In substituted alkenes γ-hydrogen rearrangement competes with allylic cleavage. In reaction 6 if R = H and R′ = CH_3, γ-hydrogen rearrangement is dominant. If R = CH_3 and R = H, allylic cleavage is more important than γ rearrangement.[18] In the latter case, the methyl group on C_1 (Figure 3) would tend to stabilize the positive charge at that carbon. The rearrangement would then have to proceed through a four-electron, five-orbital transition which would be decidedly antiaromatic. The experiments discussed above[18] can be rationalized by the observation that the electrocyclic rearrangement should not occur as a four-electron process, and the allylic cleavage should be favored by a positive charge at C_1 (the NBMO of the allyl cation has a node at C_2).

The absence of γ-alkyl migrations in the mass spectra of compounds that could give this reaction, *e.g.*, 2,2,8,8-tetramethylnonan-5-one,[19] can be easily understood in the PMO formalism. If the migration were stepwise, as indicated in reaction 6, alkyl migration should compete with hydrogen abstraction as it does in other cases. The complete absence of alkyl migration[19] supports the electrocyclic mechanism for the γ rearrangement. Alkyl migration must involve orbital inversion on the migrating carbon (as in a SN2 reaction) or extreme steric crowding. The intermediate in the hypothetical electrocyclic methyl migration in the 1-hexene molecule ion, V, has a five-orbital, five-electron cyclic conjugated system which is antiaromatic[2a] because of the single orbital inversion. The reaction should not be a class I (*i.e.*, low-lying doublet electronic state) process[1] and entropy factors could easily keep the reaction from occurring during the short lifetime of doublet excited states (class II reaction).



V

The mass spectrometric and photolytic elimination of CO_2 from pyruvic acid[20] probably proceeds through five-electron, five-orbital electrocyclic transitions that electronically resemble the γ-hydrogen rearrangement (VI).



VI

The PMO method suggests that class I electrocyclic hydrogen transfer reactions in even-electron ions should be fundamentally similar to corresponding reactions of radical cations. The transition state for γ-hydrogen rearrangement in the cleavage ion VIII from methylisopropyl-*n*-butylamine[21] (VII) should be a six-orbital, six-electron conjugated aromatic system. This rearrangement is highly selective as shown by extensive deuterium labeling studies. The selectivity must be due to the electrocyclic nature of the transformation and not to the radical character[17a] at the reaction site. The relativity low probability of γ rearrangement, as shown by the low ion current at *m/e* 72, is probably due to the fact that formation of a carbon–nitrogen π bond in VIII makes the transformation geometrically impossible (either the interaction distances must be very large, or

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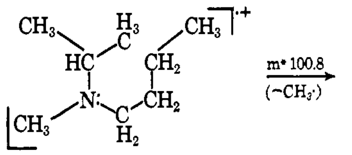
(18) F. W. McLafferty, *Anal. Chem.*, **31**, 2072 (1959).

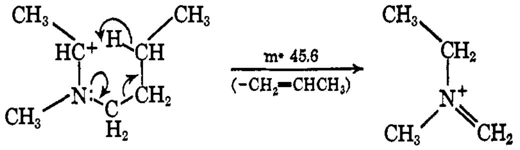
(19) R. R. Arndt and C. Djerassi, *Chem. Commun.*, 578 (1965), and papers cited therein.

(20) N. J. Turro, D. S. Weiss, W. F. Haddon, and F. W. McLafferty, *J. Amer. Chem. Soc.*, **89**, 3370 (1967).

(21) (a) S. Sample and C. Djerassi, *ibid.*, **88**, 1937 (1966); (b) C. Djerassi and C. Fenselau, *ibid.*, **87**, 5747 (1965); (c) C. Djerassi and C. Fenselau, *ibid.*, **87**, 5752 (1965); (d) C. Djerassi, M. Fischer, and J. B. Thomson, *Chem. Commun.*, 12 (1966).



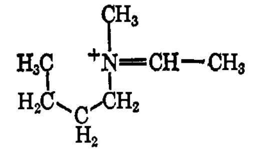
VII, *m/e* 129



VIII, *m/e* 114

severe crowding of the two carbon-bound hydrogens will occur during the transformation).

Hydrogen transfer reactions in the π-bonded conformer of VIII (VIIIa) are fundamentally different than hydrogen transfer reactions in radical cations. Electrocyclic processes which involve only the nitrogen end of the π bond are impossible because the nitrogen valence is saturated. Hydrogen transfer reactions that involve only the nitrogen center in VIIIa should be simply internal displacement reactions. The optimum size for cyclic transition states in these cases will depend more upon geometric factors than electronic factors. The nonspecificity of hydrogen transfer reactions in ions like VIIIa[21] is in accord with this view. Even-electron ions may be qualitatively dealt with as vibrationally excited protonated molecules. If the NBMO which contains the unshared pair in the molecule extends over the entire framework in excited vibrational states, proton mobility should be fairly high in even-electron ions, as has been observed.



VIIIa

Experimental Section

The mass spectra of hexahelicene and related compounds were determined by use of the direct inlet system on an A.E.I. MS-902 double-focusing mass spectrometer with the emission adjusted to 70 eV.

Acknowledgments. It is a pleasure to acknowledge useful discussions with Professors M. J. S. Dewar and M. S. Newman. Professor Newman has also supplied samples of all of the hydrocarbons we have examined. Mr. C. R. Weisenberger provided very able assistance with the mass spectrometer. The mass spectrometer was purchased with a grant from the National Science Foundation. The National Institutes of Health has generously supported our work.

Stereochemistry of the Reactions of 4-Substituted Cyclohexyl Radicals

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Abstract: The Hunsdiecker reaction with either *cis-* or *trans*-4-alkylcyclohexanecarboxylic acids (alkyl = methyl or *t*-butyl) or the bromine cleavage of *cis-* or *trans*-4-*t*-butylcyclohexylmercuric bromides yields a near-statistical distribution of bromides. In contrast, the sulfuryl chloride cleavage of either *cis-* or *trans*-4-*t*-butylcyclohexylmercuric chlorides yields a *cis*:*trans* distribution of 70:30. These isomer ratios and values in the literature from cyclohexyl and 2-norbornyl derivatives correspond well with distributions expected on the basis that torsional strain is the controlling factor. Reactions which tend more toward statistical isomer distributions are those which have low heats of reaction and which are expected to have only small structure development in their transition states. Reactions which have more bond formation in their transition states tend to give the products (axial-cyclohexyl or *exo*-norbornyl) which arise from pathways having smaller torsional strain.

Product studies of the halogen transfer reactions of 4-substituted cyclohexyl radicals provide valuable insight into the stereochemistry of atom transfer reactions. The results reported in the literature suggest that a variety of stereochemical outcomes are possible depending on the nature of the atom transfer reagent.[1-5] In the present study the Hunsdiecker reaction has been reinvestigated at a much lower temperature than used previously,[1] with both *cis-* and *trans*-4-methyl- and *cis-* and *trans*-4-*t*-butylcyclohexanecarboxylic acids. In addition, the radical halogen cleavage of alkylmercuric halides[5] has been extended to *cis-* and *trans*-4-*t*-butylcyclohexylmercuric halides. Consideration of the stereochemical results of these reactions plus the data in the literature has resulted in a unifying explanation for the diverse stereochemical product distributions obtained from halogen transfer reactions of 4-substituted cyclohexyl and 2-norbornyl radicals.

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