J. Am. Chem. Soc. **1981**, *103*, 1367–1371

A Sudden-Polarization Model To Predict Regioselectivities and Periselectivities of the 1,7-Sigmatropic Shifts and Electrocyclizations of Singlet Excited States of Cycloheptatrienes[†]

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Received July 16, 1980

Abstract: Substituted cycloheptatrienes undergo regioselective 1,7-sigmatropic shifts and electrocyclizations from singlet excited states. A model is proposed which accounts for the regioselectivities of these two reactions as a function of substituents and also shows why donor substituents promote electrocyclizations while acceptors promote sigmatropic shifts. The model is based on an excited singlet state in which a 90° rotation about one terminal double bond has occurred, accompanied by "sudden polarization" to form a zwitterionic species. Model ab initio calculations on the anionic and cationic fragments in these excited states provide support for the preferred direction of polarization in the excited singlet states.

Cycloheptatriene and substituted derivatives undergo two principal types of singlet photoisomerizations: 1,7-sigmatropic shifts[2] and [$_\pi 4_d$] electrocyclizations (Scheme I).[3] Donor and acceptor substituents have a profound influence on the regioselectivity of both of these processes and on the competition between electrocyclizations and sigmatropic shifts.[4,12] Several hypotheses have been offered to explain the electrocyclization or sigmatropic shift regioselectivity,[4,9,11,13,14] but none of these attempt to deal with competition between electrocyclic reactions and sigmatropic shifts, and none are really anything more than mnemomic generalizations. We wish to report a model which correctly rationalizes all of the reactivity and selectivity trends observed, as well as several wavelength-dependent photoreactions observed in this series. This explicit model for excited-singlet-state electonic and geometric structure is supported by model ab initio calculations reported here and indicates why the previous hypotheses are able to account for the experimentally observed directions of electrocyclizations.

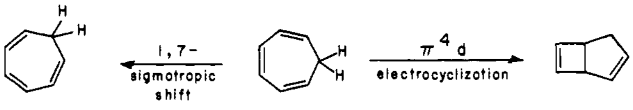
Background

Ter Borg et al.[6] reported the selectivities shown in Figure 1 for selectivities shown in Figure 1 for the photochemical reactions of 1-substituted cycloheptatrienes. The strong acceptors CN and CO_2Et[7] promote sigmatropic shifts away from the substituent, while phenyl-substituted and unsubstituted derivatives give sigmatropic shifts in both directions. Methyl, a weak donor, promotes sigmatropic shifts toward the methyl group. Increasing the strength of the donor at C-1 results in [$_\pi 4_d$] electrocyclizations involving bond formation between C-1 and C-4.

Studies of more highly substituted derivatives indicate that donor groups at carbons 1, 3, or 5 promote 1,4-electrocyclization, while acceptors at carbons 1, 3, and 5 promote 3,6-electrocyclization.[8-11] This is summarized as shown by Brember et al. in Figure 2.[11] This diagram indicates that a single donor or acceptor at the positions indicated causes electrocyclizations in the manner shown by the dashed line. Two or more substituents may reinforce this preference, or if located so as to individually favor different modes of electrocyclization, substituents at C-1 dominate over those at C-2 or C-3.[11a]

Chapman rationalized the direction of photochemical electrocyclizations of substituted tropones on the basis of charge separation in the excited states of these species.[15] Brember, Gorman, Sheridan et al. applied a similar generalization to rationalize the direction of photocyclization of substituted cycloheptatrienes.[11] The drawing shown at the bottom of Figure 2 shows the excited-state polarization proposed by Brember et al. to explain the electrocyclization regioselectivity. If this type of charge separation occurred in the excited singlet states of cycloheptatrienes, then the propensity of 1-donor cycloheptatrienes to cyclize 1,4 and 1-acceptor derivatives to cyclize 3,6 as well as the other substituent effects, could be understood. Libit carried out EHT calculations on the excited states of *planar* cycloheptatrienes and found that the electrocyclization usually occurs in such a direction so as to unite the carbons of greatest charge difference in the EHT calculations, in agreement with the Brember model.[14] However, the

Scheme I



[†] Dedicated to the memory of Ruth Wells Gandour, our friend and a superb scientist.

