The Di-π-methane and Oxa-di-π-methane Rearrangements

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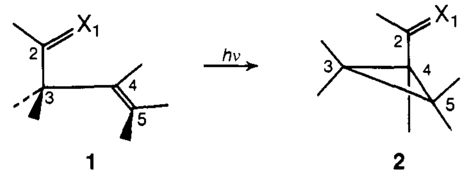
Contents

I. Introduction

In photochemistry, as in ground-state chemistry, the search for unifying principles has been of prime importance. The primary difference is that here correlations between molecular structure and reactivity must utilize the electronic makeup of the reacting excited state rather than the ground-state compound itself. A number of photochemical reactions have proven to be especially general, and it is not surprising that these have been subjected to particularly extensive investigation.

One of these has been termed the di-π-methane rearrangement by Zimmerman who first noted its generality. The reaction occurs on photolysis of molecules having two π moieties bonded to a single sp^3-hybridized (*i.e.*, saturated) carbon atom. In one variation the reactant has a carbonyl group as one π component; this is the oxa-di-π-methane reaction. The process leads to a π-substituted cyclopropane and formally involves migration of one π moiety bonded to the saturated carbon, C-3, to C-4 of the other π moiety, and concomitant three-ring formation between C-3 and C-5, as depicted in eq 1a.



(1a)

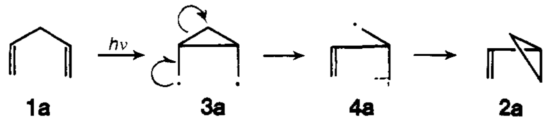
X ≡ C or O

This review summarizes both the di-π-methane and oxa-di-π-methane rearrangements. It surveys reactions in which the di-π-methane pathway is clearly operating and also those which involve di-π- and oxa-di-π-methane reactants, but without established mechanisms. Its purpose is to illustrate the significance and utility of this ubiquitous transformation and to indicate several of the interesting generalities which have developed concerning (a) the effects of structure on the excited-state multiplicity utilized by di-π-methanes for reaction, (b) the role of substituents on the π moieties in controlling the regiospecificity of the di-π-methane rearrangement, and (c) the preferred rearrangement stereochemistry in both di-π- and oxa-di-π-methane systems.

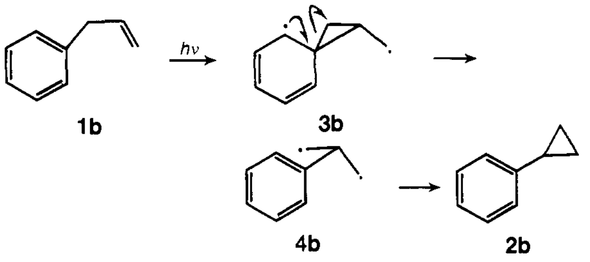
II. Di-π-methane Rearrangement

A. Exploratory Aspects and Multiplicity

It was noted by Zimmerman and coworkers[1] that the skeletal change in the di-π-methane rearrangement could be accounted for by one basic mechanism. This is expressed in the qualitative resonance terms of eq 1b; in (1b) two vinyl groups are used for simplicity, although the π systems may alternatively include phenyl (note eq 1c) or carbonyl groups.



(1b)



(1c)

It should be recognized that formulations such as those of eq 1b and 1c do not mean to imply that the species depicted along the reaction route necessarily are intermediates and thus correspond to energy minima. Rather these may just be points along the hypersurface leading from excited state of reactant to ground state of product. Each case must therefore be considered separately. Also, only in a small fraction of cases of interest is there information allowing one to specify the electronic state meant by such intermediate structures. Nevertheless, such qualitative valence-bond structures have proven exceedingly useful in describing the gross mechanism

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(1) H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966); H. E. Zimmerman, B. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969).

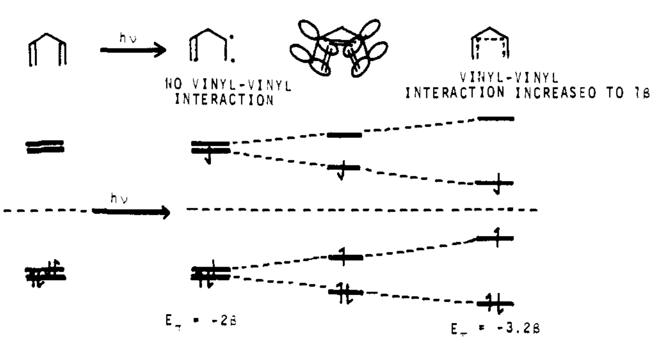
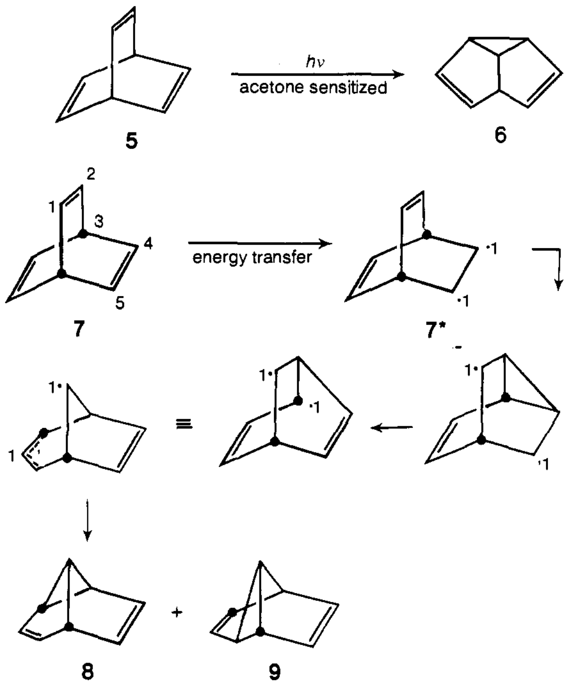


Figure 1. Results of C-2–C-4 orbital interaction in 1,4-diene excited states.

of photochemical rearrangements. Additionally, successful photochemical reactions are found to have continuous electronic redistribution pathways available, and this requirement is independent of our ability to fully specify electronic configurations and existence of energy minima for the intermediate species.

One of the first examples of the di-π-methane rearrangement was found by Zimmerman and Grunewald in the photochemical conversion of barrelene (**5**) to semibullvalene (**6**) using acetone sensitization (note eq 2a).[1] The details of the molecular reorganization occurring were demonstrated using hexadeuteriobarrelene (**7**); the disposition of the hydrogen label in the semibullvalene product corresponded to an equal composition of **8** and **9** and indicated that the pathway shown in eq 2b was being followed. This pathway for the di-π-methane rearrangement is seen to be the same as the general scheme of eq 1b.

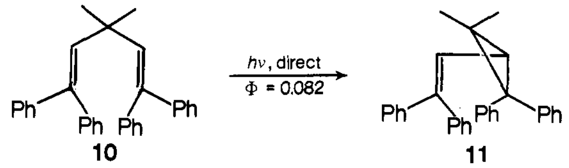


(2a)

(2b)

The vinyl-vinyl bonding during the initial steps of reorganization of an electronically excited 1,4-pentadiene system appears understandable and even predictable using first-order reasoning. It is easy to see that stabilization of either the singlet or triplet excited states of this nonconjugated diene system results when interaction of the orbitals at C-2 and C-4 occurs (note Figure 1). Thus, pathways in which this interaction takes place initially should be low-energy choices for the di-π-methane excited states (see Figure 1).

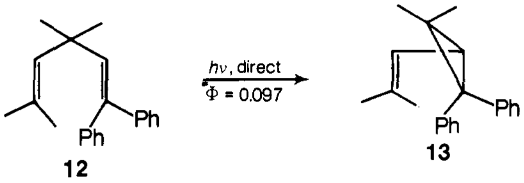
Another classic example of this rearrangement is found in the reaction of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**10**), studied by Zimmerman and Mariano.[2] This 1,4-diene rearranged readily upon direct irradiation to give 1,1-diphenyl-2,2-dimethyl-3-(2,2-diphenylvinyl)cyclopropane (**11**) with a quantum efficiency of 0.082 (see eq 3). The corresponding sensitized reactions, using



(3)

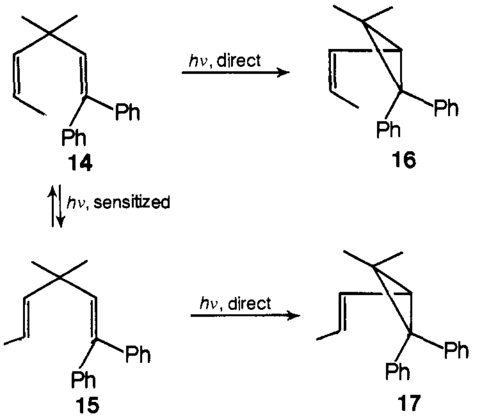
added benzophenone or acetophenone triplet sensitizers under conditions in which energy transfer to the diene occurs, failed to give detectable amounts of products. Zimmerman and Mariano[2] concluded that the di-π-methane reaction of **10** proceeds efficiently only *via* the singlet excited state manifold and that the singlet was the preferred excited state utilized by acyclic di-π-methane systems in general.

Similar results were noted by Zimmerman and Pratt[3] for 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene (**12**) which also rearranged efficiently from its singlet but not from its triplet excited state to the corresponding vinylcyclopropane **13** (eq 4). Additionally, the reaction demonstrated



(4)

remarkable regiospecificity. Another investigation by Zimmerman and Pratt[4] dealt with the photochemistry of *cis*- and *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (**14** and **15**) and the dependence of the reaction course and stereochemistry on multiplicity. Rearrangement of the cis and trans isomers occurred only upon direct irradiation and with extreme regiospecificity and striking stereospecificity. The cis isomer, **14**, yielded exclusively the *cis*-1-propenylcyclopropane **16**, and the trans isomer only the *trans*-propenyl product **17**. Owing to slow competing cis–trans interconversion of the reactants, this stereospecificity was observable only at low conversions.



(5)

In dramatic contrast to the direct irradiation (*i.e.*, singlet reactions) of dienes **14** and **15**, triplet-sensitized

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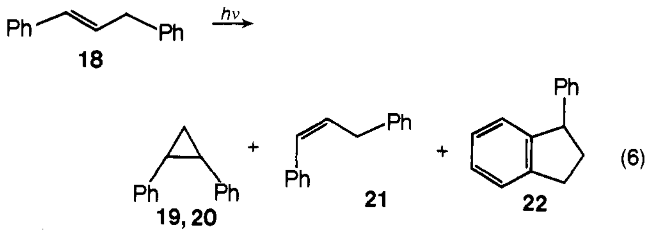
[2] H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969).

[3] H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **92**, 6259 (1970).

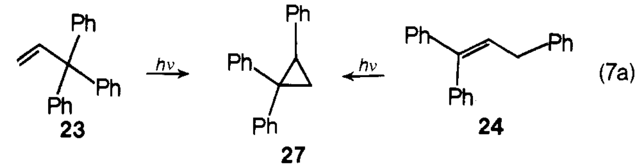
[4] H. E. Zimmerman and A. C. Pratt, *J Amer. Chem Soc.*, **92**, 6267 (1970).

photolyses failed to produce vinylcyclopropane products but, instead, led to efficient cis–trans isomerization, interconverting **14** and **15**. Thus, the answers to previous questions posed concerning the reasons why acyclic di-π-methanes are inert in the triplet manifold lie in the ability of acyclic 1,4-dienes to dissipate their triplet energies by cis–trans isomerization pathways. In the previous studies, involving the photochemistry of **10**[2] and **12**,[3] this deactivation pathway, by stereoisomerization about π bonds, was masked because of its degeneracy. Thus, the present example along with other di-π-methane rearrangements in acyclic and monocyclic systems has indeed substantiated the original proposal by Zimmerman and Mariano[2] that, in systems where free rotation about unconstrained π bonds can bring about efficient deactivation from their triplet excited states, the di-π-methane rearrangement proceeds *via* the singlet excited state.

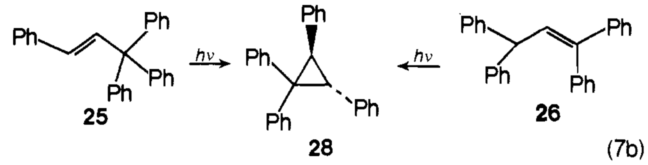
Griffin and coworkers[5,6] have extensively investigated the photochemistry of various substituted 3-phenylpropenes. These contain the di-π-methane system comprising phenyl and vinyl moieties in an acyclic arrangement. In each of these examples the rearrangement effected by direct irradiation involved phenyl migration to yield cyclopropane products. Direct irradiation of *trans*-1,3-diphenylpropene (**18**) in benzene or cyclohexane at low conversions produced a mixture of *cis*- and *trans*-1,2-diphenylcyclopropane (**19** and **20**) along with *cis*- and *trans*-1,3-diphenylpropene (**18** and **21**) and 1-phenylindan (**22**) as shown in eq 6.[5] The broad generality of this transformation is further demonstrated in the photochemistry of 3,3,3-triphenylpropene (**23**) and 1,1,3-triphenylpropene (**24**), both of which give product mixtures in which 1,1,2-triphenylcyclopropane (**27**) is the major product. Similarly, photolysis of 1,3,3,3-tetraphenylpropene (**25**) and 1,1,3,3-tetraphenylpropene (**26**) afforded the stereoisomers of 1,1,2,3-tetraphenylcyclopropane (**28**) as major components (eq **7**).[6] A final example in the series offered by Griffin and coworkers is the interesting conversion of 1,1,3-triphenylindene (**29**) to 1,2,3-triphenylindene (**30**) upon direct irradiation; the product in this case most probably arises from a secondary thermal process involving a 1,5-hydrogen shift in isoindene **31** as suggested by Griffin. Benzohousene product **32**[6] is a potential transient intermediate, and thus the reaction either is an ordinary di-π-methane type or is one where the pathway is diverted after completion of phenyl migration (as **1b** → **3b** in eq 1c).



