

STEREOCHEMISTRY AS A PROBE FOR PHOTOCHEMICAL REACTION MECHANISMS¹

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Abstract—In this publication we have reviewed examples derived from our photochemical investigations where stereochemistry provides information allowing elucidation of the mechanistic details of electronically excited state transformations. The reactions discussed include unimolecular rearrangements of both singlet and triplet excited state species.

INTRODUCTION

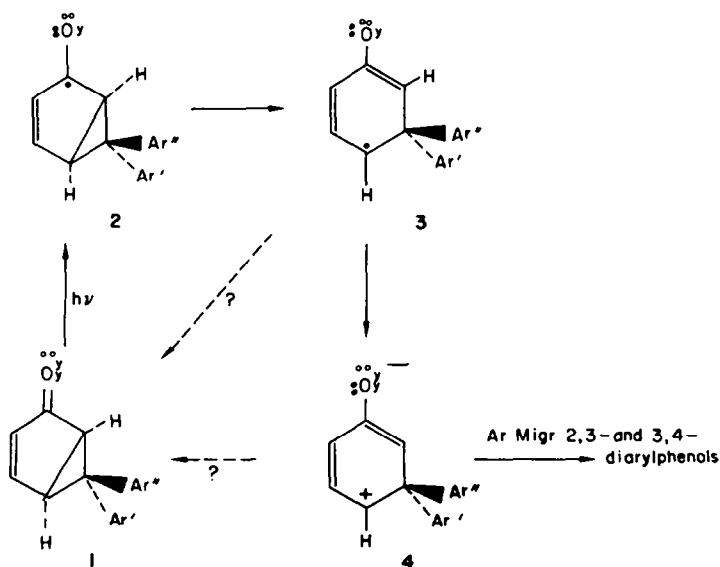
As a consequence of the author's interest in the stereochemical aspects of ground state processes², there was a logical emphasis on stereochemical techniques when the writer began his photochemical investigations in the late 1950's. Actually, stereochemistry proves to be just as powerful a tool for elucidating photochemical mechanisms as it is in the case of ground state chemistry.

AN EXAMPLE OF THE USE OF STEREOCHEMISTRY IN DETERMINING THE RATE LIMITING STEP OF A PHOTOCHEMICAL PROCESS

The Type B rearrangement of 6,6-disubstituted bicyclo[3.1.0]hex-3-en-2-ones to phenols results

from internal bond fission and migration of one of the substituents, as shown in Chart 1 where the proposed mechanism³ is depicted.

Excited state fission of the internal sigma bond accompanied or followed by electronic relaxation to ground state leads to the well established zwitterion 4. Perhaps the most cogent evidence supporting the presence of this zwitterionic intermediate is its generation by non-photochemical means under Favorskii conditions from 6-bromo-5,5-diphenyl-2-cyclohexenone.⁴ It has been shown that this type of zwitterion has been ubiquitously involved in a large number of photochemical rearrangements, so one would like to understand all the details of the reaction.



GROUND STATES

- a: Ar', Ar'' = Ph
- b: Ar' = Ph, Ar'' = *p*-CN-Ph
- c: Ar' = *p*-CN-Ph, Ar'' = Ph

Key: o represent sp hybrid electrons
 y represent in plane *p*, (i.e. n) electrons
 · represent π-system electrons

CHART 1. Stereochemistry and mechanism of the type B enone rearrangement.

One point of particular interest is the question of whether or not either the excited state 3 or the zwitterionic ground state counterpart 4 reform the internal bond to regenerate photochemical reactant, 6,6-diaryl-bicyclo[3.1.0]hex-3-en-2-one 1. It has been noted that this is an unlikely possibility since the reclosure is electronically forbidden;⁵ however, definite proof was lacking.

An answer to this question came from a stereochemical study in which the photochemistry of each of the stereoisomers of 6-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hex-3-en-2-one (1b and 1c) was investigated.⁶ It can be seen that zwitterion 4 and its excited state 3 are either planar or so close to planar that the molecule is non-diastereomeric. Thus, if internal three-ring bond fission is reversible the [3.1.0]-bicyclohexenone stereoisomers would be interconverted during reaction. However, it was found⁶ that when the photolyses of 1b and 1c were carried to partial conversion, only the starting stereoisomer was present. Therefore the processes shown with dotted arrows in Chart 1 do not occur.

STERESELECTIVITY IN THE PHENYL MIGRATION OF CYCLOHEXENONES AND HYDROCARBON ANALOGS

It has been observed that 4,4-diarylcyclohexenones rearrange photochemically to give the two stereoisomers of 5,6-diaryl-bicyclo[3.1.0]hexan-2-ones.⁷ The reaction has proved to be extraordinarily general, and in every case the *endo*-aryl isomer is kinetically preferred.⁷ A stepwise version of the mechanism in qualitative valence bond terms is given in Chart 2.

A 3-dimensional picture of the mechanism at the stage of the aryl migration from carbon-4 to carbon-3 is presented in Fig 1. It is clear that the stereochemistry shown in Fig 1 involves use of

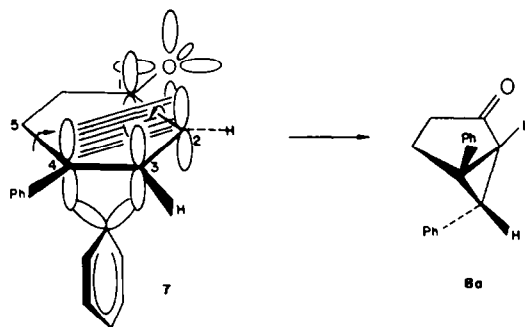


Fig 1. The intermediate bridged species and its subsequent continued migration in the rearrangement of 4,4-diarylcyclohexenones.

both lobes of the p-orbital at C-4 and thus leads to inversion of configuration at C-4. While this is ubiquitously the preferred pathway, essentially independent of substitution and other variations in structure, nevertheless, there usually is a small quantity of the minor stereoisomeric product (e.g. 1/140 in the case of 4,4-diphenylcyclohexenone). This suggests the possible intervention of diradical 6 as a discrete species (note Chart 2) to some extent. Were it not for this minor stereochemical reaction course, one might argue that structure 6 is merely a convenient formalism but that aryl migration and 3-ring formation are actually completely concerted. Our conclusion then is that the concertedness is probably weak.