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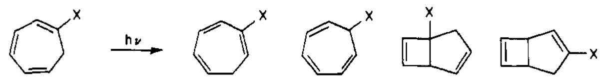

Me$_2$N	-	-	97	3
MeO	-	35	65	-
MeS	-	65	35	-
Me	2	98	-	-
H	99.8		0.2	
Ph	50	50		
CN	100	-	-	-

Figure 1. Summary of the ter Borg et al. studies of photochemistry of 1-substituted cycloheptatrienes.[6] Numbers are percentages of isolated product.

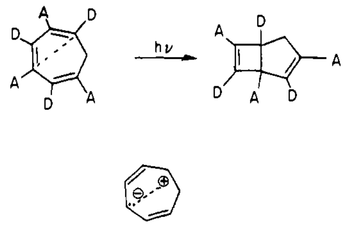

Figure 2. The Bremben et al. generalization of the regioselectivity of photochemical electrocyclization (D = donor; A = acceptor).[††] The zwitterion at the bottom of the figure indicates the excited-state model which fits this generalization.

EHT charge separation was found to be very small, and hydrogen shifts surprisingly must occur toward the more negative triene terminus, a migration which is hardly in accord with ground-state analogy, where 1,2-shifts to a cationic center are common, but those to an anionic terminus are rare. Tezuka and Kikuchi developed a new molecular orbital index, based on the Hückel charge densities in the singly occupied orbitals of the excited states of planar trienes.[13] This index correctly predicts the direction of electrocyclization of substituted cycloheptatrienes.

Chapman[15] and Jones and Jones[8,9] developed an orbital-symmetry-based explanation of the regioselectivities of 1,7-sigmatropic shifts of 1-donor substituted cycloheptatrienes. They suggested that the highest singly occupied orbital of the excited state, which is the orbital corresponding to the lowest unoccupied orbital of the ground state, has coefficient properties which only permit sigmatropic shift toward the donor substituent.

However, none of these hypotheses are based on realistic models for excited states of cycloheptatrienes, nor can they satisfactorily predict competition between electrocyclizations and sigmatropic shifts. Cycloheptatrienes not only exist as strongly puckered boat conformations in the ground state but are expected to experience substantial torsion about one or more formal double bonds in excited singlet states.

In 1975, Salem and co-workers showed that singlet excited states of polyenes may involve a rotation of one polyene terminus and "sudden polarization" as the torsion angle approaches 90° if the system is unsymmetrical.[16] The relatively low energy of zwitterionic states in ethylene was proposed on computational grounds in 1971 by Wulfman and Kumei,[17] and Dauben and co-workers proposed a zwitterionic excited state to account for the photochemical reactions of trienes.[18] Many theoretical studies have confirmed the importance of sudden polarization in singlet excited states of ethylene, dienes, and trienes.[19,20] For example, the photochemical formation of bicyclo[3.1.0]hex-2-enes from hexatrienes involves the zwitterionic excited singlet state shown in Figure 3.[19,20] The allyl anion moiety of this zwitterion cyclizes to a cyclopropyl anion which subsequently, or simultaneously, forms a second bond to give bicyclo[3.1.0]hex-2-ene.

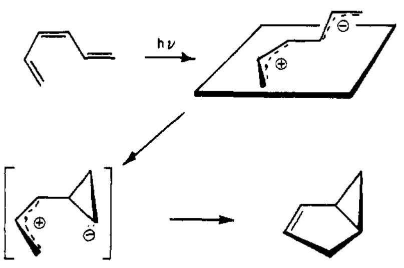

Figure 3. Singlet cyclization of hexatrienes. The formation of the "sudden-polarized" excited singlet triggers 1,3-bond formation.