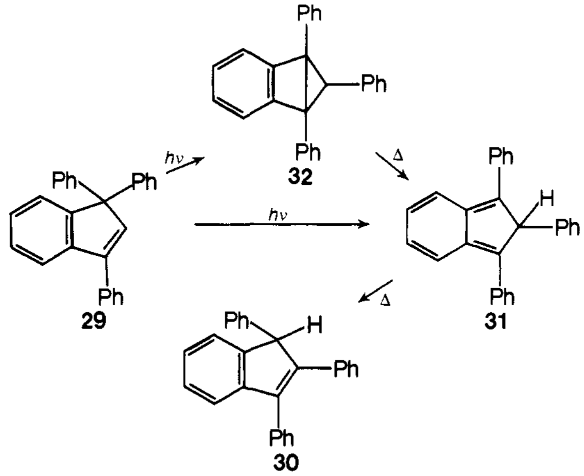
(6)



(7a)

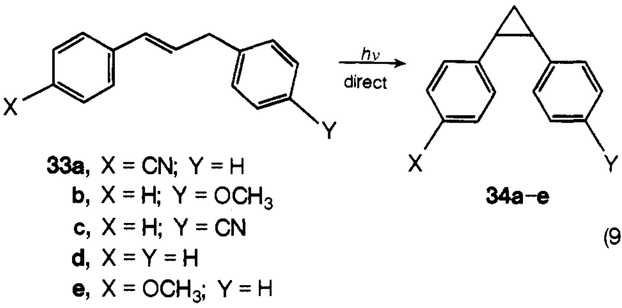


(7b)



(8)

It is important to note that, although the general di-π-methane rearrangement pathway easily explains the nature of the molecular reorganization in each of these systems, mechanisms which involve photoinduced 1,2-hydrogen shifts can equally well explain the structural aspects of the conversions of propenes **18** and **24** to their corresponding cyclopropanes, as noted by Griffin. However, in the case of **18** it has been shown by Hixson that it is indeed phenyl which migrates.[6b] In addition, although these investigations were mainly qualitative in nature and, therefore, did not delineate the multiplicities of the 3-phenylpropene excited states undergoing reaction, related systems have been shown to undergo the analogous reactions exclusively from their singlet manifold. Hixson[7] has shown that triplet-sensitized photolyses of a series of para-substituted 1,3-diphenylpropenes (**33**a–**e**) gave no detectable amounts of the 1,2-diarylcyclopropanes (**34**a–**e**), the major products of direct irradiation, but did cause extensive cis–trans isomerization (eq **9**).



(9)

Thus, the observations of singlet di-π-methane rearrangement and triplet cis–trans isomerization in the 3-phenylpropene systems add further evidence to the proposed multiplicity control of the fate of acyclic di-π-methane excited states. Additional support for this generalization is found in the transformation on direct irradiation of the 1-phenyl-2,4-pentadienes, **35**, *via* phenyl migration, to a mixture of *cis*- and *trans*-1-phenyl-2-vinylcyclopropanes, **36** and **37**, as observed by Hammond and Kristinsson (eq 10).[8]

Di-π-methanes containing one of the two π moieties in a six-ring system and lacking structural constraints which prohibit free rotation about all the π bonds also appear to undergo rearrangement to their corresponding π-substi-

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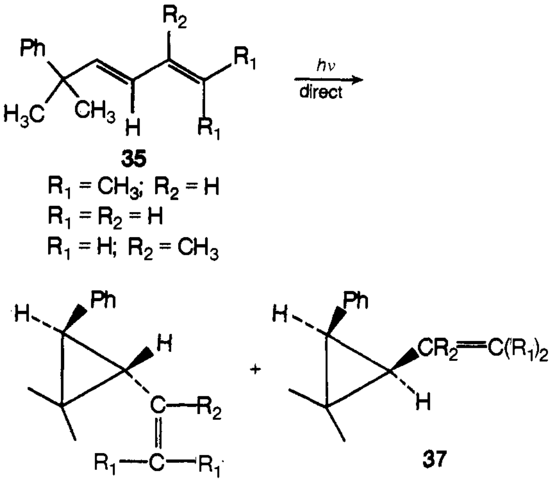
(5) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and C. Close, *J. Amer. Chem. Soc.*, **87**, 1410 (1965).

(6) (a) G. W. Griffin, A. F. Marcantonio, and H. Kristinsson, *Tetrahedron Lett.*, 2951 (1965); (b) S. Hixson, *ibid.*, 1155 (1972).

(7) S. Hixson, *J. Amer. Chem. Soc.*, **94**, 2507 (1972).

(8) H. Kristinsson and G. S. Hammond, *J. Amer. Chem. Soc.*, **89**, 5968, 5970 (1967).

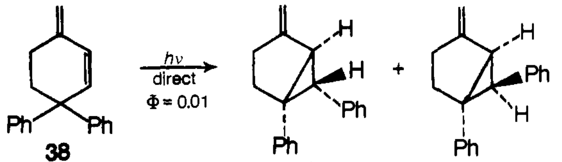


35

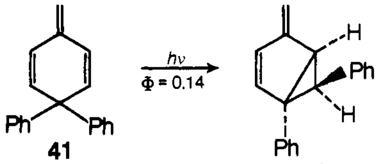
$R_1 = CH_3$; $R_2 = H$
$R_1 = R_2 = H$
$R_1 = H$; $R_2 = CH_3$

36 **37** (10)

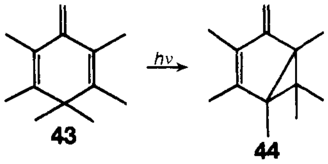
tuted cyclopropane products efficiently only from their singlet excited states. One example is the unsensitized rearrangement of 1-methylene-4,4-diphenyl-2-cyclohexene (**38**) to a mixture of the cis and trans bicyclic olefins **39** and **40**, in which the trans diastereomer predominates (eq 11).[9] Sensitized irradiation of this exocyclic methylene di-π-methane system (*i.e.*, **38**) failed to produce detectable amounts of products, showing the triplet of **38** to be unreactive. Similarly, the triene analog, 1-methylene-4,4-diphenyl-2,5-cyclohexadiene (**41**), undergoes rearrangement *via* phenyl migration only in the singlet manifold; the trans-bicyclic diene **42** is the predominant product (eq 12).[10] Analogous behavior, however involving vinyl-vinyl rather than phenyl-vinyl bonding, is displayed by the 1-methylenecyclohexa-2,5-dienes, **43** and **45**, as depicted in eq 13.[11,12]



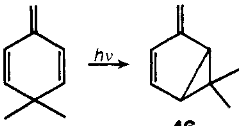
38 **39** **40** (11)



41 **42** (12)

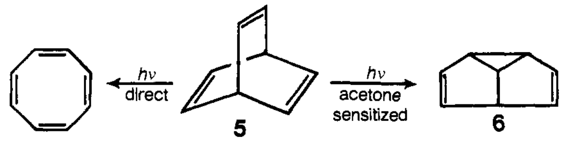


43 **44** (13a)

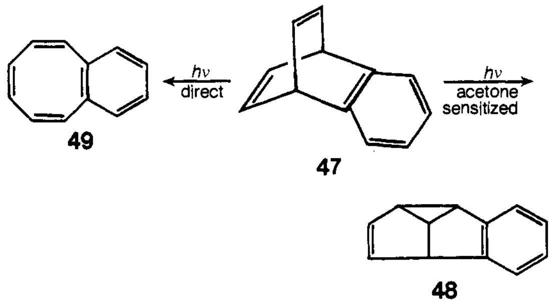


45 **46** (13b)

The contrasting di-π-methane reactivity of various bicyclic systems like barrelene (**5**), which contain both π moieties within rigidly structured environments, and the acyclic and exocyclic methylene monocyclic systems is dramatic in that in the former the triplet multiplicity is required for rearrangement. Zimmerman and coworkers[1] have shown, as discussed above, that barrelene (**5**) rearranges by the di-π-methane pathway to semibullvalene (**6**) solely with acetone sensitization. In contrast, cyclooctatetraene is the major product of direct irradiation. The case of benzobarrelene (**47**) is similar in that rearrangement to benzosemibullvalene (**48**) occurs from the triplet while benzocyclooctatetraene (**49**) is produced on direct irradiation (eq 14).[13] A number of similar examples exist, each demonstrating the general phenomenon of preferred triplet multiplicity for di-π-methane rearrangements in rigidly constrained systems, *i.e.*, in structures which prohibit free rotation about the π bonds. Characteristic of these are the observations of Edman[14] of the acetophenone-sensitized transformation of benzonorbornadiene (**50**) to the benzotricycloheptene, **51**; of Brewer and Heaney[15] where tetrafluorobenzobarrelene (**52**) rearranged to the corresponding semibullvalene, **54**; of Liu[16] in which 2,3-bistrifluoromethylbarrelene (**55**) underwent sensitized rearrangement to the three semibullvalenes **56–58**; and of Ciganek[17] and Friedman[18] of the efficient sensitized conversion of dibenzobarrelene (**59**) to dibenzosemibullvalene (**60**), as summarized in eq 15a–d.



5 **6** (14a)



49 **47** **48** (14b)

The structure-multiplicity relationships generally adhered to in the di-π-methane rearrangement (Table I) appear to result from several governing factors. The triplet excited states of the acyclic and methylene monocyclic di-π-methanes appear to have more efficient pathways available for dissipation of the excited-state energy than for rearrangement to π-substituted cyclopropanes. These energy dissipation pathways involve free rotation about nonconstrained π bonds. Such energy dissipation was directly observable (*vide supra*) in the example of Zimmerman and Pratt[3] in the photochemistry of *cis*- and *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (**14** and **15**) where cis–trans isomerization was actually found. In contrast, rapid di-π-methane isomerization pathways are

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(9) H. E. Zimmerman and G. E. Samuelson, *J. Amer. Chem. Soc.*, **91**, 5307 (1969); **89**, 5971 (1967).

(10) H. E. Zimmerman, P. Hackett, D. F. Juers, and B. Schroder, *J. Amer. Chem. Soc.*, **93**, 3653 (1971); **89**, 5973 (1967).

(11) H. Hart, J. D. DeVrieze, R. M. Lange, and A. Sheller, *Chem. Commun.*, 1650 (1968).

(12) H. E. Zimmerman, D. F. Juers, J. M. McCall, and B. Schröder, *J. Amer. Chem. Soc.*, **93**, 3662 (1971).

(13) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J Amer. Chem. Soc.*, **90**, 4194, 6090 (1968).

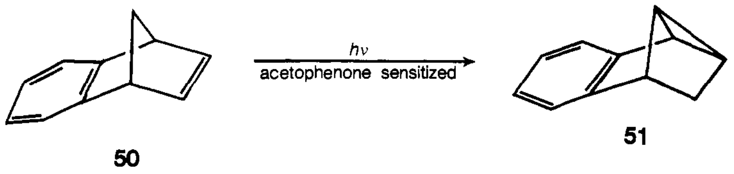
(14) J. R. Edman, *J. Amer. Chem. Soc.*, **91**, 7103 (1969).

(15) J. P. N. Brewer and H. Heaney, *Chem. Commun.*, 811 (1967).

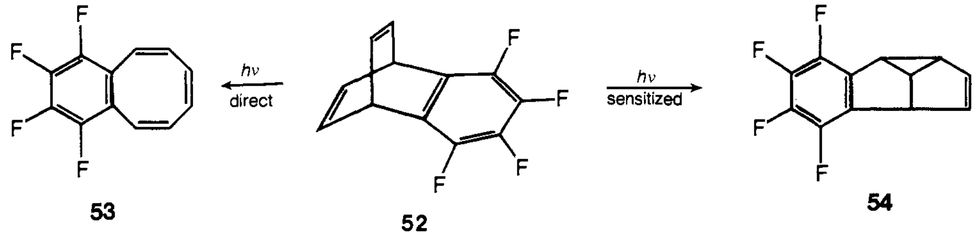
(16) R. S. H. Liu, *J. Amer. Chem. Soc.*, **90**, 802 (1968).

(17) E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 2882 (1966).

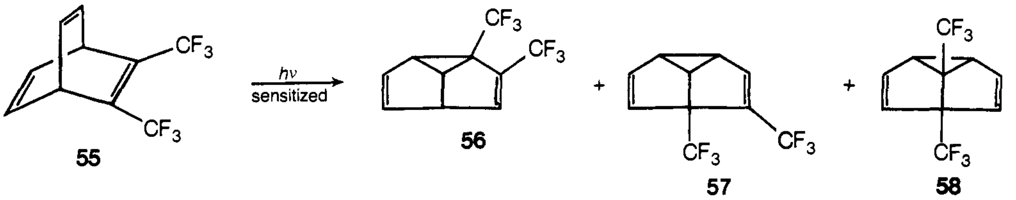
(18) P. W. Rabideau, J. B. Hamilton, and L. Friedman, *J. Amer. Chem. Soc.*, **90**, 4465 (1968).



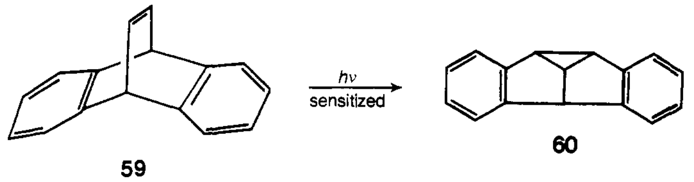
(15a)



(15b)



(15c)



(15d)

TABLE I. Structure–Multiplicity Relationship in the Di-π-methane Reaction

Di-π-methane structural feature	Singlet excited state	Triplet excited state
Presence of nonconstrained or free π moiety	Efficient	Inefficient
Absence of nonconstrained or free π moiety	Inefficient	Efficient

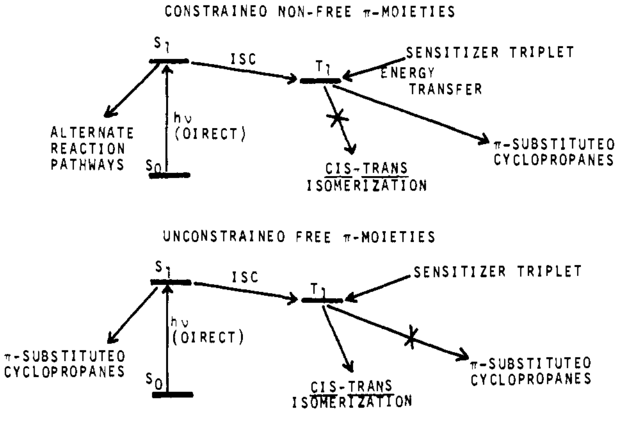


Figure 2. Pathways for di-π-methane excited state deactivation.

available to the properly substituted singlets of flexible di-π-methane systems. Moreover, in these systems competing singlet reactions are commonly not available. However, whenever alternative and more efficient reaction pathways are open, the singlet excited di-π-methane to π-substituted cyclopropane transformation becomes unobservable. These alternate singlet pathways are exemplified in barrelene and benzobarrelene photochemistry in which 2 + 2 cycloaddition, leading eventually to the cyclooctatetraene products, overwhelmingly predominates (see eq 14 and 15). On the other hand, the triplet excited states of bicyclic systems are incapable of "free-rotor" energy dissipation due to their rigid structures; thus, the pathways for triplet transformation in these cases involve conversion to π-substituted cyclopropanes. The patterns of behavior are summarized in Figure 2.