Interestingly, this stereochemistry is not limited to phenyl and aryl migration in cyclohexenones but is also encountered in the photochemistry of olefin analogs of both cyclohexenones and 2,5-cyclohexadienones.^{8,9} Examples are depicted in equations 1, 2 and 3. Even though rearrangements

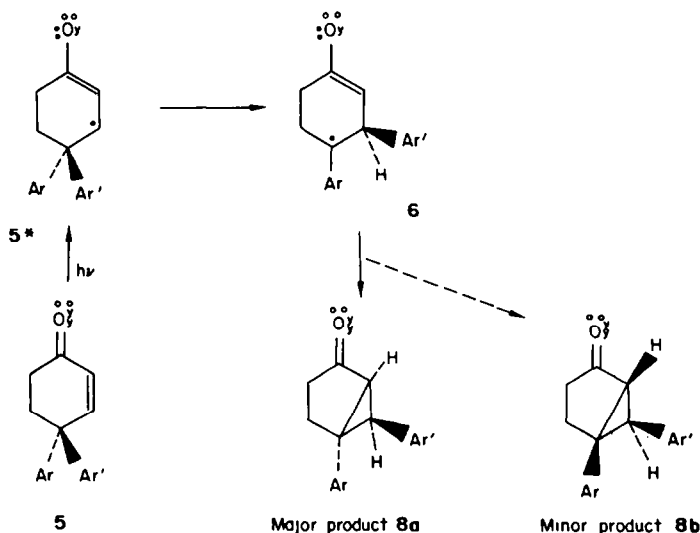
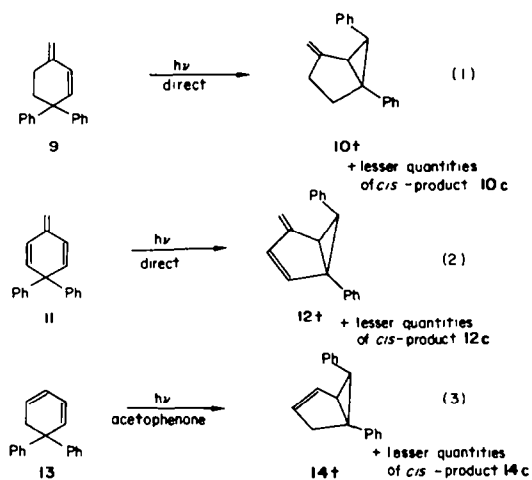


CHART 2. Stereoselectivity of the 4,4-diarylcyclohexenone rearrangement.



(1) and (2) in the hydrocarbon cases are singlet processes (in contrast to the triplet rearrangements of the cyclohexenones), the stereochemistry is the same, with a preference for formation of the *endo*-phenyl product. In case (3), that of 6,6-diphenyl-1,3-cyclohexadiene¹⁰, where the rearrangement does occur from the triplet state of a hydrocarbon, the *endo*-phenyl stereochemistry is still kinetically preferred.

THE USE OF STEREOCHEMISTRY IN DETERMINING THE NATURE OF EXCITED STATE CYCLOPROPANE RING OPENING REACTIONS

A number of photochemical reactions proceed by mechanisms in which a 3-membered ring of reac-

tant is opened transiently during the process, either with stereoisomerization or with a more drastic change in molecular structure. Often stereochemistry can be used to elucidate the nature of the photochemical reaction.

One intriguing example is the photochemical interconversion of *cis*- and *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one stereoisomers (**8b** and **8a**) via the triplet excited states. One can envisage two quite reasonable reaction mechanisms. These differ in whether it is the internal three-ring bond *b* (path B) or the external bond (path A) which is opened and then reclosed. The two possibilities are shown in Chart 3.

Both processes are mechanistically plausible in that the antibonding electron in the $n-\pi^*$ excited state would be expected to weaken an adjacent three ring bond (*i.e.* *a* or *b*). Interestingly, it is apparent that if one starts with one enantiomer of the *trans*-bicyclohexanone reactant (*e.g.* **8a'**), one will obtain different enantiomers of *cis*-product depending on which reaction mechanism is followed. Thus, a mechanism involving external 3-ring bond fission (*i.e.* fission of bond *a*, path A) gives rise to enantiomer **8b'** while a mechanism involving scission of the internal bond *b* followed by reclosure with phenyl groups *cis*, leads to enantiomer **8b''**. It is also noted that if bond *c* were broken and reclosed after rotation about bond *a*, one would obtain the same product **8b'** deriving from bond *a* fission; however, excitation is heavily localized in the CO group and the bonds conjugated with it making bond *c* fission less likely.

The answer to this mechanistic problem was

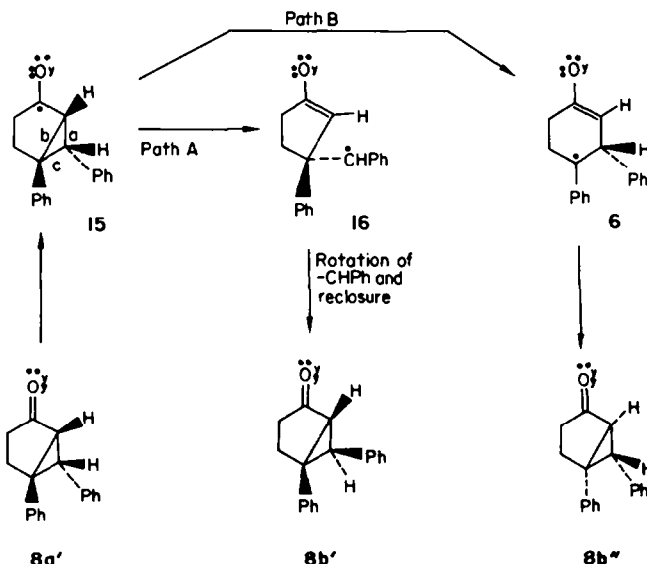


CHART 3. Mechanisms for stereoisomerization of the 5,6-diphenylbicyclo[3.1.0]hexan-2-ones.*

a. prime and double prime refer to enantiomers.