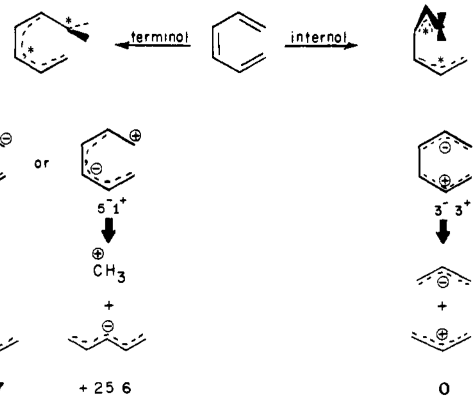

Figure 4. Definitions of "terminal" and "internal" rotations of a triene. Neglecting unsymmetrical distortions, the single zwitterion shown is possible upon internal rotation, while two are possible upon terminal rotation. Relative energies are from STO-3G calculations.

These results, along with the dramatic influence of donor and acceptor substituents on the photochemistry of cycloheptatrienes, suggested to us that the excited singlet states of these species might well involve "sudden polarized" zwitterionic states as well.

A Zwitterionic Model for the Excited Singlet States of Cycloheptatrienes

There are two types of rotations of a triene system which could lead to zwitterionic excited states, which we will refer to as "terminal" and "internal" rotations (Figure 4). In hexatriene itself, central rotation is preferred, as indicated by the chemistry observed and by many calculations on the excited singlets of hexatrienes.[20] Because of the expense of calculations on excited singlet states of the large systems in which we were interested, the known central rotation in hexatriene was used as a test case to explore whether simple model calculations could be used to estimate the relative energies of various zwitterionic excited states of polyenes.

Instead of carrying out excited-singlet-state calculations with sufficient configuration interaction to adequately describe such species, we have crudely modeled such zwitterionic states by summing the energies of ionic fragments computed individually with use of ab initio calculations[22] with the STO-3G basis set with

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Table I. STO-3G Energies of Species Used to Model Zwitterionic Excited Singlets of Cycloheptatrienes

molecule	energy, au	geometry	ref
methyl·	−39.07701	full opt[h]	e
methyl⁻	−38.83473	full opt[h]	e
methyl⁺	−38.77948	full opt[h]	e
allyl·	−115.05429	full opt[h]	e
allyl⁺	−114.80953	full opt[h]	e
allyl⁻	−114.83660	b	f
pentadienyl⁻	−190.82592	b	this work
pentadienyl⁺	−190.79277	a	this work
aminomethyl⁺	−93.23485	full opt[h]	e
aminomethyl⁻	−93.16710	full opt[h]	g
cyanomethyl⁺	−129.32438	full opt[h]	this work
cyanomethyl⁻	−129.48098	full opt[h]	this work
1-aminopentadienyl⁺	−245.16886	a	this work
1-aminopentadienyl⁻	−245.14206	c, d	this work
1-cyanopentadienyl⁺	−281.32797	a	this work
1-cyanopentadienyl⁻	−281.43124	c	this work

[a] Heavy-atom bond lengths and angles were varied, while CH bond lengths were fixed at 1.08 Å and bond angles were fixed at 120°. [b] Heavy-atom bond lengths and all angles were varied, while CH bond lengths were fixed at 1.08 Å. [c] Bond angles were fixed at optimized geometries of the parent pentadienyl anion, and heavy-atom bond lengths were reoptimized. [d] The amino group has the lone pair coplanar with the pentadienyl system. [e] Whiteside, R. A.; Binkley, J. S.; Krishnan, R.; DeFrees, D. J.; Schlegel, H. B.; Pople, J. A. "Carnegie-Mellon Quantum Chemistry Archive"; Carnegie Mellon University: Pittsburgh, 1980. [f] Boerth, D. W.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* 1978, *100*, 750. [g] Clark, T.; Körner, H.; Schleyer, P. v. R. *Tetrahedron Lett.* 1980, 743. [h] Full opt: full optimization.

full or partial geometry optimizations (Table I). In the actual zwitterionic excited states, the polarization is not as large as in our models, and the Coulombic attraction between the ionic fragments will be large due to the close proximity of these partial ions.[20] One ionic fragment also strongly perturbs the other, so that the charge is expected to be somewhat concentrated on atoms connected by the 90° twisted bond. Nevertheless, this fragment model may be able to predict qualitatively the relative energies of various zwitterionic species.