This rationale of the structure–multiplicity relationships merely on the basis of the presence or absence of structural features which provide mechanisms for energy degradation seems reasonable in light of recent observations of Dauben,[19] Zimmerman,[20] and Swenton.[21] Zimmerman and Samuelson[9] had shown earlier that the triplet excited state of the exocyclic methylene monocyclic di-π-methane **38**, formed by benzophenone sensitization, was inert, and that this could be ascribed to "free-rotor" deactivation about the exocyclic π bond. In accord with this view, the structurally related endocyclic diene **61**[20,21] and monoolefin **62**[19] upon sensitized photolyses proceed smoothly to their corresponding π-substituted cyclopropane products **63**, **64** and **65**, **66**, respectively, as outlined in eq 16. This remarkable restoration of triplet di-π-methane reactivity is reasonably attributed to the absence of any exocyclic π bonds in cyclohexene **62** and cyclohexadiene **61**, thereby eliminating the alternative pathway for triplet energy dissipation by simple stereoisomerization. In addition, the singlet photochemistry of 5,5-diphenylcyclohexadiene (**61**) emphasizes that one always has to consider competing and more efficient types of reaction. In this case the formation of triene **67** from the singlet suggests that the electrocyclic opening is very facile.

It is interesting to speculate further on the mechanism for energy dissipation from triplet excited states of both

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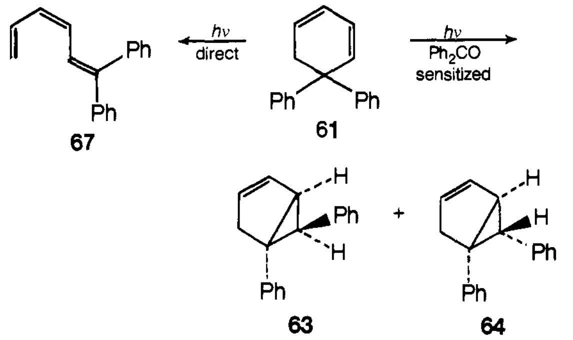
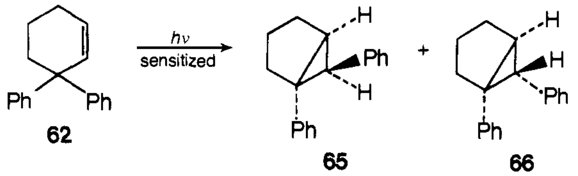
[19] W. G. Dauben and W. A. Spitzer, *J. Amer. Chem. Soc.*, **92**, 5817 (1970).

[20] H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, **92**, 1411 (1970).

[21] J. S. Swenton, A. L. Crumrine, and T. J. Walker, *J. Amer. Chem. Soc.*, **92**, 1406 (1970).

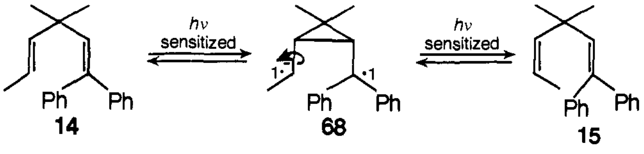


(18a)



(16b)

acyclic and methylene monocyclic di-π-methanes. While one possible mechanism involves the triplet double bond isomerization already discussed and observed in a multitude of olefinic systems, an alternative involves reversible formation of the triplet cyclopropyl-dicarbinyl-diradical species written in the di-π-methane rearrangement mechanism. Thus, in the case of diene **14** rotation about the 1-2 and 4-5 bonds in the species **68** formed by 2-4 bonding leads to loss of stereochemistry, and the energy is dissipated as this diradical reverts to diene **14** or **15**.

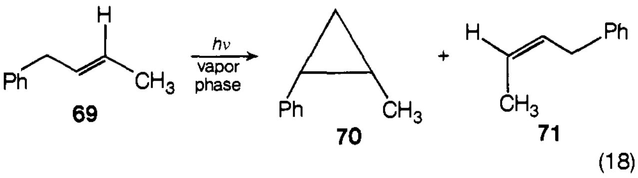


(17)

This latter explanation seems more plausible when consideration is taken of the relative triplet energies of the π chromophores involved. In the case of excited 1,4-dienes, **14*** and **15***, the triplet energy should be heavily localized in the diphenylethylene moiety and not the propenyl group, so that isomerization about the propenyl π bond would not ordinarily be expected.

Although the generalities stated above derive from numerous examples of di-π-methane photochemistry in acyclic, monocyclic, and bicyclic systems and therefore appear to be the rule rather than exception, it is worthy to note that several exceptions do exist.

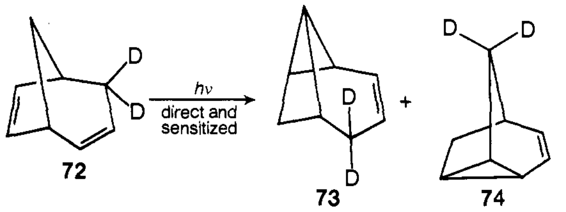
Comtet[22] has concluded, for instance, from studies of the gas-phase photochemistry of *trans*-1-phenyl-2-butene (**69**), that di-π-methane rearrangement to 1-phenyl-2-methylcyclopropane (**70**) proceeds *via* the second triplet.



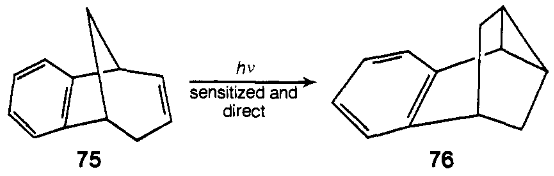
(18)

These conclusions were based upon the inability to quench formation of the cyclopropane product under conditions which effectively reduced the fluorescence quantum yield and sensitization studies in which acetophenone efficiently sensitized cis-trans isomerization but not cyclopropane formation.

Another interesting case is found in the photochemistry of 4,4-dideuteriobicyclo[3.2.1]octa-2,6-diene (**72**) which rearranges to a mixture of tricyclic olefins **73** and **74** upon both direct and sensitized irradiation (eq **19**a).[23] Related to this are the observations by Hahn and Rothman[24] on the photochemistry of the benzo analog **75**, which rearranges to the benzotricyclooctane **76** on direct irradiation. These cases are summarized in eq **19**a and **19**b. Whether these two cases really are exceptions to the multiplicity generalization is uncertain. It is possible that, in absence of a facile singlet process, intersystem crossing affords the triplet which rearranges. Alternatively, it is perfectly possible that a singlet di-π-methane rearrangement really does occur in bicyclic examples when a facile simple electrocyclic process does not compete.

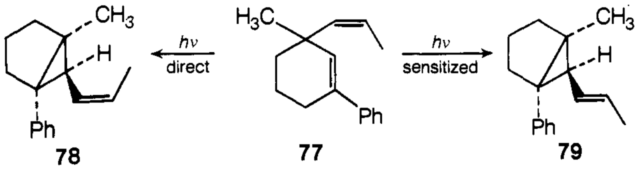


(19a)



(19b)

An exception of another type, namely where a free rotor present does not inhibit di-π-methane triplet reactivity, is apparent in the work of Mariano and Ko[25] on the singlet and triplet di-π-methane reactivity of 1-phenyl-3-methyl-3-(*cis*-1-propenyl)cyclohexene (**77**) as summarized in eq **19**c. A second exception is found in the work of Kende (see ref 36) discussed below in connection with regiospecificity. Here benzomethylenebicyclononatriene (**126**) was found to exhibit di-π-methane reactivity (note eq 28c) despite the presence of an *exo*-methylene potential free rotor.



(19c)

It is obvious that a free rotor is capable of destroying a triplet only if its rate of energy dissipation by 90° rotation is faster than the rate of di-π-methane rearrangement. That free rotor energy dissipation will necessarily inhibit all di-π-methane reactions then can be seen to be an overstatement. Ideally, an investigation of the rates of a series of triplet di-π-methane transformations and comparison of these with the rate of the free rotor process would cast more light on the matter. Presently, it is sufficient to note that the free rotor effect inhibits most di-π-methane processes of triplets.

In addition to the above examples of the di-π-methane reaction, studied mainly with the idea of gathering information on the mechanistic and structural features of the rearrangement, many other systems are known to undergo the reaction. Some of these examples have well-stud-

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(22) M. Comtet, *J. Amer. Chem. Soc.*, **91**, 7761 (1969); **92**, 5308 (1970).

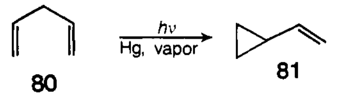
(23) R. S. Sauers and A. Shurpik, *J. Org. Chem.*, 33, 799 (1968).

(24) R. C. Hahn and L. J. Rothman, *J. Amer. Chem. Soc.*, **91**, 2409 (1969).

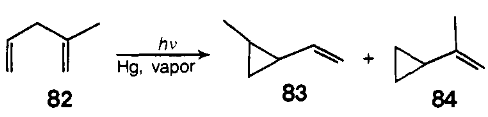
(25) P. S. Mariano and J. K. Ko, *J. Amer. Chem. Soc.*, **94**, 1766 (1972).

ied mechanisms and have been recognized as proceeding by di-π-methane pathways while others have not but, on reflection, appear to fit into the general patterns discussed.

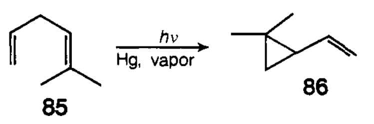
In comprehensive studies by Meinwald[26] and Srinivasan,[27] the mercury-sensitized, vapor-phase photochemistry of a series of 1,4-pentadienes was reported. The parent compound, **80**, was shown to yield mainly vinylcyclopropane (**81**) plus several other products in trace amounts on mercury ($^3P_1$) sensitized irradiation.[27] The other systems studied by these workers include 2-methyl-1,4-pentadiene (**82**), 5-methyl-1,4-hexadiene (**85**), 3,3-dimethyl-1,4-pentadiene (**87**), and 1,1-divinylcyclohexane (**89**), the results of which are summarized in eq 20a–e. In addition and related to these is the observation of Reusch[28] of the mercury-sensitized isomerization of 3,3,6,6-tetramethyl-1,4-cyclohexadiene (**92**) to 4,4,6,6-tetramethylbicyclo[3.1.0]-2-hexene (**93**) (note eq 20f).



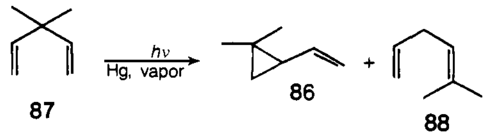
(20a)



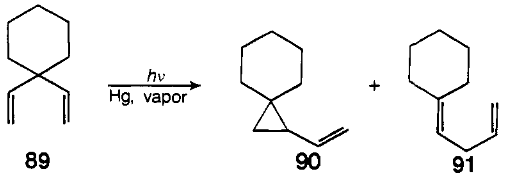
(20b)



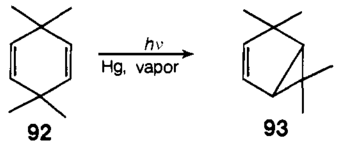
(20c)



(20d)



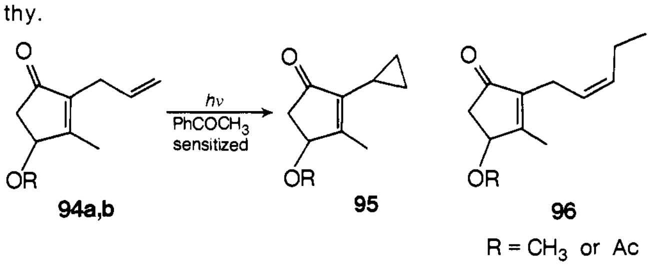
(20e)



(20f)

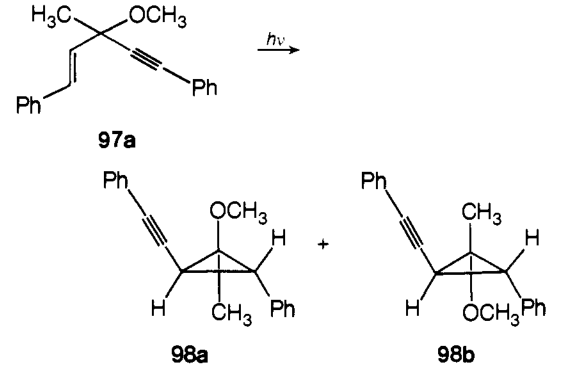
The vapor-phase photolyses of eq 20a–f are included for completeness. These probably proceed by triplet energy transfer from the Hg($^3P_1$) triplet to give vibrationally excited diene triplets. In contrast to the solution-phase photochemistry discussed thus far, the reacting excited states possess excess vibrational energy, and one would not expect the various generalizations (*e.g.*, the free rotor effect) to necessarily hold. Thus, for example, solution phase photosensitization of **87** with acetone does not afford the vapor-phase product **86**.[26]

A rather unusual example of an apparent di-π-methane rearrangement of a 1,4-diene has been uncovered by Bullivant and Pattenden[29] in their study of the 2-allylcyclopentenones, **94** and **96**. Triplet-sensitized photolyses of **94** led to efficient formation of the 2-cyclopropylcyclopentenones, **95**, while similar irradiation of the analogous 1-(2-pentenyl) system, **96**, caused only stereoisomerization about the exocyclic π bond even after extended irradiation. Although an alternative hydrogen shift mechanism may be operating in the rearrangement of **94**, the unusual disparity between the reactivity of **94** and **96**, the successful rearrangement of the triplet of **94**, and the unusual regiospecificity in rearrangement are all noteworthy.

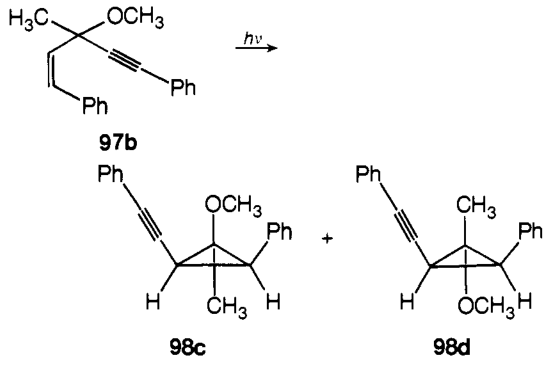


(21)

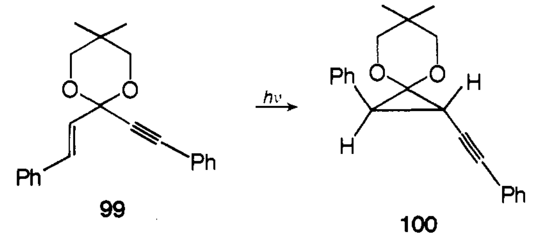
Griffin and coworkers[30] have recently studied several novel di-π-methane systems having π moieties other than phenyl or vinyl. Both *trans-* and *cis*-1,5-diphenyl-3-methoxy-3-methylpent-1-en-4-yne (**97a** and **97b**) undergo rearrangement upon direct irradiation to their corresponding acetylenic cyclopropanes, **98a–d**, and the cyclic ketal analog **99** similarly rearranges to **100** as depicted in eq 22. Additionally, the allenyl-vinyl methanes **101** and **104**



(22a)



(22b)



(22c)

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[26] J. Meinwald and G. W. Smith, *J. Amer. Chem. Soc.*, **89**, 4923 (1967).