found¹¹ in the optical resolution of *trans*-bicyclic ketone **8a** and correlation of the configuration of *trans*-ketone **8a** with that of the *cis*-ketone **8b**. It was thus observed that the *trans* to *cis* (i.e. **8a** to **8b**) conversion proceeds exclusively via mechanism A while the *cis* to *trans* conversion (i.e. **8b** to **8a**) utilizes route A to the extent of 86% and route B to the extent of 14%. This means that there appears to be a violation of microscopic reversibility. The violation, however, is superficial since in each case it is the excited state of reactant proceeding to ground state of product, and thus the *cis* to *trans* and the *trans* to *cis* reactions are not the exact reverse of one another.

The preference for bond *a* fission is understandable if one recognizes that this bond has its orbitals nearly parallel to the antibonding carbonyl π^* orbital and thus overlap favors opening this bond over bond *b*. Hence, this example has been one where stereochemistry has helped elucidate the reaction mechanism and the mechanism, in turn, has had stereochemical implications.

Another intriguing example of 3-ring photochemical stereoisomerizations is that of the 1-benzoyl-2-aryl-3-phenylcyclopropanes. In this case, our interest was in the nature of the excited state leading to stereoisomerization of the cyclopropyl ketones and also in the electronic charge distribution along the reaction coordinate. Chart 4 provides an example. Thus the 2-*trans*-*p*-cyanophenyl-3-*trans*-phenyl-*r*-1-benzoylcyclopropane (**17**) has been observed¹² to rearrange to the *cis*-*trans* (i.e. **19**) and the *trans*-*cis* (i.e. **20**) stereoisomers with a preference for formation of the *cis*-*trans* isomer in which the *p*-cyanophenyl group has become *cis* to benzoyl.

In Chart 4 we have pictured the excited state of **17** rather ambiguously with an asterisk and a dagger to represent free valences which may be +, - or -, + or -, ; the question, in fact, is just how the excited state should be pictured both initially and as the molecule proceeds along the reaction coordinate. As in the preceding bicyclohexanone study, it is a very reasonable initial guess that the excited state undergoes fission of either bond *a* or bond *b* followed by free-rotation processes and reclosure.

The situation is somewhat esoteric as can be seen from inspection of Chart 4 which reveals that *cis*-*trans* product **19** can arise from two structurally different mechanisms. One mechanism is fission of bond *a* followed by single rotation about bond *c* and reclosure to form a 3-ring. The other mechanism is fission of bond *b* followed by a double rotation involving single rotations about bonds *a* and *c*.

However, if one begins with one enantiomer of the *trans*-*trans* reactant (**17**(+)) the two mechanisms are seen to lead to different enantiomers of the *cis*-cyanophenyl stereoisomer **19**. The single rotation mechanism gives the stereoisomer labeled **19**(-) in Chart 4 while the double rotation mechanism

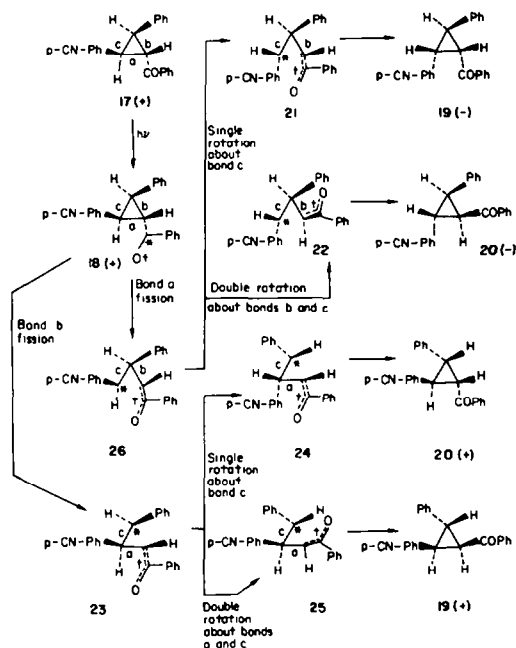


CHART 4. Mechanisms for stereoisomerization of 2,3-disubstituted cyclopropanes.

ism gives the **19**(+) enantiomer of **19**. In the solution of this problem the configurations of starting material and products were correlated and thus the rotation of each diastereomer isolated indicates what linear combination of alternative mechanisms is operating. One can actually dissect the transformations into the extent of single rotations involved vs double rotations and also into the relative amount of bond *a* vs bond *b* breakage. Chart 5 gives a summary of the pathways actually followed by the excited state of the starting cyclopropyl ketone **17**.

The observed results were: (1) the ratio of the *cis*-*trans* isomer **19** to the *trans*-*cis* isomer **20** was 3.5:1; (2) the major product **19** was optically pure with the indicated relative configuration (Chart 5); (3) the minor product **20** was racemic. The relative rates derived from this information are indicated at the bottom of Chart 5. We see that opening of bond *a* is more rapid than opening of bond *b* by a factor of 8 and that single rotations are preferred over double rotations by a factor of 7.