The relative energies given in Figure 4 provide a test of this simple model. The fragment model for the zwitterion resulting from internal rotation is considerably more stable than the two possible zwitterions arising from terminal rotation, in accord with the preference for excited singlets of acyclic trienes to undergo internal rotation. The Coulombic interactions between ionic fragments in these various models should be similar, so that the relative energetic order is unlikely to be changed in the actual excited-state calculations.

This crude model also gives the correct order of magnitude of excited-state energies of the "sudden-polarized" butadiene singlet, although the overestimation of polarization in this model gives an energy which is too low. The energy of methyl⁻ plus allyl⁺ is calculated to be 13.3 eV higher than that of methyl radical plus allyl radical, but when separated by the distance of an sp^2–sp^2 single bond (1.48 Å), a positive and a negative point charge are stabilized by 9.7 eV (Coulomb's law). The simple model predicts that the zwitterionic excited state of butadiene is 13.3 − 9.7 = 3.6 eV higher than the corresponding diradical. Salem's[21] calculations indicate that the energy difference is about 5.6 eV.

Returning to the quantities given in Figure 4, internal rotation is clearly favored over terminal rotation in the excited singlet of hexatriene. However, large internal rotations are impossible in cycloheptatriene since the two termini cannot be bridged effectively by a single methylene group. Figure 5 shows internally and terminally rotated hexatrienes with asterisks indicating those bonds that would have to be united to a single methylene group in the cycloheptatriene analogue. Because of the steric impossibility of internal rotation in cycloheptatriene, we postulate that a zwitterionic excited state can only be formed from cycloheptatriene by terminal rotation.

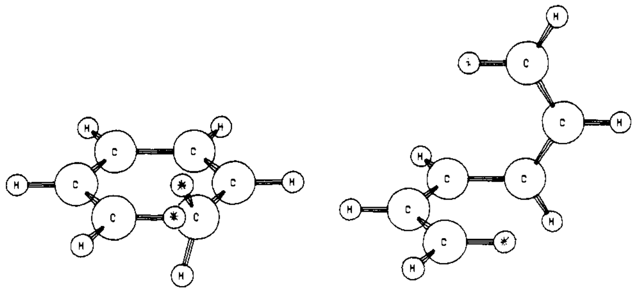

Figure 5. Terminal and internal rotations of *cis*-hexatriene. Asterisks indicate sites which join to a single methylene group in cycloheptatriene.

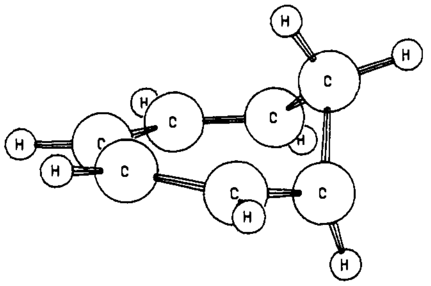

Figure 6. PROPHET model for the terminally rotated zwitterionic excited state of cycloheptatriene.[23]

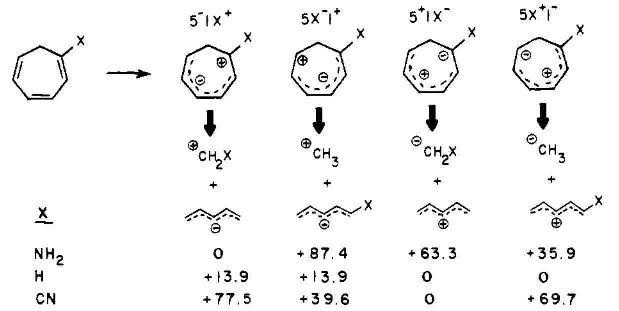

Figure 7. The four possible zwitterionic states of cycloheptatriene and STO-3G relative energies for the fragment models.