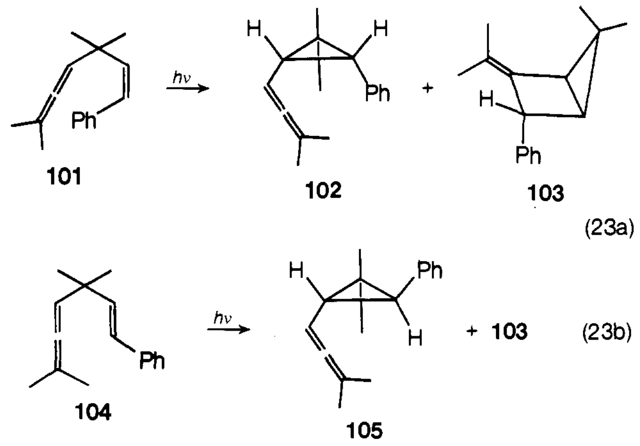
[27] R. Srinivasan and K. H. Carlough, *J. Amer. Chem. Soc.*, **89**, 4932 (1967).

[28] W. Reusch and D. W. Frey, *Tetrahedron Lett.*, 5193 (1967).

[29] M. J. Bullivant and G. Pattenden, *J. Chem. Soc., Chem. Commun.*, 864 (1972).

[30] B. Halton, M. Kulig, J. Perreten, D. M. Gibson, and G. W. Griffin, *J. Amer. Chem. Soc.*, **93**, 2327 (1971); D. J. Keyton, J. J. Brophy, and G. W. Griffin, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, No. ORGN-91; G. W. Griffin, J. Perreten, D. C. Lankin, and D. M. Chihal, presented in preliminary form at the 27th American Chemical Society Southwest Regional Meeting, San Antonio, Tex., 1971; and private communication of most recent results.

produce minor amounts of the allenylcyclopropanes **102** and **105**, respectively; in both of these systems, however, the methylenehousane **103** is the major component in the product mixture (eq 23). Not only do these reactions represent interesting extensions of the general rearrangement to new di-π-methane systems, but also they reflect the considerable regiospecificity that is characteristic of unsymmetric di-π-methanes.



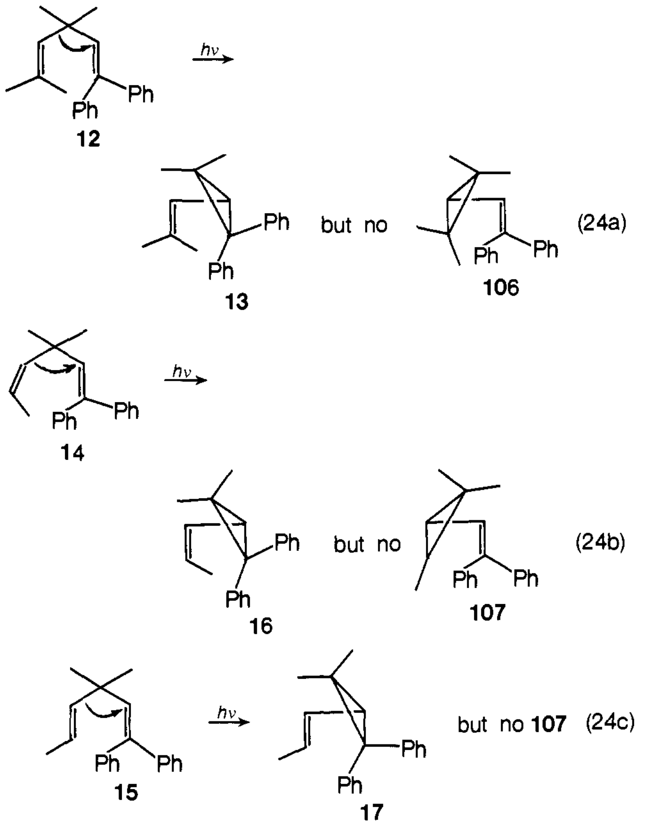
B. Regiospecificity

Zimmerman and Pratt[3,4] were the first to recognize and explain the extreme regiospecificity of the di-π-methane rearrangement, *i.e.*, the strong preference for migration of one of the two different π moieties attached to the saturated carbon in an unsymmetric di-π-methane system.

The controlling factors are best illustrated by the examples of the singlet isomerizations of 3,3,5-trimethyl-1,1-diphenyl-1,4-hexadiene (**12**)[2] and the cis (**14**) and trans (**15**) isomers of 1,1-diphenyl-3,3-dimethyl-1,4-hexadiene[3] as described by Zimmerman and Pratt. In each of these cases the sole product isolated (eq 24a–c) resulted from a pathway involving migration of the less conjugated π moiety to the more conjugated one; *e.g.*, **13** and not **106** is the sole product from photolysis of **12.** These observations were rationalized by Zimmerman and Pratt on the basis of a preferred direction of ring opening of the cyclopropyldicarbinyl diradical species. Thus opening of **108** proceeds preferentially by pathway b to give **110** and thence **13.** The controlling factor is maintenance of maximum odd-electron stabilization during the three-ring opening process. Route a leads to loss of benzhydryl delocalization while pathway b does not.

It should be noted that this rationale does not require a nonconcerted mechanism. The species in eq 25a and 25b may just be points on a potential energy surface and then not represent energy minima. To the extent that these species are useful in depicting odd-electron disposition along the reaction coordinate, one can expect predictions based on such models to correlate with experiment.

In another instructive case, Zimmerman and Baum[31] observed a striking predominance for formation of the α-styrylcyclopropane (**114**) over the β-diphenylvinylcyclopropane (**116**) in the singlet transformation of 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene (**111**). Here the unzipping process a in eq 26 is preferred over opening b since less delocalization energy is lost. This example is of further importance, since in contrast to the previous example the difference in singlet excitation energy of the two moieties is very small. This means one can rule out control by relative energy of the two π moieties.



Thus far, qualitative resonance (*i.e.*, electron pushing) reasoning has been employed in discussion of the di-π-methane rearrangement. It has been noted that this is just a convenient notation which allows resonance structures to depict the molecule at various stages along the reaction coordinate.

An alternative but equivalent view is given in Figure 3 which depicts the orbital array at midreaction. Here the old bonds are between orbitals c and d (*i.e.*, the old π bond between atoms 1 and 2), between orbitals e and f (*i.e.*, the old σ bond holding vinyl group 1–2 to the methane carbon 3), and between orbitals a and b (*i.e.*, the second initial π bond). New overlap occurs between orbitals b and c (corresponding to vinyl–vinyl bonding), between orbitals e and d (regenerating a π bond between atoms 1 and 2), and between orbitals a and f (forming the three ring). The last overlap seems to lag behind the other processes from evidence available. There is the exciting point that despite appearances, the 1,2 π′ bond of the product is really not the π bond of the reactant.

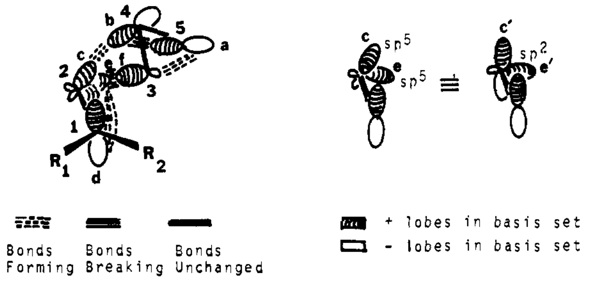


Figure 3. Orbital array during the di-π-methane rearrangement. Note that the orbitals shown are basis orbitals before any MO mixing and bonding or antibonding is not implied by overlap between pairs.

It has been noted by Zimmerman[2-4] that this picture constitutes a Möbius cyclic array of six orbitals in the se-

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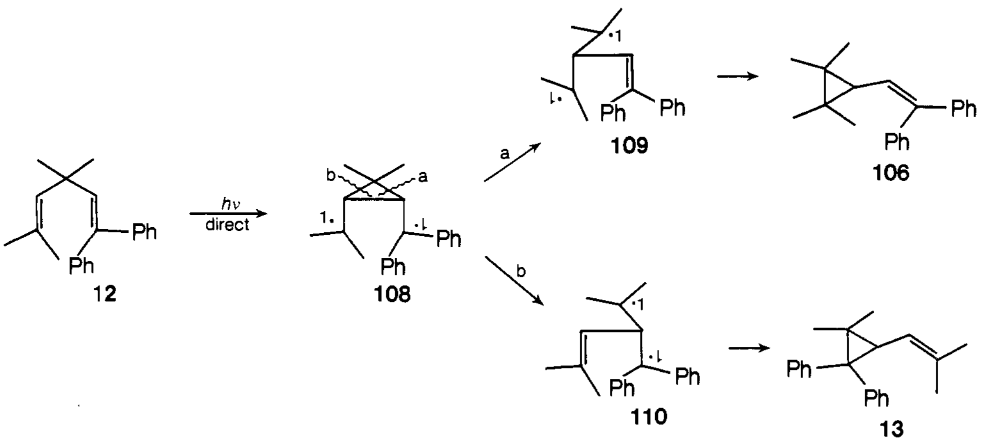
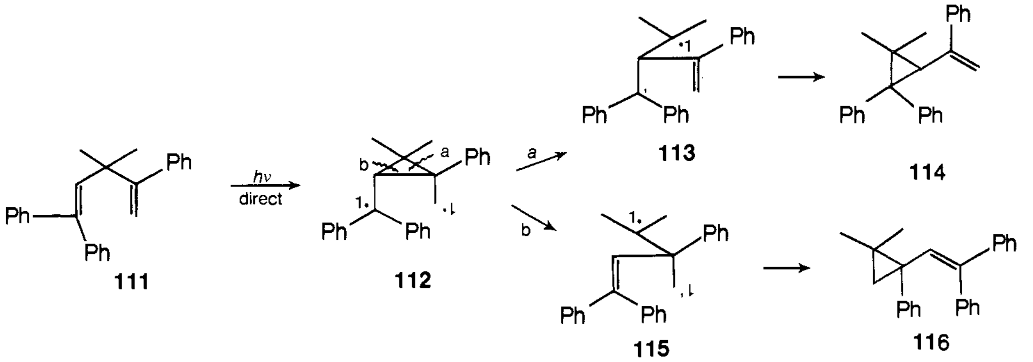
(31) H. E. Zimmerman and A. Baum, *J. Amer. Chem. Soc.*, **93**, 3646 (1971).



(25a)

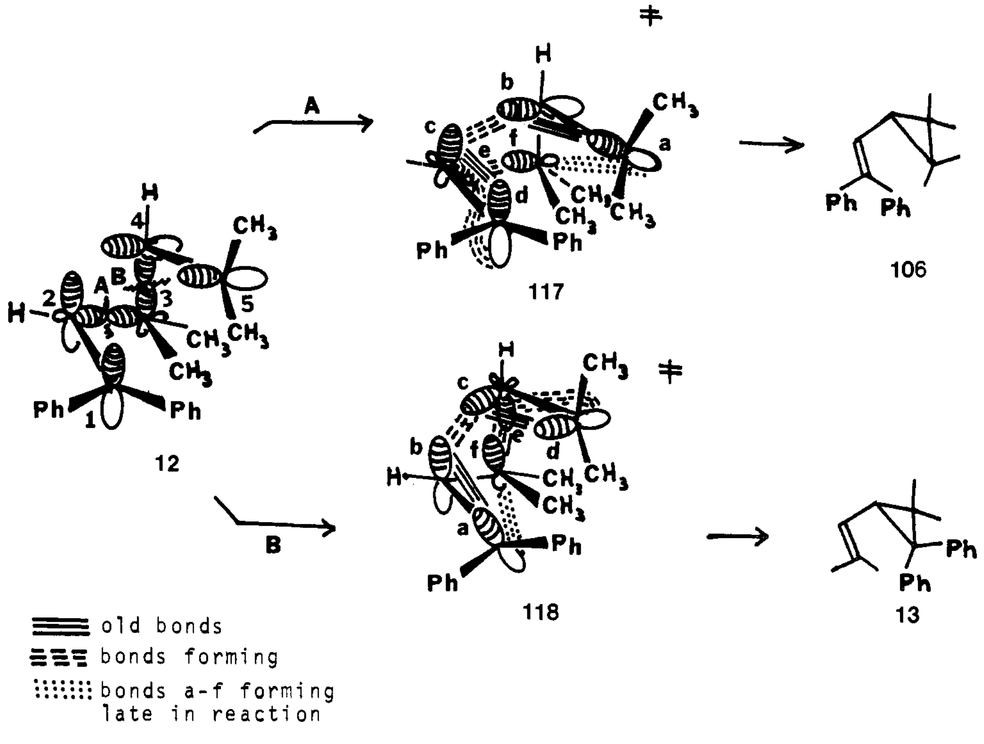
(25b)



(26a)

(26b)

CHART I



quence a–b–c–d–e–f, since the overlap between orbitals e and d is of the +− variety while all other overlap is ++ or −−. This odd number of sign inversions between pairs of basis orbitals in the cyctic array categorizes the system as Mobius.[32] While a Mobius system in the ground state is antiaromatic with six electrons, it is aromatic and stable in the excited state. Thus, the present transformation depicted in Figure 3 is an allowed one.

When extended to the di-π-methane reaction of the diphenyl-tetramethyl-diene **12**, the orbital representation is as shown in Chart I. Another aspect is seen if we recognize that the bonding between orbitals a and f is minimal early along the reaction coordinate. Then one can understand the preference for the pathway leading to product **13** rather than **106**. We note that in the array (*i.e.*, **118**) leading to **13** the phenyl substitution is at orbital a, which

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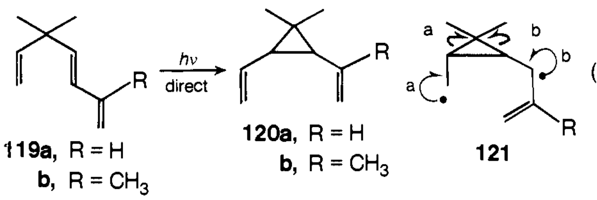
[32] (a) H E. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971); (b) *J. Amer. Chem. Soc.*, **88**, 1564 (1966).

as an approximation can be considered the end of the six-orbital chain Ph$_2$-a-b-c-d-e-f. Here we neglect overlap a-f which develops only later after the rate-limiting stage of the reaction. In contrast, array **117** has the phenyl substitution at orbital d of the array a-b-c-d(Ph$_2$)-e-f. Both arrays are hexatriene-like, and it is clear that the lower energy excited state is obtained with phenyl substitution at the end of the chain. Independent of the mechanistic model used, it is the less substituted vinyl group which ends up migrating.