With regard to the question of intervention of any bond *c* opening, we note that this could not account for formation of enantiomer **20**(-), since this enantiomer differs in configuration at the carbon α to the carbonyl, and this α -carbon configuration is not affected by bond *c* opening. Also, to the extent that there is any bond *c* fission, it will lead by symmetry to equal amounts of **19**(-) and **20**(+). But the latter is only 11% of the product. Furthermore, **20**(+) can also be formed by bond *b*

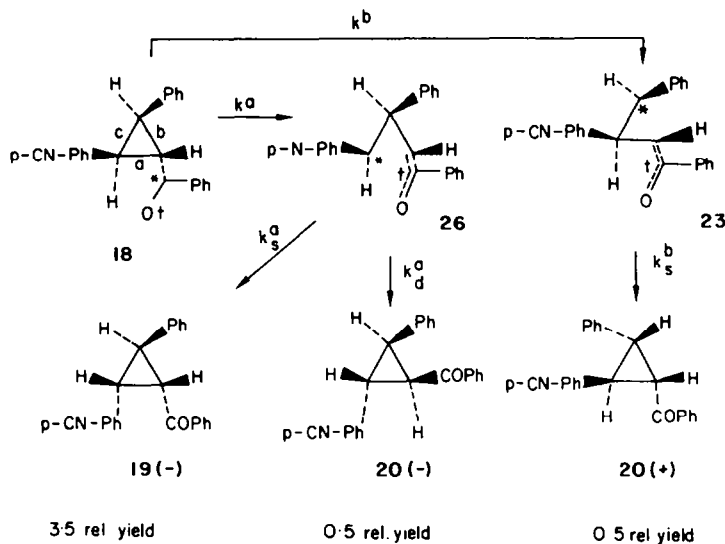


CHART 5. Summary of observed bond openings and rotations.

scission as shown in Chart 5. Hence any bond *c* cleavage must be considerably below 11%. Any involvement of bond *c* fission, in fact, increases the k^a/k^b ratio and leaves the single to double rotation situation essentially unchanged.

From the preference for bond *a* fission it could be concluded that the excited state and the excited state transition state leading from this could not be pictured as having an electron rich CO group and electron deficient 3-ring. A parallel study in which the two aryl groups were *p*-methoxyphenyl and phenyl,¹³ again showed the preference for fission of the bond bearing *p*-substituted aryl group. In this case one can conclude that the CO group is not electron deficient with the 3-ring being electron rich.¹³ As a consequence, it was possible to deduce that the excited state and the transition state for stereoisomerization were best presented by odd-electron free valences.

The reaction efficiencies of the stereoisomerizations of these molecules proved to be very high. The cyanophenyl ketone 17 had a quantum yield of 0.81,¹² that for the anisyl analog had an efficiency of 0.76¹³ and that for the unsubstituted 1-benzoyl-2,3-diphenylcyclopropane isomerizing from *trans-trans* to *cis-trans* proved¹⁴ to be 1.0. A comparison of the rates of the three reactions did reveal a difference with the cyanophenyl isomer being most rapid.¹⁴ Since cyanophenyl is a particularly good odd-electron stabilizing group, this confirms the conclusions about the nature of the ring opening process.

Other 3-ring stereoisomerization processes occur photochemically without the presence of a CO group. For example, *trans,trans*-2,3-diphenyl-1-(α -styryl)cyclopropane (27), which is the methylene analog of the benzoyl-cyclopropane derivative

discussed above, stereoisomerizes photochemically to the *cis-trans* isomer (28).¹⁵ While the reaction does proceed on direct irradiation ($\phi = 0.023$), the benzophenone sensitized reaction was much more efficient ($\phi = 0.34$). This provides unambiguous evidence that the triplet undergoes the stereoisomerization with facility but it only suggests that on direct irradiation intersystem crossing is occurring to give the triplet which then rearranges. The reaction mechanism is given in Chart 6.

Another example of a vinylcyclopropane reaction involving stereochemistry was encountered in the photochemistry of the isomeric *cis*- and *trans*-5,6-diphenylbicyclo-[3.1.0]-2-hexenes (31a and b) and the *cis*- and *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexenes (32a and b).¹⁰ Again the device of utilizing optically active material and interrelating configurations was employed.¹⁰ For these molecules, two types of reactions were observed, *cis-trans* stereoisomerization and 1,3-sigmatropic migrations interconverting the 5,6-isomers and the 4,5-compounds. While the sigmatropic rearrangement can proceed only by internal bond involvement, the stereoisomerization can be seen to be possible, *a priori*, either by internal bond fission or by external bond fission followed by reclosure after conformational change. In the case of the *cis-trans* isomerization, the possible mechanisms are outlined in Chart 7 for the case of the 5,6-isomers 31a and 31b and with the *trans* to *cis* isomerization given for illustration. External bond fission is seen to give product 31a' with retention of configuration at C-5 while internal bond fission gives enantiomer 31a'' in which C-5 is inverted.

It turns out that the stereoisomerization behavior depends in one instance on the multiplicity (*i.e.* singlet vs triplet) of the excited state reacting,

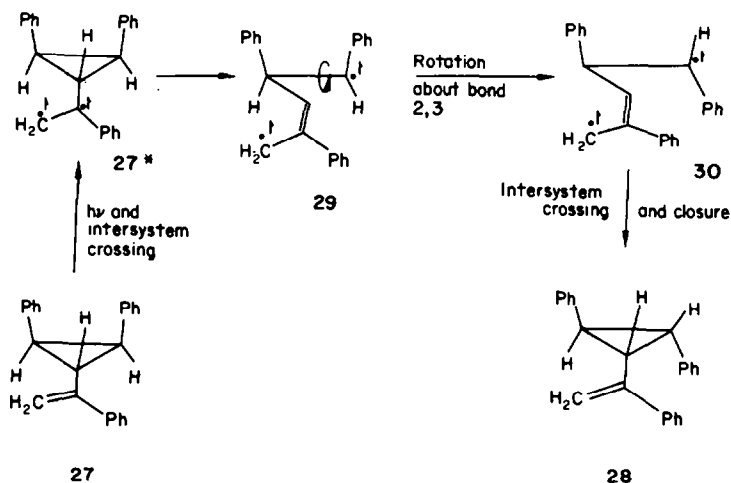


CHART 6. Mechanism of stereoisomerization of *trans,trans*-2,3-diphenyl-1-(α -styryl)cyclopropane (1) to *cis,trans*-2,3-diphenyl-1-(α -styryl)cyclopropane (2).