A reasonable geometric model for a terminally rotated cycloheptatriene was constructed in the following manner with use of the molecular graphic capabilities of the PROPHET computer system.[23] The bond lengths and angles of the pentadienyl anion were used for the pentadienyl moiety; this fragment was joined to a methyl cation fragment with the local planes of each fragment fixed at 90°, and these were joined by a standard methylene group. So that this could be effected in a reasonable way, the pentadienyl unit could not be kept planar; each CCCC dihedral angle in the pentadienyl fragment was changed to 5° in order to close the last CC bond in the model which is shown in Figure 6.

Two zwitterionic states with this structure are possible, one with delocalized pentadienyl cation and localized anion moieties and the other with the opposite polarization. These will be referred to as 5^+1^- and 5^-1^+ states, respectively. To obtain a qualitative estimate of which of these is of lower energy in the parent and substituted cases, we have calculated the relative energies of models for the 5^+1^- and 5^-1^+ zwitterions shown in Figures 4 and 7.

For the parent species (Figure 4), the 5^-1^+ excited state is predicted to be 13.9 kcal/mol less stable than the 5^+1^-. However, a more realistic model should give a large preference for the 5^-1^+

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(23) PROPHET is a national computer resource sponsored by the Division of Research Resources of the National Institutes of Health.

zwitterion. That is, in the C_7H_8-$5^{-}1^{+}$ species, the cation is secondary, which should cause appreciable stabilization. At the STO-3G level, conversion of the methyl to the isopropyl cation results in a 56 kcal/mol stabilization relative to the corresponding alkane. In C_7H_8–$5^{+}1^{-}$, the 5^{+} is terminally dialkylated but this should be less stabilizing since less than a full positive charge is located at each terminus. Alkyl groups have very small effects on anion energies, so they should not affect the energy estimates much.

Once the $5^{-}1^{+}$ zwitterion has been identified as the most probable structure of the polarized, and geometry relaxed, excited singlet state of cycloheptatrienes, it is possible to understand the substituent effects on the basis of various ground-state analogies for the behavior of ionic species.

We postulate that in $5^{-}1^{+}$, a rapid hydrogen shift can occur from the methylene group to the cationic center. Presumably the pseudoequatorial hydrogen shifts more rapidly since this CH bond is nearly coplanar with the vacant p orbital of the cationic center (Figure 6). This hydrogen shift will produce a new species which is more or less like an isomeric $5^{-}1^{+}$ species, although simultaneous molecular relaxation could give the ground state of cycloheptatriene in the same process. Qualitatively, however, this 1,2-shift is expected to be rapid if the new zwitterion is equal to or lower in energy than the original zwitterion. If the 1,2-shift produces a less stable zwitterion, then this process should be very slow or should not occur at all.

Our second hypothesis has to do with the direction of cyclization of the $5^{-}1^{+}$ zwitterion. There are a number of modes of cyclization possible, but the union of the cationic (1^{+}) center to the center carbon of the dienyl anion (5^{-}) system should be preferred for several reasons. From Figure 6, it can be determined that a vacant p orbital at the 1^{+} center should point approximately toward the p orbital of the central carbon of the pentadienyl anion system. Furthermore, these two carbons are the site of highest plus and minus charge densities, respectively. Also, 1^{+} has a low-lying LUMO consisting of a vacant p orbital, while the HOMO of the 5^{-} fragment has its largest coefficient at the central carbon. These sites should experience a strongly stabilizing HOMO–LUMO interaction. All of these factors should promote $1^{+}5(\text{C-3})^{-}$ cyclization. There is no driving force for internal cyclization of the 5^{-} moiety, which should, in any case, lead to 1,5- and not 1,4-cyclization. This excited-state model provides a viable explanation of the polarization and direction of cyclization postulated by Brember et al.[11]

With these postulates, we turn to a consideration of how substituents should influence each of these processes and the competition between them.

A 1-substituted cycloheptatriene can give rise to four different zwitterionic states, depending on the $5^{+}1^{-}$ or $5^{-}1^{+}$ polarizations and upon whether the substituted (1–2) or unsubstituted (5–6) terminal bonds rotate. These four states are represented for donor or acceptor substituted species by calculations on model fragments at the STO-3G level with cyano and amino substituents, summarized in Figure 7. Relevant energies and levels of geometry optimization are given in Table I.