An interesting example was reported by Roth and Peltzer[33] and later by Japanese researchers[34] (note eq 27).



119a, R = H
b, R = CH$_3$

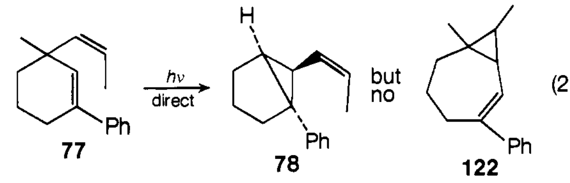
120a, R = H
b, R = CH$_3$

121

(27)

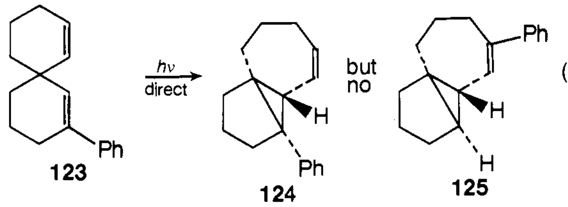
In both cases it is seen that the reasoning employed above nicely rationalizes the directionality of opening intermediate **121** and hence the product structure. For example, using resonance reasoning, we note in species **121** process a is favored over opening b since the electron density needed for the former (*i.e.*, a) is more available due to diminished initial delocalization.

There are additional examples which confirm the preference for migration of the less conjugated to more conjugated π chromophore. Several of these are the singlet transformation of propenylcyclohexene **77**[25] and spirodiene **123**[35] and photoisomerization of the benzomethylenebicyclononatriene **126**,[36] all depicted in eq 28a-c.



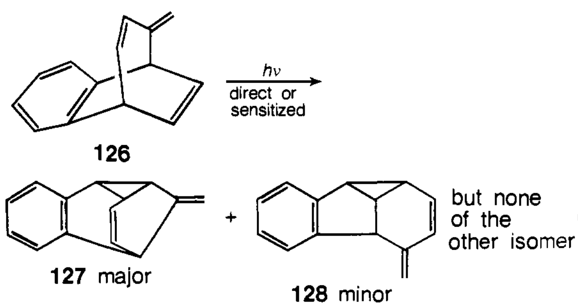
77 **78** **122**

(28a)



123 **124** **125**

(28b)



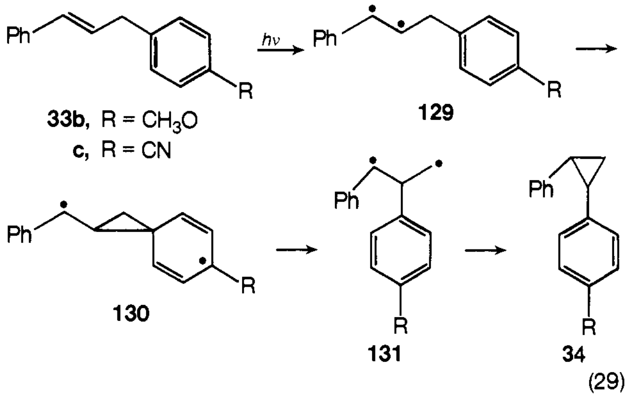
126

127 major

128 minor

but none of the other isomer (28c)

Finally, there are some studies by Hixson on the singlet migratory aptitudes for aryl-vinyl systems. In the rearrangement of **33b** and **33c** it was observed that both *p*-methoxyphenyl (*i.e.*, in **33b**) and *p*-cyanophenyl (*i.e.*, in **33c**) have excited singlets which rearrange more rapidly than the parent compound. This is consistent with a rearrangement in which the migrating group moves to an odd-electron center.[7]



33b, R = CH$_3$O
c, R = CN

129

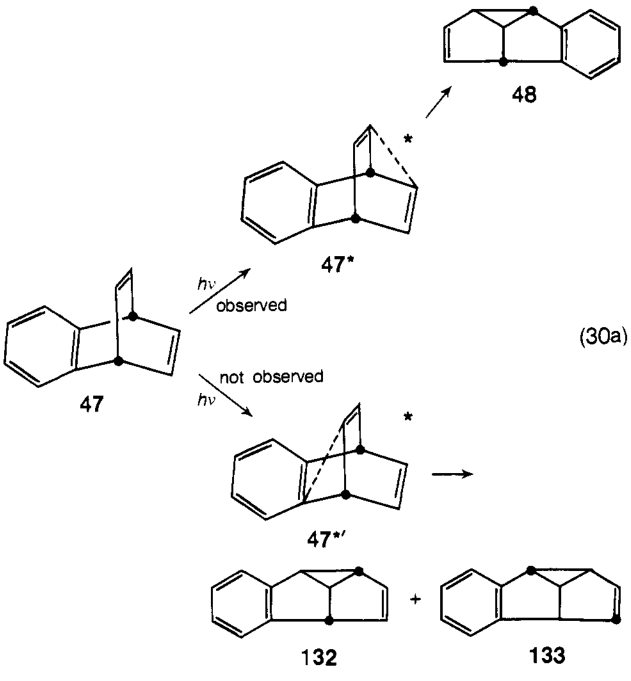
130

131

34

(29)

Bicyclic di-π-methanes also show regiospecificity in their triplet reorganization reactions, but the factors which control migratory preferences appear more complex than those of the singlet di-π-methane rearrangements discussed above. Zimmerman and coworkers[13] observed the preference for vinyl over benzo migration in the benzobarrelene (**47**) to benzosemibullvalene (**48**) sensitized transformation. This was demonstrated by the relative deuterium distribution in **48**-d_8 and explained in terms of energy minimization by interaction between the π moieties (note eq 30a). The initial interaction between vinyl chromophores leads to a system (*i.e.*, **47***′) isoconjugate with triplet butadiene and, therefore, of lower triplet energy (E_T = *ca.* 58 kcal/mol) than the species formed by vinyl-benzo interaction (*i.e.*, **47***″) and resembling styrene (E_T = *ca.* 64 kcal/mol). Note that this reasoning utilizes similar models as discussed above (see Figure 1) originally to understand why the di-π-methane rearrangement has such an efficient deactivation pathway open to most di-π-methane systems. The related 1,2- and 2,3-naphthobarrelenes **134** and **137** rearrange from their triplet excited states, again with remarkable regiospecificity, to their respective 1,2- (**135** and



48

47*

47

47*′

132 **133**

● ≡ H

(30a)

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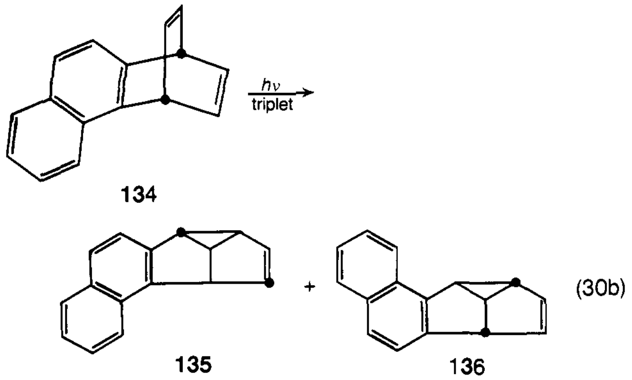
[33] W. R. Roth and B. Peltzer, *Justus Liebigs Ann. Chem.*, **685**, 56 (1965).

[34] T. Sasaki, S. Eguchi, M. Ohno, and T. Umemura, *Tetrahedron Lett.*, 3895 (1970).

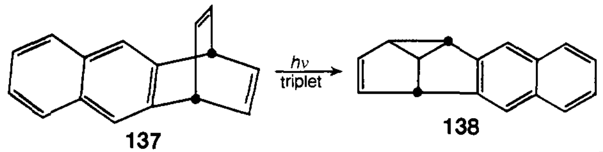
[35] P. S. Mariano, R. B. Steittle, and J. K. Ko, Contributed Papers, IVth IUPAC Symposium on Photochemistry, Baden-Baden, Germany, 1972, p 156.

[36] Z. Goldschmidt and A. S. Kende, *Tetrahedron Lett.*, 4625 (1971).



134

135 + **136** (30b)



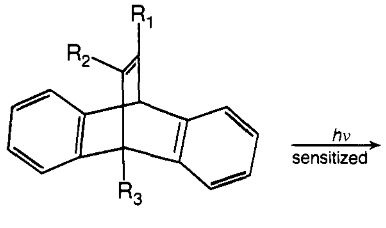
137 **138** (30c)

• ≡ H

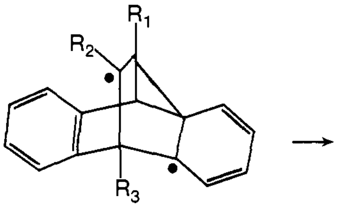
136) and 2,3-naphthosemibullvalenes (**138**), as shown in eq 30b,c.

Studies by Zimmerman and Bender[37] of deuterium-labeled systems demonstrate that the vinyl–vinyl bridging pathway is again preferred in the transformation of the deuterio-2,3-naphtho isomer **137**, but that, on the contrary, 1-naphtho to vinyl migration is followed by **134**. It is remarkable but comforting that the migratory aptitudes in all of these reacting systems can be correlated quite well with the comparative triplet energies of simple conjugated π models derived from inspection of the interacting π moieties in the competing pathways.

The photochemical conversions of several dibenzobarrelenes studied by Ciganek[17] and Friedman[18] indicate that other factors are capable of controlling the regiospecificity in π migration. The reactivity seen in formation of the major dibenzosemibullvalene product **140d**, from triplet-sensitized irradiation of **139d**, seems readily explainable on the basis of odd-electron stabilization by the carbomethoxy group in the same manner considered earlier for the acyclic singlet processes. Thus **141** is the favored bridged species where R_2 = $COOCH_3$ (*i.e.*, in **141d**) is the only stabilizing group. The case of **139c** is less understandable since electron delocalization cannot be controlling. It would appear that there is a reluctance to have the electronegative carbomethoxyl group held by a bond which becomes heavy in s character.



139a, $R_1 = R_2 = CO_2CH_3$; $R_3 = H$
b, $R_1 = R_2 = CN$; $R_3 = H$
c, $R_3 = CO_2CH_3$; $R_1 = R_2 = H$
d, $R_1 = H$; $R_2 = COOCH_3$; $R_3 = H$



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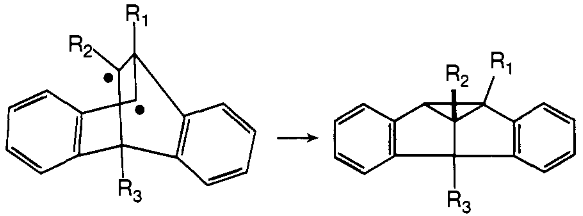
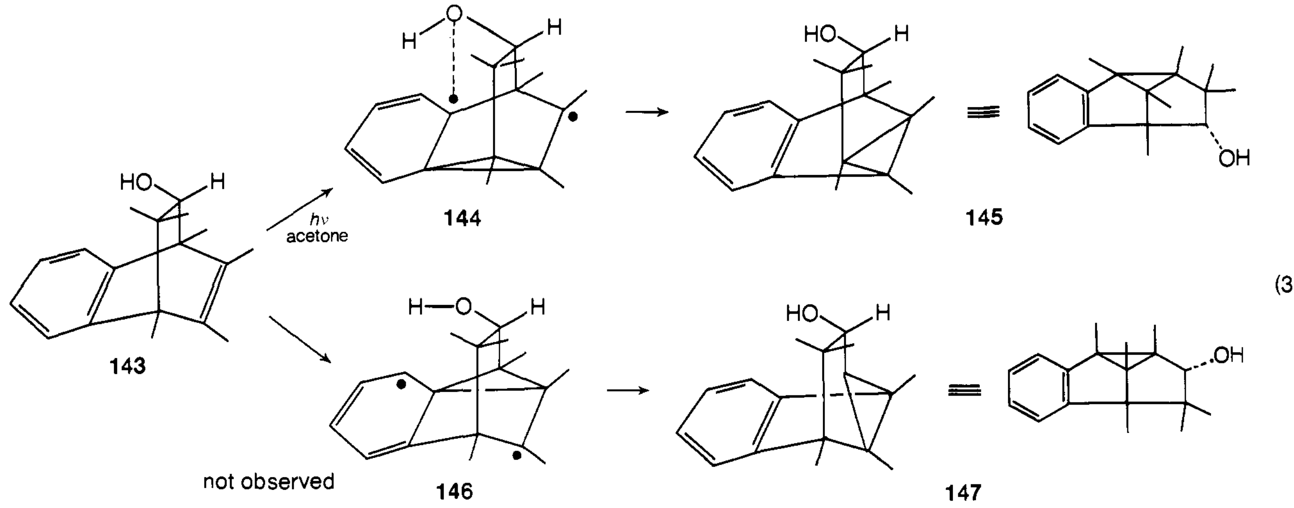


142 **140** (31)

It is interesting to note that Hart and Murray[38a] have uncovered an example in which stabilization of intermediate diradicals appears to control the direction of π migration in bicyclic systems. The observation of exclusive formation of the 6-hydroxydihydrobenzosemibullvalene (**145**) from *syn*-7-hydroxy-6,7-dihydrobenzobarrelene (**143**) can be attributed to selective stabilization of the intermediate diradical **144** by the 7-hydroxy substituent over the competing diradical **146**, as summarized in eq 32a. Additional confirmation of this control is offered in the photochemistry of the 7-*anti*-dihydrobenzobarrelenol (**148**) which produces a mixture of both 6- and 7-hydroxydihydrobenzosemibullvalenes, **149** and **150**, in which the 6 isomer predominates. Subsequent results[38b] indicate that



143 **144** **145** **146** **147** (32a)

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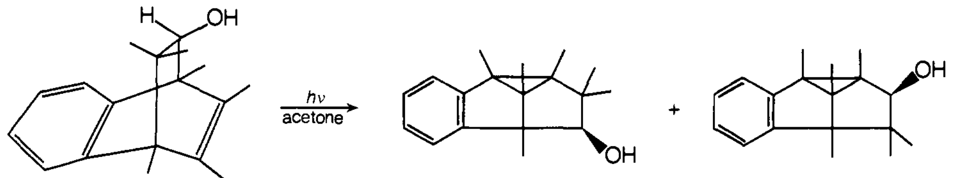
(37) H. E. Zimmerman and C. O. Bender, *J. Amer. Chem. Soc.*, **92**, 4366 (1970); **91**, 7516 (1969).