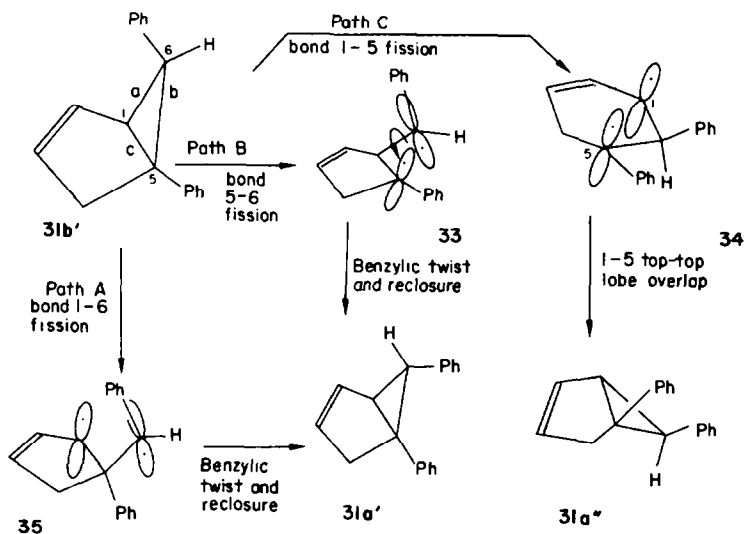


CHART 7. Possible mechanisms of *trans* to *cis* stereoisomerization of 5,6-diphenylbicyclo[3.1.0]-2-hexene.

and this situation is summarized in Table 1. It can be seen that the preferred reaction pathway, however, is primarily that which involves external bond fission (pathway A or B). One exception is the reaction of *cis*-5,6-olefin excited singlet where about 20% of the pathway involves internal bond fission. Also, we see that at least in the singlet reactions microscopic reversibility appears to be violated, since the mechanism followed by *cis* to *trans* isomerization is not exactly that followed by the *trans* to *cis* conversion. Again, as discussed earlier we note that this means that the excited states of

reactant and product are not interconverted. Rather, excited state of reactant goes directly to product ground state and microscopic reversibility does not really apply.

Table 2 considers the data from another viewpoint and gives the total amount of internal vs external bond fission with both stereoisomerization and sigmatropic rearrangement being included. For each excited state the ratio k_{ext}/k_{int} is given where these are the rates of external and internal bond fission from that excited state. Of course, external bond fission leads only to stereoisomerization while

Table 1. Extent of external versus internal bond fission mechanisms in stereoisomerization*

Reactant	Multiplicity	External bond fission, %	Internal bond fission, %
<i>trans</i> -5,6 Olefin	Singlet	97.5	2.5
<i>trans</i> -5,6 Olefin	Triplet	96.9	3.1
<i>cis</i> -5,6 Olefin	Singlet	80.3	19.7
<i>cis</i> -5,6 Olefin	Triplet	97.5	2.5

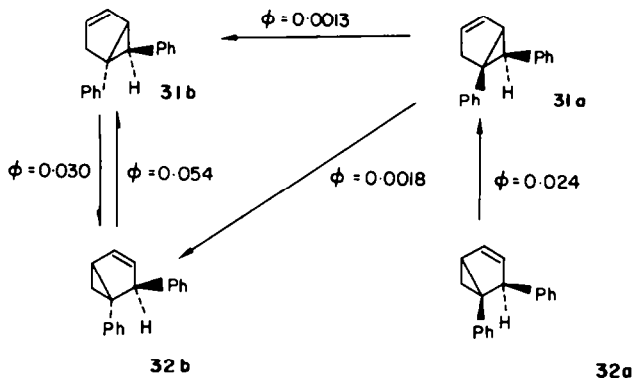
*Derived from the relative amounts of retention and inversion observed.

Table 2. Total amounts of internal vs external bond fission

Reactant	Multiplicity	Percentage reaction with internal bond involvement		k_{ext}/k_{int}
		Sigmatropic rearrangement	Stereoisom. ^a	
31a	Singlet	81	0.05	0.2
31a	Triplet	30	2	2.1
31b	Singlet	21	16	1.7
31b	Triplet	0	2	49.0

^aOverall percentage: equal to the product of the percentage of reaction which is stereoisomerization and the fraction of isomerization occurring by internal bond fission.

A Singlets



B Triplets

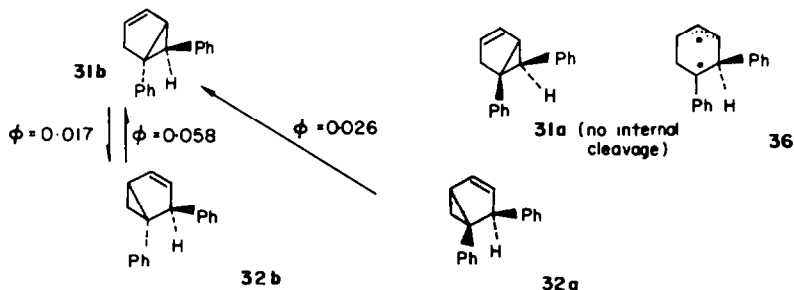


CHART 8. Singlet and triplet rearrangements involving internal bond fission (contributions due to external bond fission are excluded)

internal bond fission gives rise to both stereoisomerization and sigmatropic rearrangement.

If one now directs attention just to internal bond fission mechanisms, it is possible to summarize the situation as in Chart 8 which dissects the internal bond fission processes into reactions of the singlet and separately of the triplet. A most exciting result is that the pattern of reactivity exhibited by the singlet is quite different than that for the triplet. Another intriguing point is that, since the *cis*-4,5-isomer **32a** kinetically gives the *cis*-5,6-isomer **31a**, which differs from the kinetic behavior of all the other isomers, there cannot be a common allylic biradical (*i.e.* **36**) involved in these interconversions. Rather they must proceed by concerted processes.

The mechanisms for the interconversions are pictured in Chart 9.

The reactions can be seen to involve cyclic arrays of four orbitals. Each array can be analyzed further as having either zero or an even number of sign inversions and thus to consist of a Hückel basis set array.^{16,17} With the four delocalized electrons in each case, the reaction then is excited state allowed.^{16,17} The Woodward-Hoffmann rules¹⁸ predict the same allowedness.