Beginning our discussion with the strong donor substituted species, the $5^{-}1NH_2{}^{+}$ species is clearly most stable, as expected, since the amino group is a potent cation stabilizer. Thus, we postulate that the $5^{-}1NH_2{}^{+}$ species is the lowest energy polarized excited singlet state. This species can undergo either ring closure corresponding to 1,4-cyclization or a hydrogen shift of the pseudoequatorial hydrogen from C-7 to C-1. These are summarized at the top of Figure 8. However, the hydrogen shift leads to a less stable system since initially the developing p orbital at C-7 is more or less orthogonal to the pentadienyl anion π system. Thus, with strongly stabilizing groups at C-1, e.g., Me_2N, this hydrogen shift is suppressed and 1,4-electrocyclization is favored (Figure 1). The small amount of 3,6-electrocyclization may result from a higher excited state ($5NH_2{}^{+}1^{-}$), as discussed below in more detail for cyano.

As the donor group at C-1 is made weaker, the 7 → 1 hydrogen shift becomes competitive with electrocyclization (OMe, SMe) and then dominates (Me, H). In all of these cases, the $5^{-}1^{+}$ zwitterion is expected to be more stable than the $5^{+}1^{-}$, but with weak donors, the hydrogen shift becomes rapid because the cationic center is not highly stabilized.

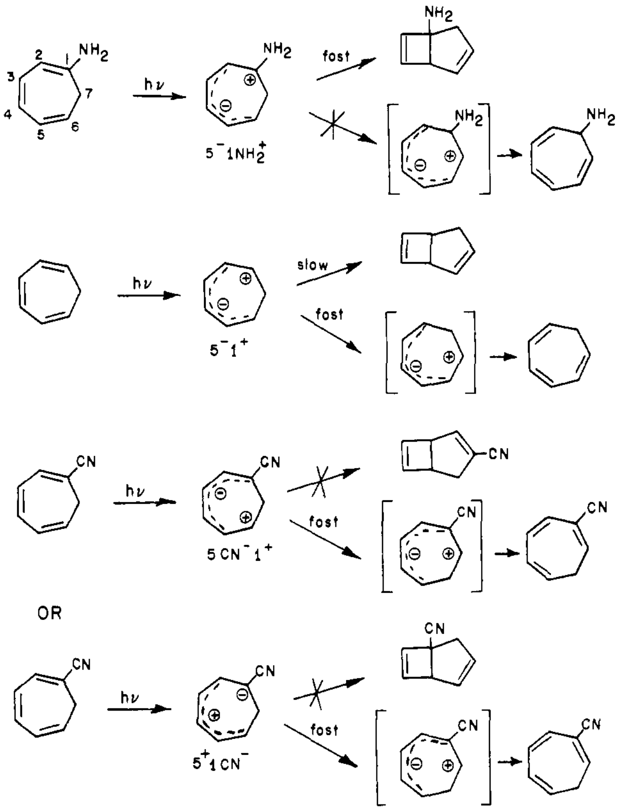

Figure 8. Summary of preferred pathways for substituted cycloheptatrienes.

The strongly electron-accepting cyano group makes the $5^{+}1CN^{-}$ state more stable than all the others according to our model calculations. However, these models are relatively crude, and the absolute difference in energy of $5^{-}1^{+}$ and $5^{+}1^{-}$ is not known with certainty, as discussed earlier. Since the relative stability of $5^{-}1^{+}$ is probably underestimated, it is possible that either $5CN^{-}1^{+}$ or $5^{+}1CN^{-}$ is the lowest energy zwitterionic state, even though our model calculations favor the latter by 39.6 kcal/mol (Figure 7). Because of this uncertainty, the probable fates of both of these states will be considered and are outlined in the lower portion of Figure 8.