(38) (a) H. Hart and R. K. Murray, *J. Amer. Chem. Soc.*, **91**, 2183 (1969); (b) H. Hart and G. M. Love, *ibid.*, in press.



148 **149** **150**

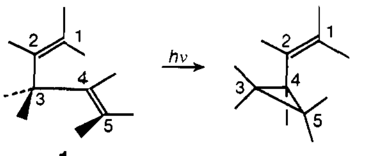
3 : 2

(32b)

the corresponding acetates show similar selectivity; additionally, high regioselectivity diminished with extent of methyl substitution on the reactant double bond. The suggestion of odd-electron stabilization by an oxygen unshared pair seems particularly attractive.

C. Reaction Stereochemistry

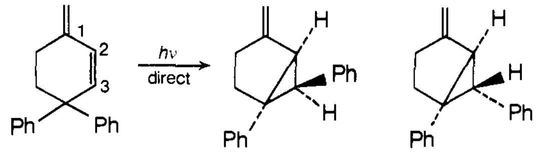
A final aspect of both the singlet and triplet di-π-methane reactions, which relates directly to the mechanisms for these processes and requires more discussion, is stereochemistry. This has been considered only briefly with respect to the stereochemical course at C-1. However, stereochemistry exists at C_1, C_3, and C_5 in the reacting di-π-methane system.



1 **2**

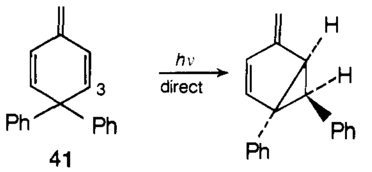
(33)

In two independent studies on the singlet excited-state chemistry of 1-methylene-4,4-diphenyl-2-cyclohexene (**38**) and its 2,5-cyclohexadiene analog, **41**, Zimmerman and coworkers[9,10] have noted preferential formation of the *trans*-5,6-diphenylbicyclo[3.1.0]hexyl products, **40** and **42.** The major pathways in each of these reactions involve inversion at C-3 in the di-π-methane network and require disrotatory three-ring formation as depicted in the transition-state orbital geometry, **151**. In addition, these results are not consistent with mechanisms which invoke the intermediacy of long-lived diradicals, like **152.**



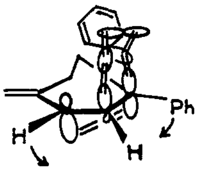
38 **40** (major) **39** (minor)

(34a)



41 **42**

(34b)



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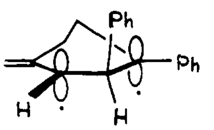
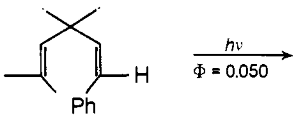


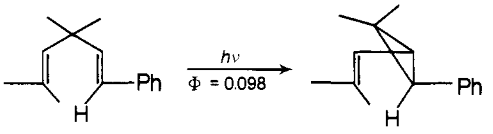
152

Further investigations by Zimmerman and coworkers[4,39] on the singlet di-π-methane rearrangement of appropriately substituted 1,4-dienes have elucidated the stereochemistry at C_1 and C_5. Direct irradiation of both *cis*- and *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene (**14** and **15**) led to stereospecific production of the respective *cis*- and *trans*-propenylcyclopropanes, **16** and **17**, as noted above (see eq 5).[4] Also, the singlet reactions of *cis*- and *trans*-1-phenyl-3,3,5-trimethyl-1,4-hexadiene (**153** and **155**) produced stereospecifically the phenylvinylcyclopropanes **154** and **156**, respectively (eq 35).[39] Together, these observations indicate that the preferred pathways for rearrangement involve retention of stereochemical integrity about the migrating π bond and specific motion at C-5, requiring utilization of the anti lobe in bonding with C-3, and can best be rationalized in terms of a concerted reaction mechanism for singlet di-π-methanes *via* lowest energy transition state orbital geometries like **158**, in general. Griffin and coworkers[30] have offered further confirmatory evidence from observation on the vinyl and allenyl acetylenic systems **97a**, **97b**, **99**, **101**, and **104** as described above in eq 22 and 23.



153 **154**

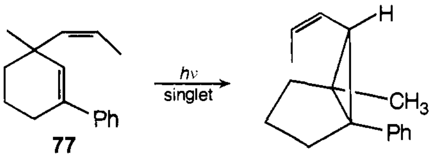
(35a)



155 **156**

(35b)

Additional information regarding the stereospecificity of the di-π-methane process is present in the studies of Mariano and Ko[25] on the singlet conversion of 1-phenyl-3-methyl-3-(*cis*-1-propenyl)cyclohex-1-ene (**77**) to 1-methyl-5-phenyl-6-*endo*-*cis*-1-propenylbicyclo[3.1.0]hexane (**78**), exclusively. A strong preference for disrotatory C-3, C-5 ring closure, anti to the migrating *cis*-propenyl moiety, is exhibited. All these examples support concerted mechanisms for the singlet di-π-methane process. Using the accepted transition-state π-electron treatments[32] (*vide supra*), the excited state transition state orbital geometry, represented by **158** (anti-disrotatory), necessary to explain the stereochemical results, is predicted to be allowed or of lowest energy compared to the others involving conrotatory motion of C-3 and C-5. However, the other disrotatory motion pathway involving overlap of the syn lobes at C-3 and C-5 is predicted to proceed through a transition state of equal energy to **158**; it is apparently not preferred in the rearrangements discussed above since exactly opposite stereochemistry at C-3 and C-5 would have resulted. When the di-π-methane



77 **78**

(36)

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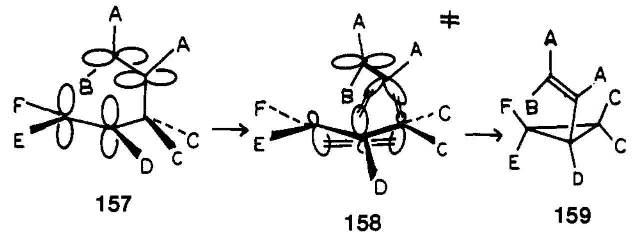
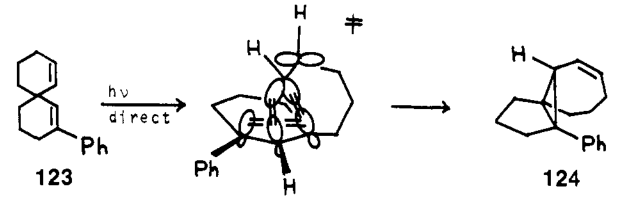
[39] H. E. Zimmerman, P. Baeckstrom, T. Johnson, and D. W. Kurtz, *J. Amer. Chem. Soc.*, **94**, 5504 (1972).

CHART II

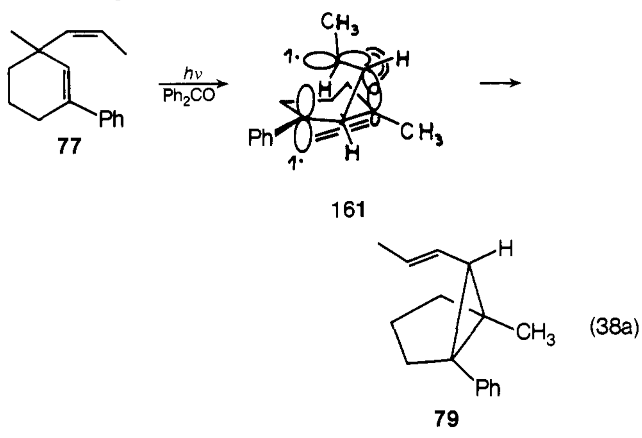


system is sufficiently constrained to prohibit transition states like **158**, the alternative syn-disrotatory mode through transition state **160** is followed, as shown in the results of Mariano and coworkers[35] from studies on the spirodiene (**123**) to tricycloundecene (**124**) transformation (eq 37).

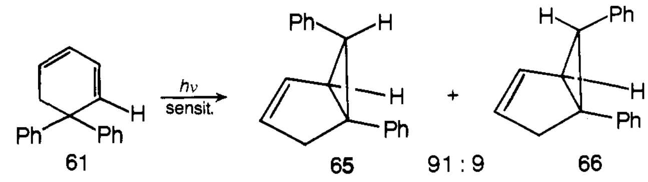


(37)

The stereochemistry of the triplet di-π-methane rearrangement has not been extensively investigated, and the number of examples from which to develop patterns are few. It is relevant to discuss several observations which suggest that the process in the triplet manifold proceeds also with stereospecificity in C-3, C-5 ring closure. Triplet-sensitized photolysis of the *cis*-propenylcyclohexene **77** yields solely the *trans-endo*-propenylbicyclohexane **79**.[25] Similarly, triplet rearrangement of 5,5-diphenyl-1,3-cyclohexadiene (**61**) proceeds with almost total stereospecificity in forming predominantly *trans*-5,6-diphenylbicyclo[3.1.0]hex-2-ene (**65**).[20,21]



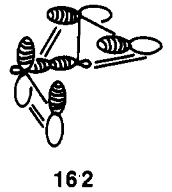
(38a)



(38b)

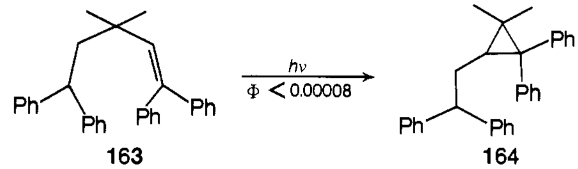
D. Question of a $\sigma + \pi$ vs. the Di-π-methane Rearrangement Mechanism

One might ask if the six-orbital scheme of Figure 3 really is unnecessarily complex; such a mechanism, taken in conjunction with the stereochemistry elucidated, constitutes a ${}_{\pi}2_{a} + {}_{\pi}2_{a} + {}_{\sigma}2_{a}$ process. Alternatively, one might consider just a ${}_{\sigma}2_{a} + {}_{\pi}2_{a}$ mechanism in which the σ bond initially holding on vinyl group adds across the other π bond. This is shown in structure **162**. Such a mechanism leads equally well to a prediction of excited state allowedness since it is a four-electron Hückel system (note ref 32).



162

However, this mechanism does differ operationally in not involving one vinyl group of the di-π-methane system. Evidence is available that this second π bond is, indeed, needed for efficient rearrangement. Thus, photolysis of **163** has been shown by Zimmerman and Little[40] to give no di-π-methane or σ plus π rearrangement. Hence the necessity of the second π bond in a successful di-π-methane rearrangement is established.



(39)

Many other examples of the di-π-methane rearrangement are present in the literature, some of which contain information that directly confirms patterns of reactivity discussed above and others which demonstrate the unusual number of transformations in a variety of systems. It would be unwise to attempt to review in detail all of these. However, several of the more unusual and demonstrative examples are included in eq 40,[41] 41,[42] 42,[43] 43,[44] 44,[45] and 45[46] with the purpose of indicating the extraordinary generality of this most general of excited-state molecular reorganization processes.

III. Oxa-di-π-methane Rearrangement

A. General

Attention is now turned to the variation of the reaction termed the oxa-di-π-methane rearrangement. It has been known for some time that β,γ-unsaturated ketones undergo a rearrangement involving a formal 1,2-acyl migration and three-ring formation. The reaction is formally analogous to the di-π-methane rearrangement. A di-π-methane-like mechanism was first suggested by Swenton[47] while the relationship to the ordinary di-π-methane rearrangement was first noted by Givens.[48] Appropriately, this process has been termed the "oxa-di-π-methane rearrangement" by Dauben.[49] Although competitive pho-

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(40) H. E. Zimmerman and R. D. Little, *J. Amer. Chem. Soc.*, **94**, 8256 (1972).

(41) T. D. Walsh, *J. Amer. Chem. Soc.*, **91**, 515 (1969); N. J. Turro, M. Tobin, L. Friedman, and J. B. Hamilton, *ibid.*, **91**, 516 (1969).

(42) M. J. Jones, Jr., S. D. Reich, and L. T. Scott, *J. Amer. Chem. Soc.*, **92**, 3118 (1970).

(43) T. J. Katz, J. C. Carnahan, Jr., G. M. Clarke, and N. Acton, *J. Amer. Chem. Soc.*, **92**, 734 (1970).

(44) L. A. Paquette and J. R. Malpass, *J. Amer. Chem. Soc.*, **90**, 7151 (1968).

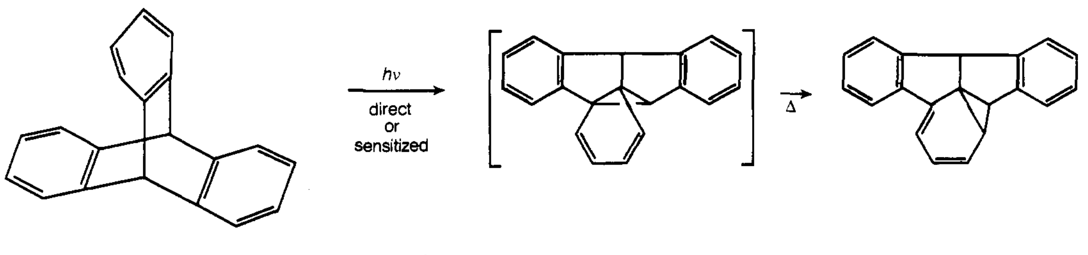
(45) H. Prinzbach and M. Thyes, *Chem. Ber.*, **104**, 2489 (1971).

(46) B. Haton, M. Kulig, M. A. Battiste, J. Perreten, D. M. Gibson, and G. W. Griffin, *J. Amer. Chem. Soc.*, **93**, 2327 (1971)

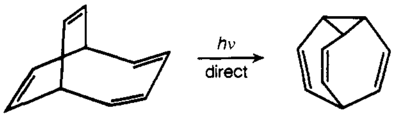
(47) J. S. Swenton, *J. Chem. Educ.*, **46**, 217 (1969).

(48) R. S. Givens and W. F. Oettle, *Chem. Commun.*, 1164 (1969).

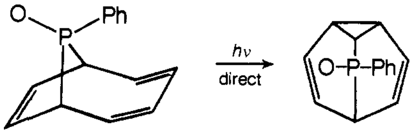
(49) W. G. Dauben, M. S. Kellog, J. I. Seeman, and W. A. Spitzer, *J. Amer. Chem. Soc.*, **92**, 1786 (1970).