Of the three sigmatropic rearrangements in Chart 9, the singlet conversion of *cis*-5,6-bicyclic olefin

31a is unique in proceeding *via* a 1,3-antarafacial migration with inversion of the migrating group (*i.e.* note transition state **38'**). This contrasts with the conversion of *trans*-5,6-bicyclic olefin **31b** giving *trans*-4,5-bicyclic olefin **32b** and the conversion of *cis*-4,5-bicyclic olefin **32a** giving *cis*-5,6-bicyclic olefin **31a**. These two processes are suprafacial with retention of the migrating group. We note, however, that the antarafacial process accounts for just about 50% of the reaction course of *cis*-5,6-olefin **31a** (note Chart 8, Singlet Processes).

Also we note in Chart 9 that the flattened species **36** is only different from transition state **38** in minor detail; yet this is what one might term the diradicaloid transition state.

In looking at the reactions of these systems (note Table 2), one can draw a general conclusion. It can be seen that the electrocyclic processes, in which all the orbitals are closely compressed, are preferred by the singlet while the triplet excited state prefers external bond fission which provides a mechanism for separating two electrons of opposite spin.^{10,19}

"SLITHER" PROCESSES IN STEREOCHEMISTRY PHOTOCHEMISTRY AND THEIR

One fascinating type of photochemical reaction is one in which a divalent carbon moiety may

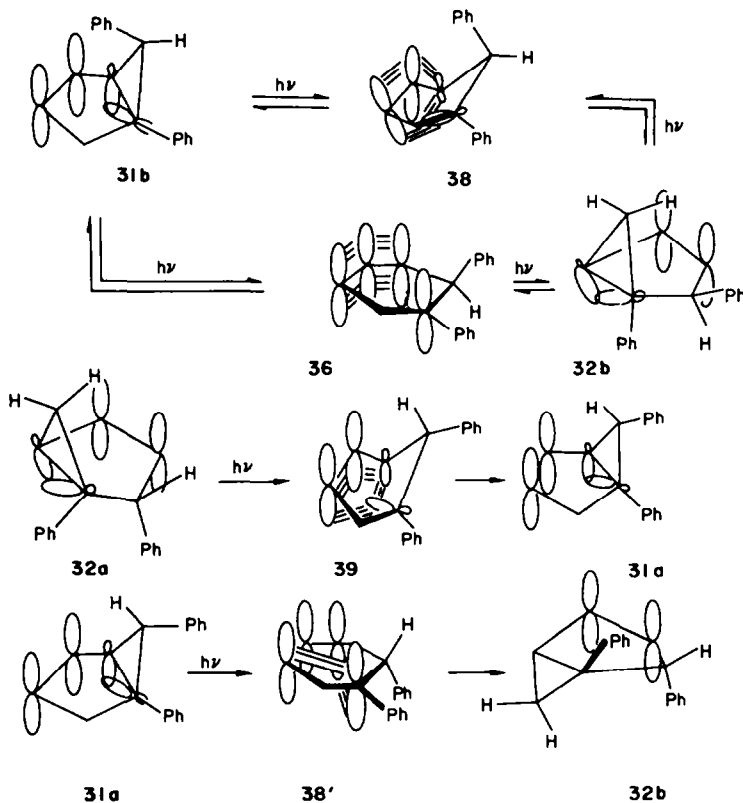
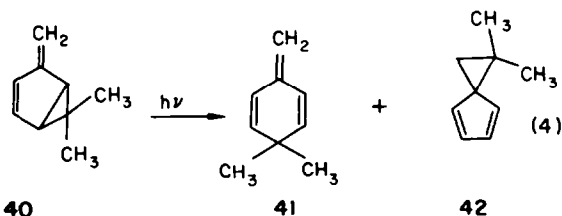
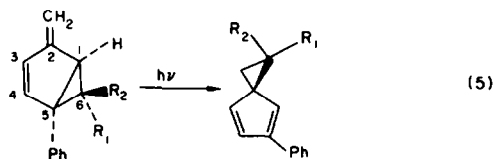


CHART 9. Mechanisms of the sigmatropic rearrangements.

"slither" along the surface of a π -system. One example is found in the photochemistry of 2-methylenebicyclo[3.1.0]-3-hexenes which are converted into spiro[2.4]-4,6-heptadienes. Both reactants and products can be visualized as formal adducts of a divalent carbon atom and a fulvene moiety. Thus, 2-methylene-6,6-dimethylbicyclo[3.1.0]-3-hexene (**40**) reacts *via* its singlet to give 1,1-dimethylspiro[2.4]-4,6-heptadiene (**42**) and 1-methylene-4,4-dimethylcyclohexadiene (**41**)²⁰ (Eq 4). Similarly, irradiation



of the stereoisomeric 2-methylene-5,6-diphenylbicyclo[3.1.0]-3-hexenes (**43a** and **b**, resp.) led stereospecifically to the *syn*- and *anti*-1,5-diphenylspiro[2.4]-4,6-heptadienes (**44a** and **b**, resp.) with the *cis*-bicyclic diene **43a** giving the *syn* product **44a** and the *trans*-bicyclic diene **43b** giving primarily the *anti* isomer **44b**. This is depicted in Eq 5. An additional clue to the reaction mechanism was given by the formation of 2,4-diphenyltoluene, 2,5-diphenyltoluene, 3,5-diphenyltoluene and 3,4-diphenyltoluene as by-products of the reaction (*vide infra*). Chart 10



43a $R_1 = \text{Ph}$, $R_2 = \text{H}$

44a $R_1 = \text{Ph}$, $R_2 = \text{H}$

43b $R_1 = \text{H}$, $R_2 = \text{Ph}$

44b $R_1 = \text{H}$, $R_2 = \text{Ph}$

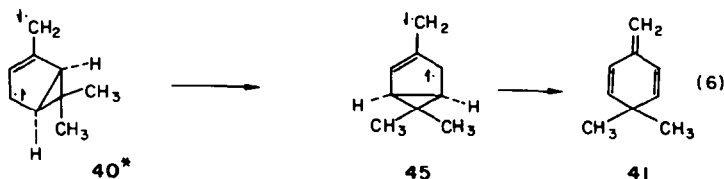
outlines a qualitative valence bond picture of the possible reaction mechanisms for the rearrangement in the case of the diphenylbicyclic olefins **43a** and **43b** and the dimethyl analog **40** rearranging to their spiro-isomers. Eq 6 gives an equivalent mechanism, starting with the excited state of the dimethyl analog **40** (*i.e.* **40***), but leading to 1-methylene-4,4-dimethylcyclohexadiene (**41**)

which is the second photoproduct observed in this case.