We start with $5CN^{-}1^{+}$; this species should undergo a very rapid 1,2-shift since the rearranged zwitterion is equal to or lower in energy than $5CN^{-}1^{+}$. The lifetime of $5CN^{-}1^{+}$ should be too short to permit electrocyclization. The sigmatropic shift corresponds to a 7 → 6 sigmatropic shift as is observed experimentally.

If $5^{+}1CN^{-}$ is the lowest energy zwitterionic excited state, then a 1,2-shift to the terminus of the pentadienyl cation occurs faster than ring closure. Interestingly, this would most likely involve a shift of the pseudoaxial hydrogen and would give the same zwitterion as formed by rearrangement of $5CN^{-}1^{+}$. However, the electrocyclic ring closure products formed from $5^{+}1CN^{-}$ and $5CN^{-}1^{+}$ are different; in some cases of acceptor substituted cycloheptatrienes, the 3,6-electrocyclization product is observed. This is expected to be formed from $5CN^{-}1^{+}$, suggesting that this zwitterionic species is the lowest lying even in acceptor substituted cycloheptatrienes.

Although no calculations have been performed which have direct bearing on the photoreactions of 1-phenylcycloheptatriene or similar cycloheptatrienes with conjugating substituents, the experimental results can be rationalized by postulating the nearly equal energies of $5^{-}1Ph^{+}$ and $5Ph^{-}1^{+}$ zwitterions, which would give 7 → 1 and 7 → 6 sigmatropic shifts, respectively. Phenyl is unique among the series of substituents given in Figure 1, since it can strongly stabilize both anions and cations, so that the

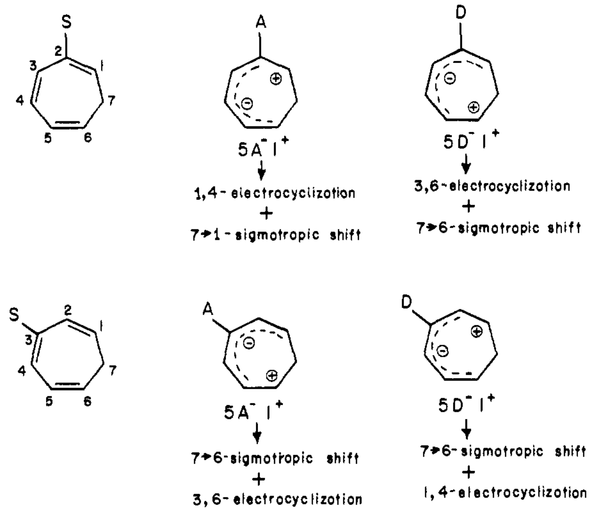

Figure 9. Predictions of the lowest zwitterionic excited states and photochemical reaction products of 2- and 3-substituted cycloheptatrienes.

postulate of two excited states with similar energies is not unreasonable.

Although calculations have not been carried out on all the appropriate models, the photochemical behavior of 2- and 3-substituted cycloheptatrienes may be predicted in a similar way. Figure 9 summarizes these predictions. We have assumed as before that the 5^-1^+ species are always preferred and have chosen the more stable of these on the basis of the idea that acceptors stabilize a pentadienyl anion most when attached to C-1 or C-3, while donors destabilize these species least when attached at C-2. Thus, a 2-acceptor should lead to preferential formation of $5\mathrm{A}^-1^+$, which can undergo 1,4-electrocyclization or a slightly endothermic 7 → 1 sigmatropic shift. Linstrumelle found that the 1,4-electrocyclization and 7 → 6 (not 7 → 1) sigmatropic shift occur in a ratio of 3:1 with 2-(ethoxycarbonyl)cycloheptatriene.[7,11d] However, he also found that the product of a 7 → 1 shift is rapidly converted to 2-ethoxycarbonyl)cycloheptatriene, so that the final product ratios may not reflect the fastest processes. In any case, this result is not in agreement with prediction.