(40)



(41)



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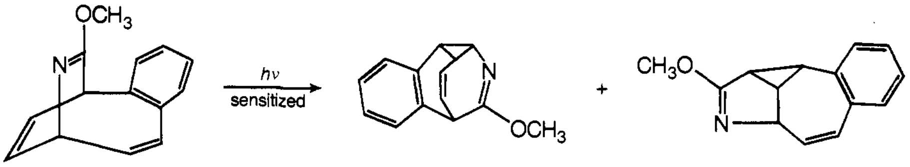
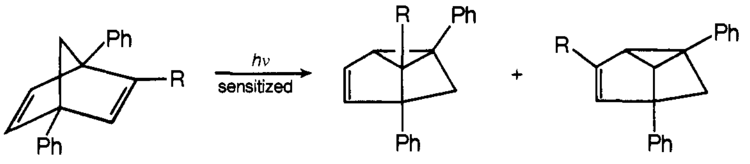
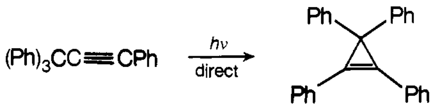


(43)



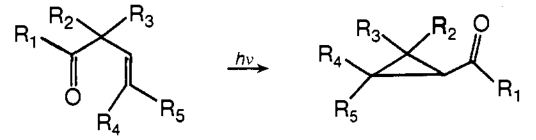
(44)

R = CO_2CH_3 or H



(45)

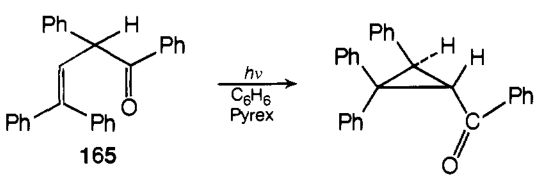
tochemistry is often encountered, discussion will be limited presently to the oxa-di-π-reaction except for examples where alternative reactivity is particularly relevant.



(1d)

1c **2c**

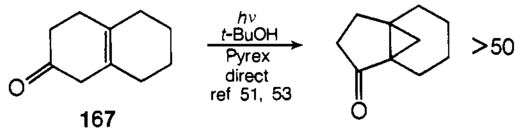
One of the earliest examples of this photochemical rearrangement was reported by Tenney, *et al.*, in 1966.[50] Thus, irradiation of 1,2,4,4-tetraphenyl-3-butenone (**165**) gave a 7% yield of 2,2,3-triphenyl-1-benzoylcyclopropane (**166**). Both C-14 and deuterium labeling studies showed that this rearrangement indeed occurs by migration of the benzoyl group and not by phenyl migration (eq 46).



7% (46)

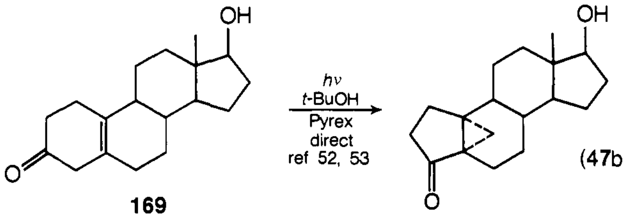
165 **166**

Closely following the observations of Tenney were reports by Williams and Ziffer[51-53] describing the rearrangement of unsaturated ketones **167** and **169** to the corresponding cyclopropyl ketones **168** and **170**, respectively.



>50% (47a)

167 **168**



(47b)

169 **170** (55%)

Following these initial reports, many examples of the oxa-di-π-methane reaction have been brought to light. Several interesting examples giving strained small ring compounds are summarized in eq 48a,[54,55] 48b,[54,55] 48c,[56] 48d,[57-59a] 49a,[60,61] and 49b[60,61] and further in ref 95.

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(50) L. P. Tenney, D. W. Boykin, Jr., and R. E. Lutz, *J. Amer. Chem. Soc.*, **88**, 1835 (1966).

(51) J. R. Williams and H. Ziffer, *Chem. Commun.*, 194 (1967).

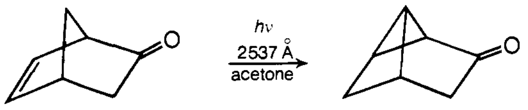
(52) J. R. Williams and H. Ziffer, *Chem. Commun.*, 469 (1967).

(53) J. R. Williams and H. Ziffer, *Tetrahedron*, **24**, 6725 (1968).

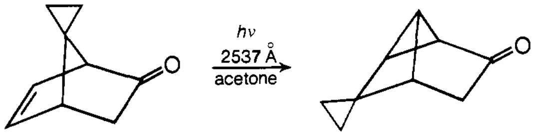
(54) J. Ipaktschi, *Tetrahedron Lett.*, 2153 (1969).

(55) J. Ipaktschi, *Chem. Ber.*, **105**, 1840 (1972).

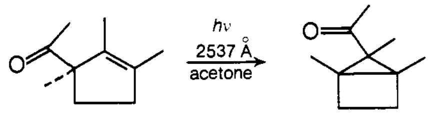
(56) E. Baggiolini, K. Schaffner, and O. Jeger, *Chem. Commun.*, 1103 (1969).



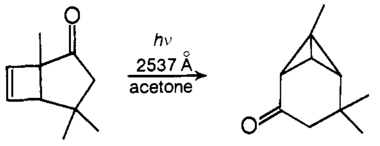
171 **172** (75%) (48a)



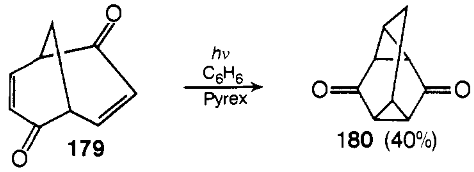
173 **174** (60%) (48b)



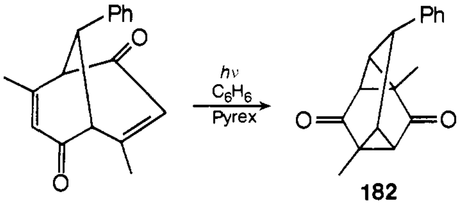
175 **176** (48c)



177 **178** (70%) (48d)



179 **180** (40%) (49a)

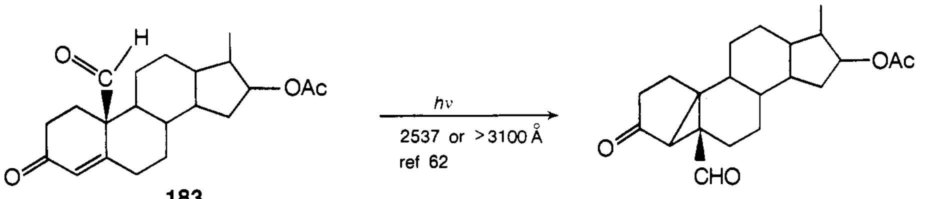


181 **182** (49b)

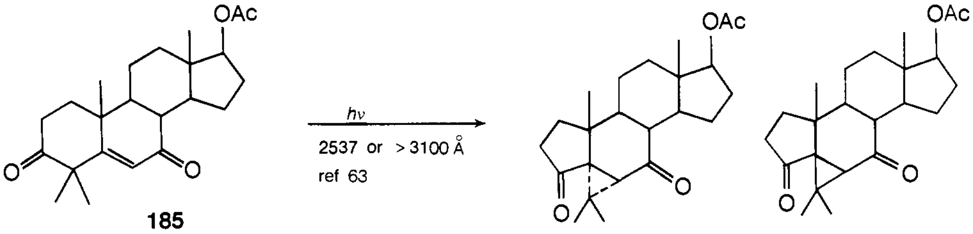
The cases of bis-β,γ-unsaturated ketones **179** and **181**[60,61] are especially intriguing in that the products, **180** and **182**, respectively, appear to result from two successive oxa-di-π-methane rearrangements. However, a single photon process is possible, and the question is open to experimental test. The reaction likewise occurs in systems where the olefin part of the β,γ-unsaturated carbonyl group is simultaneously part of an α,β-unsaturated ketone system. Thus, note the behavior of steroid systems **183**[62] and **185**[63,64] (eq 50a and 50b). The example[65] of trienone **187** is also of interest; here the olefinic portion is a diene moiety.

In the cases of ketones **189**[66-69] and **191**[55] (note eq 50d and 50e), where both the di-π-methane and oxa-di-π-methane mechanisms are available, only the oxa-di-π-methane route is followed. Thus, deuterium labeling studies[68] show that enone **189** rearranges to product **190** solely by acyl migration and not by benzo migration.[69]

Although almost all of the reported examples of the oxa-di-π-methane reaction occur with systems in which the double bond is contained within a ring, this is apparently not absolutely necessary. There is, of course, the example of Tenney, *et al.*[50] (eq 46). Likewise, Dauben[49] has found that the styryl substituted ketone **193** yields cyclopropyl ketone **194** in quite high yield. Commonly it is found that the carbonyl group does not have to be part of a ring.[49,50,56,62,70]



183 **184** (50a)



185 **186a** (major product) **186b** (50b)

Other carbonyl-containing chromophores have also been found to undergo formal photochemical 1,2-carbonyl shifts analogous to those above, for example, ester **195**[70] and imide **197**[71] (note eq 51a and 51b),

(57) J. Ipaktschi, *Tetrahedron Lett.*, 3179 (1970).

(58) D. I. Schuster and D. H. Sussman, *Tetrahedron Lett.*, 1661 (1970).

(59) (a) See D. I. Schuster, G. R. Underwood, and T. P. Knudsen, *J. Amer. Chem. Soc.*, **93**, 4304 (1971), footnote 6, for a discussion of the discrepancy in results noted in ref 57 and 58. (b) Recently an example of a triplet state 1,3-acyl migration has been reported by P. S. Engel and M. A. Schexnayder, *ibid.*, **94**, 9252 (1972).

(60) P. A. Knott, *Tetrahedron Lett.*, 1829 (1970).

(61) P. A. Knott and J. M. Mellor, *J. Chem. Soc., Perkin Trans. 1*, 1030 (1972).

(62) E. Pfenninger, D. E. Poel, C. Berse, H. Wehril, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **51**, 772 (1968).

(63) S. Domb, G. Bozzato, J. A. Saboz, and K. Schaffner, *Helv. Chim. Acta*, **52**, 2436 (1969).

(64) For other examples, see T. Matsuura and K. Ogura, *Chem. Commun.*, 1247 (1967); *J. Amer. Chem. Soc.*, **89**, 3850 (1967); G. F. Burkinshaw, B. R. Davis, and P. D. Woodgate, *J. Chem. Soc. C*, 1607 (1970); D. A. Plank and J. C. Floyd, *Tetrahedron Lett.*, 4811 (1971).

(65) K. N. Houk and D. J. Northington, *J. Amer. Chem. Soc.*, **94**, 1387 (1972).

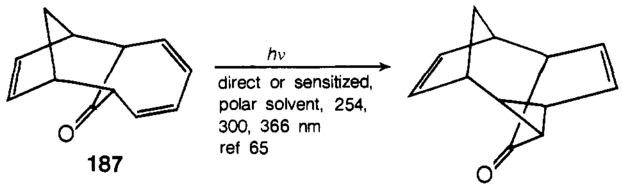
(66) J. Ipaktschi, *Tetrahedron Lett.*, 215 (1969).

(67) R. S. Givens, W. F. Oettle, R. L. Coffin, and R. G. Carlson, *J. Amer. Chem. Soc.*, 93, 3957 (1971).

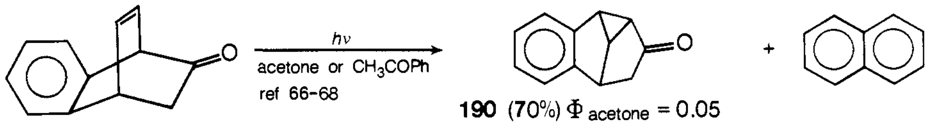
(68) R. S. Givens and W. F. Oettle, *J. Amer. Chem. Soc.*, **93**, 3963 (1971).

(69) The hexamethyl analog of **189** behaves similarly: H. Hart and R. K. Murray, *Tetrahedron Lett.*, 379 (1969).

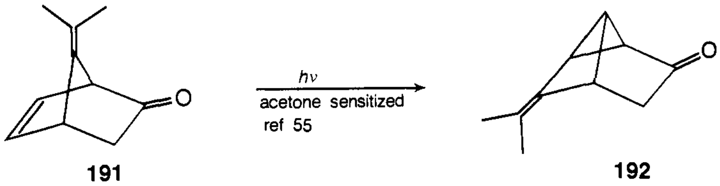
(70) J. S. Swenton and D. M Madigan, *Tetrahedron*, **28**, 2703 (1972).



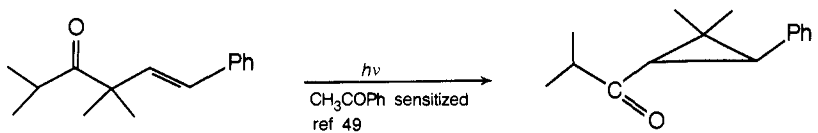
187 → **188** (60%) (50c)



189 → **190** (70%) $\Phi_{\text{acetone}} = 0.05$, $\Phi_{\text{CH}_3\text{COPh}} = 0.12$ (50d)

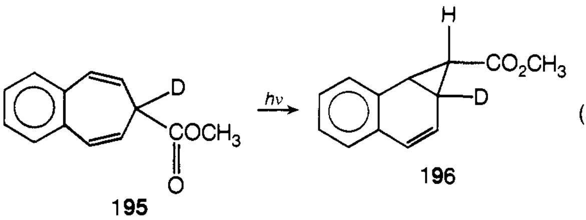


191 → **192** (50e)

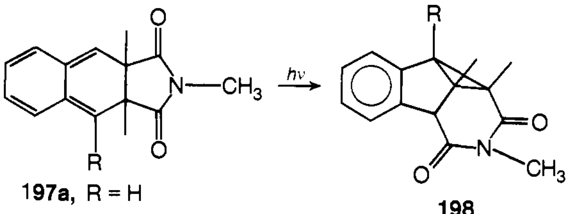


193 → **194** (93%) (50f)

though in the cases of **195** to **196** alternatives to the oxa-di-π-methane pathway were postulated as possibilities. This review, however, will concentrate on ketones and aldehydes.