If one follows the slither mechanism in Chart 10, he notes that carbon *e* migrates from *a* and *b* to *b* and *c* to give diradical species **48** (or **49** in the case of the dimethyl series); it then migrates to carbons *c* and *d* to give spiro product (*i.e.* **44** or **42**). Since stereochemistry is maintained this can be pictured as a slither process in which the divalent carbon then moves along the skeleton of the 5-ring. An alternative stepwise mechanism is also shown, but this variation of the slither seems unlikely since it proceeds through diradical intermediates which do not easily account for the stereospecificity of the reaction. Still another mechanism proceeds *via* a bicyclo[3.2.0]-intermediate **52** (and **53**). Such an intermediate would go onward thermally to product^{21,22} if formed.

The main evidence in favor of the slither mechanism is the isolation of all possible 6-ring products resulting from the divalent carbon stopping along the slither route with internal bond fission and hydrogen shift. Thus, the 3,4-diphenyltoluene observed can arise from internal bond fission of excited state **43**. The 2,4-diphenyltoluene similarly derives from internal bond fission of diradical **48** (note Chart 10). However, the mechanism in Chart 10 involves a counter-clockwise slither of the divalent carbon; and a clockwise slither is also possible. In the case of the dimethyl series the 1-methylene-4,4-dimethylcyclohexadiene (**41**) formation as depicted in Eq 6 can be seen to proceed *via* a clockwise slither. Similarly, in the case of the *trans*-diphenyl bicyclic olefin **43b**, species **57** deriving from two clockwise slither processes can be seen (Chart 11) to afford the 3,5-diphenyltoluene; and the diradical species **58**, resulting from still another clockwise slither leads to the 2,5-diphenyltoluene found. Finally, in the case of the *trans*-diphenylbicyclic reactant (*i.e.* **43b**) there was observed some loss in stereospecificity which affords 22% of the *syn*-phenyl isomer **44a**. This can be seen from the divalent carbon taking the long route and slithering clockwise via diradical **58** as shown in Chart 11. That only the *trans* system affords clockwise slither products makes sense when one notes that in the *cis* system two bulky phenyl groups would have to pass one another for clockwise slithering but not for counterclockwise motion.

Finally, it needs to be stated that the species in Charts 10 and 11 as well as in Eq 6 are just convenient valence bond representations; they should not



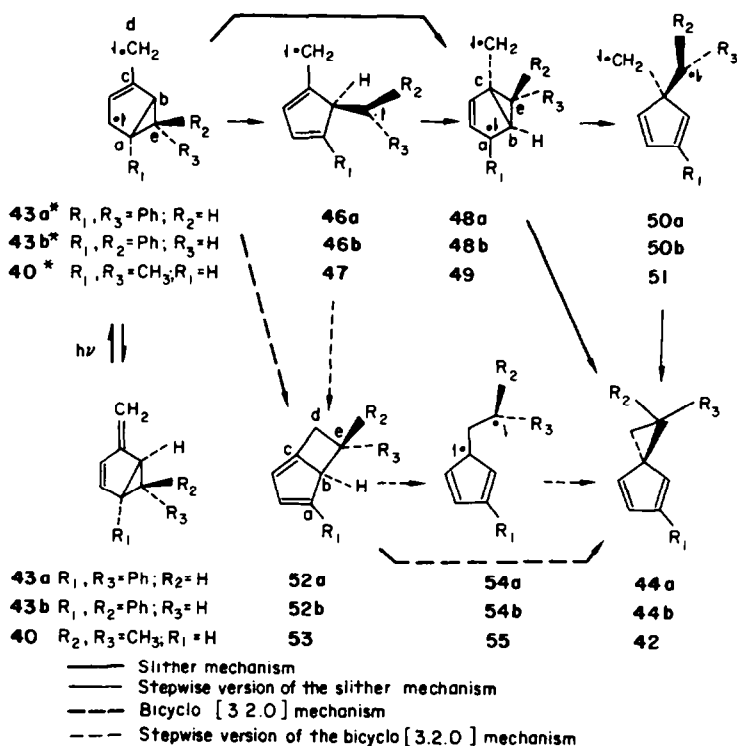
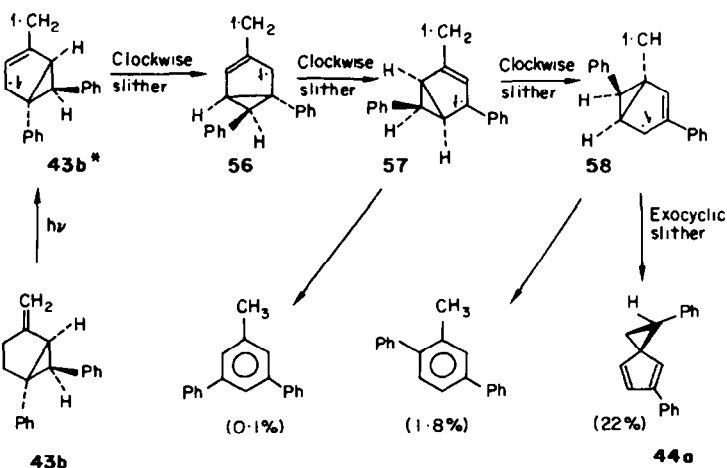


CHART 10. Mechanistic variations for the rearrangement of 2-methylenebicyclo[3.1.0]-3-hexenes.