A 2-donor should promote rotation of the unsubstituted double bond, and both 3,6-electrocyclization and 7 → 6 sigmatropic shifts are expected to ensue. Both of these processes are observed with 2,7,7-trimethylcycloheptatriene.[8b]

The 3-acceptor and donor substituted species are expected to undergo both electrocyclization and sigmatropic shifts but with opposite regioselectivities in the case of donor and acceptor substituents. The predicted processes are observed with 3-(ethoxycarbonyl)cycloheptatriene[11b,d] and with 3,7,7-trimethylcycloheptatriene[8a] as examples of 3-acceptor and 3-donor substituents.

Finally, the model is capable of rationalizing several interesting wavelength-dependent photoreactions uncovered by Freestone and Gorman.[12] Two methoxycycloheptatriene esters each gave a single photoproduct upon irradiation at 313 nm, while an additional product is formed at 254 nm, as shown in Figure 10. The species $5\mathrm{E}^-1\mathrm{D}^+$ is expected to be most stable regardless of the position of the ester group because of the strong stabilization of the cationic center by the methoxy substituent. The 1,4-electrocyclization should occur readily, but a 7 → 1 sigmatropic shift is expected to be relatively inefficient, as is the case for 1-methoxycycloheptatriene. Freestone and Gorman find that the 7 → 1 shift occurs slowly in competition with electrocyclization, There are three candidates for zwitterionic upper excited singlet states. We postulate that either of the structures shown at the top of Figure 10 could be the state responsible for the additional 3,6-electrocyclization product observed at 254 nm. The 5^-1^+ species is expected to have a higher propensity for sigmatropic shift than the lower energy excited state, since the cation is now destabilized. On the other hand, the 5^+1^- structure is stabilized by both substituents and would not undergo a 7 → 6 sigmatropic shift, which has not been observed.

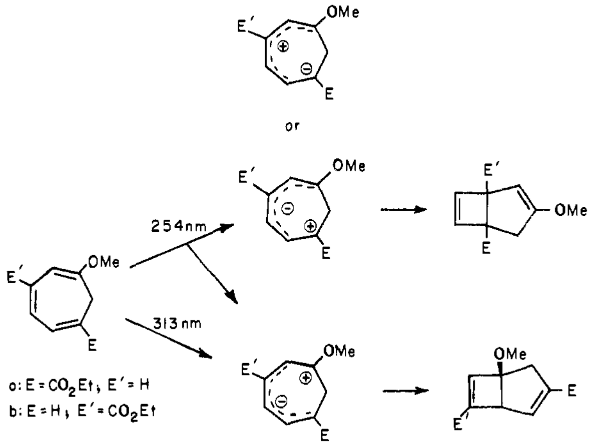

Figure 10. Rationalization of wavelength dependence observed experimentally in 3(or 6)-(ethoxycarbonyl)-1-methoxycycloheptatriene.

Conclusions

The "sudden-polarized", or zwitterionic, excited-state model for excited singlet states of substituted cycloheptatrienes is equivalent to, but more detailed than, the Bremher et al. model for cycloheptatriene electrocyclization, During the course of this work, Gorman and co-workers elaborated on the polarized excited-state model and proposed that an excited singlet of C_2 symmetry is favored for cycloheptatrienes.[11d] We believe, however, that the less symmetric excited state shown in Figure 6 is necessary to account for the charge separation in the excited state, since no polarization occurs in a symmetrical molecule. Our model identifies the geometric changes as rotation around a bond which is a double bond in the ground state rather than about single bonds as in the Gorman model.[11d] The regioselectivity of 1,7-sigmatropic shifts and the competition between the two pericyclic processes also can be accounted for most satisfactorily on the basis of the sudden-polarized model.

As computational methods and speed develop, we expect to be able to carry out computations on the excited-state surfaces responsible for these reactions and to test the accuracy of the ground-state analogy we have developed for polarized excited states. In the meantime, a reliable technique for the prediction of regioselectivities and periselectivities of cycloheptatriene reactions is available. Such a model should also be applicable to the excited-singlet-state reactions of other substituted polyenes.

Acknowledgment. We are grateful to the National Science Foundation (Grant No. CHE 79-08543 to K.N.H,) for financial support of this research.