CHART 11. Minor pathways in the rearrangement of the *trans*-bicyclic *trans*-diphenyl bicyclic system.

be construed to mean that the divalent carbon is free of the π -surface of the five ring or that the odd-electron densities are sufficiently localized to allow free rotation.

One other example of a slither rearrangement was observed in a study which was termed "photochemistry without light".²³ This latter term was in-

duced by our research group to designate the non-photochemical generation of species involved in photochemical reactions. These species do not have to be excited states since often many unstable subsequent species are an integral part of a photochemical reaction.

Presently, the species of interest is the zwitterion

postulated by us years earlier as involved in a very large fraction of 2,5-cyclohexadienone photochemistry. We termed this the Type A zwitterion.³

We were able to generate the Type A zwitterion in two different ways.²³ One is illustrated in Chart 12. It can be seen that there are two *a priori* stereochemical courses for the rearrangement of this zwitterion to the bicyclic enone which is the photochemical product but one cannot tell which pathway is utilized. However, with one of these being *p*-bromophenyl, the two pathways are differentiated and it is the slither mechanism which is observed.

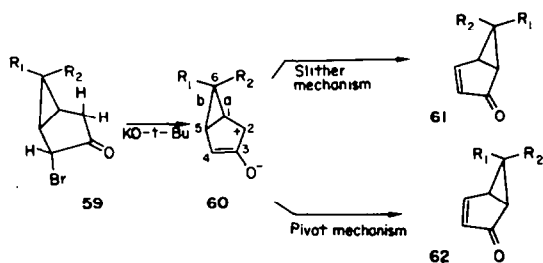


CHART 12. Slither and pivot mechanisms in the type A rearrangement.

The pivot mechanism can be pictured as a process (see Chart 12, structure 60) in which bond *a* remains intact and bond *b* is broken; thus carbon-6 detaches itself from C-5, there is pivoting about bond *a* and carbon-6 bonds to carbon 2 with retention of configuration at C-6.

The slither mechanism can be envisaged as a process in which bond *a* is broken as carbon-6 bonds to C-2 and concerted with this bond *b* is broken as carbon-6 begins to use its second valence to bond to carbon-1. An alternative view of the slither process is that bond *a* remains intact throughout, that bond *b* breaks as carbon-6 bonds to C-2 with inversion of

configuration at C-6. The pivot and slither transition states are shown in Chart 13. For the slither process, we arbitrarily select one of the two equivalent versions for illustration, this being the one with sp^2 hybridization at C-6 and both lobes of the *p*-orbital at this carbon being used.

In Chart 13, one observes that slither (or inversion) transition state 63 consists of a cyclic array of five orbitals (*i.e.* 1, 2, 3, 4 and 6a). As an approximation we omit sigma orbitals 5 and 6b as well as the oxygen π -system orbital. The cyclic system we have chosen has four delocalized electrons. In looking at this array, we find one site of inter-orbital sign inversion (*i.e.* between orbitals 1 and 6a) and the system is therefore Möbius.¹⁷ If we selected a different orientation for one of the cyclic array *p*-orbitals, we would still have an odd number of sign inversions and the system would still be termed Möbius. With four electrons and the ground state reaction, a Möbius system is aromatic and the transition state is allowed.¹⁷

Conversely, in transition state 64 for the pivot mechanism, we have a Hückel system¹⁷ made up of the array of the five orbitals 1, 2, 3, 4 and 6c. Were we to select one of the *p*-orbitals in the set as inverted, we would have two inversions between orbitals, but there would still be an even number and the system would still be Hückel. With 4 electrons a ground state Hückel system is antiaromatic and the transition state is forbidden.¹⁷ Hence, we can understand the preference for the slither, or inversion, stereochemistry.

We note that the inversion hybridization, that is, $sp^2 + p$, is equivalent to having two sp^3 hybrids at carbon-6. Thus, whether we picture carbon-6 as undergoing inversion of its *p*-orbital or instead slithering around the five ring with its two sp^3 orbitals acting as front and rear wheels of a bicycle, we are nevertheless dealing with two seemingly different but quantum mechanically equivalent pictures.

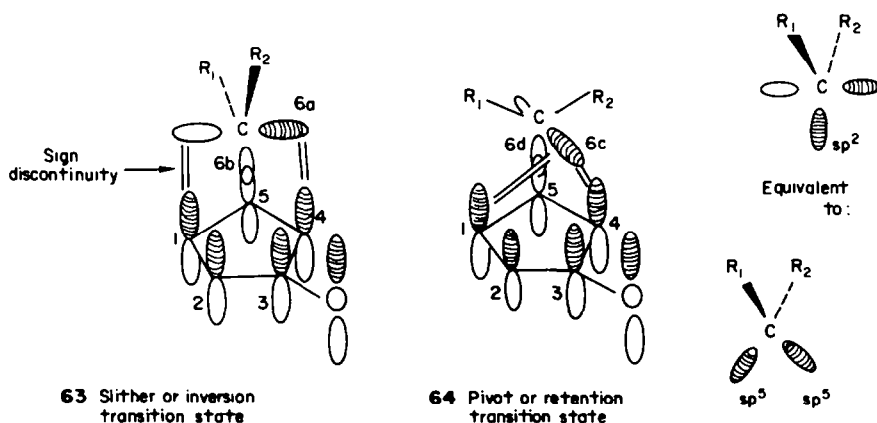


CHART 13. Pivot (retention) and slither (inversion) transition states and their basis orbital arrays.

CONCLUSION

Clearly there are a myriad of photochemical reactions involving stereochemistry and where stereochemistry allows mechanistic conclusions. We have dealt only with a review of photochemistry carried on in our own laboratories. Also, we are omitting a discussion of the di- π -methane rearrangement and its stereochemistry, since this has recently been reviewed exhaustively.²⁴

We conclude that stereochemistry is an integral part of mechanistic organic photochemistry and provides a powerful probe for many mechanistic questions.

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