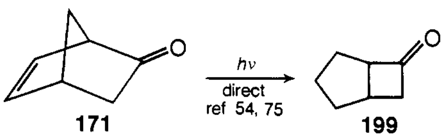
195 → **196** (51a)



197a, R = H
b, R = Ph
→ **198** (51b)

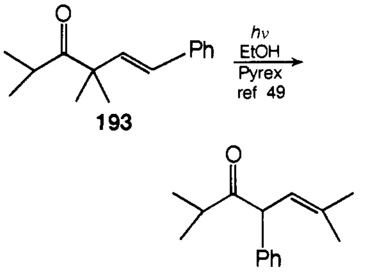
B. Multiplicity Studies

In contrast to the di-π-methane rearrangement which has been found to occur from both singlet and triplet states, the oxa-di-π-methane reaction appears to take place solely from the triplet state. Thus far no sensitization or quenching results have been inconsistent with this conclusion in the case of ketones although ester **195** is an exception if it does rearrange by the oxa-di-π-methane pathway since it appears to rearrange *via* the singlet.[70] Indeed, for the most part, direct irradiation of β,γ-unsaturated ketones gives reactions other than the oxa-di-π-methane process. This suggests inefficient intersystem crossing. The singlet photochemistry observed under direct photolysis of β,γ-unsaturated ketones consists of 1,3-acyl migration[72] and/or decarbonylation, although other processes are observed.[73] Thus, it is frequently found that direct irradiation of a β,γ-unsaturated ketone yields an isomeric β,γ-unsaturated ketone, whereas triplet sensitization yields a cyclopropyl ketone. Examples are shown below.[74]



171 → **199** (mostly) (52a)

$$171 \xrightarrow[\text{sensitized ref 54}]{h\nu} 177 \qquad (48a)$$



193 → **200** + decarbonylation products (52b)

$$193 \xrightarrow[\text{sensitized}]{h\nu} 194 \qquad (50f)$$

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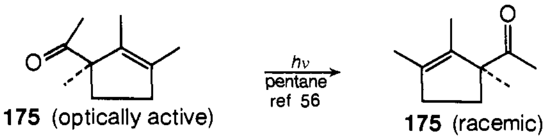
(71) D. W. Jones and G. Kneen, *J. Chem. Soc., Chem. Commun.*, 1038 (1972).

(72) See, for example, H. Sato, N. Furutachi, and K. Nakanishi, *J. Amer. Chem. Soc.*, **94**, 2150 (1972); N. Furutachi and K. Nakanishi, *ibid.*, **91**, 1028 (1969); W. F. Erman, *ibid.*, **89**, 3842 (1967); G. Buchi and E. M. Burgess, *ibid.*, **82**, 4333 (1960).

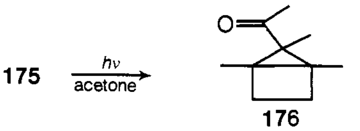
(73) See, for example, R. C. Cookson and N. R. Rogers, *J. Chem. Soc., Chem. Commun.*, 809 (1972); R. C. Cookson, *et al.*, *Tetrahedron*, **24**, 4353 (1968); E. F. Kiefer and D. A. Carlson, *Tetrahedron Lett.*, 1617 (1967).

(74) Small amounts of 1,3-acyl migration products formed at sensitized irradiations most likely arise as a result of absorption of light by the β,γ-unsaturated ketone or singlet energy transfer.

(75) D. I. Schuster, M. Axelrod, and J. Auerbach, *Tetrahedron Lett.*, 1911 (1963); G. O. Schenck and R. Steinmetz, *Chem. Ber.*, **96**, 520 (1963).

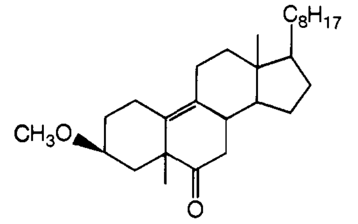


175 (optically active) **175** (racemic) (52c)

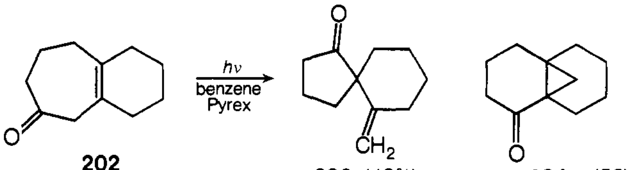


175 **176** (48c)

However, the oxa-di-π-methane rearrangement is not the only possible reaction of triplet β,γ-unsaturated ketones. Other processes such as photoreduction,[76a] cis–trans isomerization,[76b] 2 + 2 cycloaddition,[76c] and epimerization[76d] have been found to occur. For example, on acetone sensitization steroid methoxy-enone **201** gives predominantly the C-5 epimeric ketone and no cyclopropyl ketone.[76d] Likewise bicyclic enone **202** on direct irradiation gives spiro-enone **203**, the product of 1,3-acyl migration, whereas sensitization was reported to afford no **203** or **204**.[77]



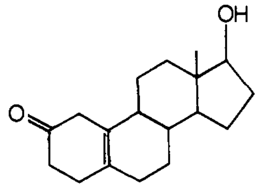
201



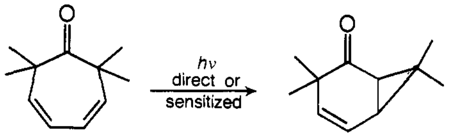
202 **203** (40%) **204** (53)

As in the cases of ketones **201** and **202** the reason for the nonobservation of the oxa-di-π-methane rearrangement of triplet-state β,γ-unsaturated ketones is not always clear. From the fact that steroid enone **205** does not form a cyclopropyl ketone while the structural isomer **169** does, Williams and Ziffer[53,77] concluded that geometrical factors in the transition state are important, but these remain unspecified.

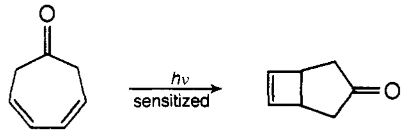
In certain cases, however, quite plausible reasons for the unreactivity may be put forth. Whereas Paquette[78] found that cycloheptadienone **206** affords bicyclic ketone **207** on direct and triplet-sensitized photolysis, the triplet of the corresponding demethylated ketone **208** affords only **209**, the formal product of electrocyclic closure, upon triplet sensitization.[79] It was suggested[79,80] that the isomerization of **208** proceeds *via* initial cis–trans isomerization about one of the double bonds to form a highly strained *cis,trans*-3,5-cycloheptadienone which then closes thermally in a conrotatory fashion to bicyclic ketone **209**. The methyl groups in **206** would inhibit such a cis–trans isomerization. As a result, isomerization to **207** becomes the favored process of triplet **206**.[80] However, a different rationale has been provided by Houk[65] (*vide infra*).



205

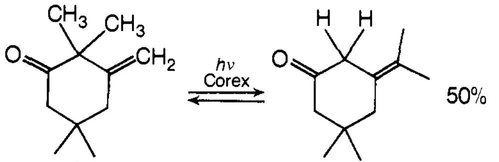


206 **207** (~20%) (54)

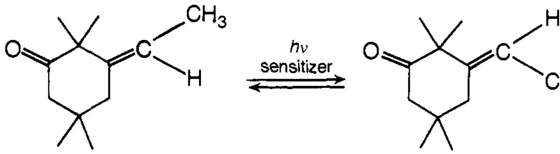


208 **209**

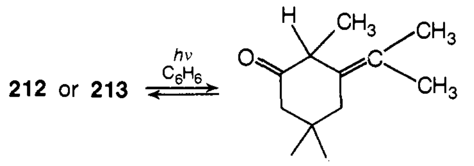
Related to this are the definitive studies of Hancock[81,82] on six-ring ketones **210–214** in which the β,γ-double bond is exocyclic (note eq 55a,b). Direct irradiation of **210** gives **211**; the process is reversible and cannot be sensitized or quenched, indicative of a singlet-state process. The triplet of **210** is apparently unreactive. This lack of reactivity is both interesting and revealing when it is considered that the nearly isosteric ketone **215** readily undergoes triplet-state rearrangement to **216**[83] (eq 56).



210 **211** (55a)



212 **213** (55b)



214 (55c)

It is proposed[81] that the triplet of **210** is only apparently unreactive and that it is deactivated by an

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(76) (a) R. L. Cargill, T. Y. King, A. B. Sears, and M. R. Willcott, *J. Org. Chem.*, **36**, 1423 (1971); (b) H. Morrison, *Tetrahedron Lett.*, 3653 (1964); (c) P. S. Engel and M. A. Schexnayder, *J. Amer. Chem. Soc.*, **94**, 4357 (1972); (d) R. J. Chambers and B. A. Marples, *Tetrahedron Lett.*, 3747, 3751 (1971).

(77) J. R. Williams and G. M. Sarkisian, *Chem. Commun.*, 1564 (1971).

(78) L. A. Paquette, R. F. Eizember, and O. Cox, *J. Amer. Chem. Soc.*, **90**, 5153 (1968).

(79) D. I. Schuster, B. R. Schnolick, and F.-T. H. Lee, *J. Amer. Chem. Soc.*, **90**, 1300 (1968).

(80) Schuster's arguments[79] have since been modified in light of his failure to trap the *trans,cis*-3,5-cycloheptadienone [D. I. Schuster and D. J. Blythin, *J. Org. Chem.*, **35**, 3190 (1970)]. However, the same sort of reasoning given by Paquette[78] could still apply.

(81) K. G. Hancock and R. O. Grider, *Tetrahedron Lett.*, 1367 (1972).

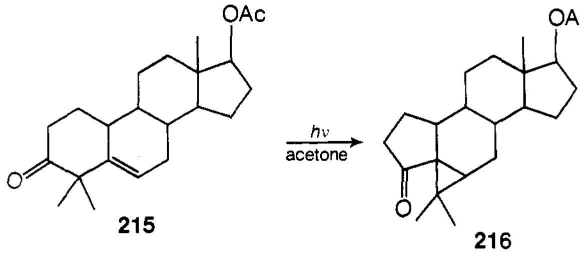
(82) K. G. Hancock and R. O. Grider, *Tetrahedron Lett.*, 4281 (1971).

(83) K. Kojima, K. Sakai, and K. Tanabe, *Tetrahedron Lett.*, 1925, 3399 (1969).

TABLE II. Triplet Lifetimes of β,γ-Unsaturated Ketones[a]

Compd	E_t, kcal/mol[b]	τ, msec[c]
210	70.7	205
212, 213	68.9	156
171	69.5	190[e]
Cyclooct-3-en-1-one	68.4[d]	95[d]
	68.8[e]	5.4[e]
2,2-Dimethylcyclohept-3-en-1-one	68.8	44
Chrysanthenone	69.2	34
193	68.8	49
17β-Acetoxy-4β,19-oxido-androst-5-en-3-one	73.7	55[e]
185	68.9	28
215	68.9	48
189	60.9	210

[a] From ref 85. [b] ±1.5 kcal/mol; in both ethanol and isopentane glasses: 77°K. [c] n-π^* excitation, ±10-15%. [d] Ethanol glass. [e] Isopentane glass.



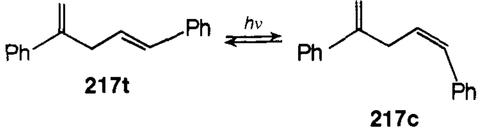
18.5%

215 **216** (56)

unobservable isomerization of the double bond—a "free rotor" effect analogous to that observed in flexible di-π-methane triplets. Sterically constrained **215** has no such facile deactivation pathway to it and accordingly undergoes the oxa-di-π-methane reaction as the next best choice. Phosphorescence studies (*vide infra*) support this conjecture.

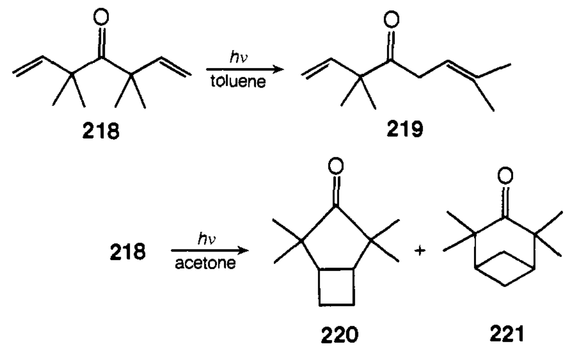
Concrete evidence for this proposal comes from the finding that **212** and **213** undergo interconversion when sensitized with sensitizers of triplet energy of 65-74 kcal/mol.[82] (The triplet energies of **212** and **213** are 69 ± 2 kcal/mol.) On direct irradiation **212** and **213** interconvert with **214**. The free rotor effect in these molecules therefore seems well established.

However, the free rotor effect does not eliminate the oxa-di-π-methane reaction in all cases where the double bond is not contained within a small ring, for as mentioned above **193** affords **194** in high yield *via* its triplet state[49] and **165** yields **166.**[50] Of course, high isolation yield does not prove high quantum efficiency. It is interesting to note, though, that **217**, which is quite similar to **193**, undergoes facile triplet trans-cis isomerization upon irradiation.[84] No cyclopropyl ketone was observed, although a small amount of an unidentified photoproduct did accumulate upon prolonged irradiation. Evidently olefin isomerization is the preferred process in this case.



217t **217c** (57)

Along this line is the interesting study of Engel[76c] of the bis-β,γ-unsaturated ketone **218**. Upon direct irradiation **218** gave the usual 1,3-acyl shift and decarbonylation products. However, upon acetone sensitization neither typical lack of reactivity nor the oxa-di-π-methane process is observed. Instead bicyclic isomers **220** and **221** are formed by simple 2 + 2 cycloaddition



218 **219**

220 **221** (58)

Evidently the free rotor effect does not prevent reactions from acyclic triplets in all cases. It is most likely a matter of delicate balance of relative rates, the cis-trans isomerization process usually being the fastest but not always the exclusive reaction. Ideally one needs quantitative evidence for adequate interpretation of each individual case.

C. Configuration of the Reactive Triplet State

Evidence that the reactive triplets of ketones undergoing the oxa-di-π-methane rearrangement are of a π-π^* configuration has been provided by Hancock[85] in a study of the triplet energies (0-0 band) and triplet lifetimes of 11 β,γ-unsaturated ketones (Table II).[85]

No sizable difference in triplet energy or lifetime was found between samples run in ethanol or in isopentane except with the cyclooctenone. The long observed lifetimes suggest that all the enones (except 3-cyclooctenone in isopentane) possess π-π^* emitting triplets at 77°K. Where observable, solvent shifts and vibrational spacings were also consistent with this assignment. The π-π^* configuration for the lowest triplet of **185** was confirmed by other workers using the polarized phosphorescence technique.[86] If one assumes that the configuration of the reactive triplets of these ketones at room temperature is the same as that of the lowest triplet at 77°K in a rigid glass and that the emitting triplet is the reacting one, it would appear that the oxa-di-π-methane reaction proceeds from a π-π^* state. However, where π-π^* and n-π^* states are close in energy, the emitting triplet may not be the reacting one.

Evidence that the configuration of the lowest triplet of an oxa-di-π-methane system can be important has been provided by Houk.[65] Direct or sensitized photolysis of **187** in polar solvents provides **188** in 60% yield *via* a 1,2-acyl shift shown by deuterium labeling. In cyclohexane solution dimerization *via* the triplet to **222** (70%) is the most important process. In solvents of intermediate polarity both products are found. Calculations indicate that **187** has three lowest triplet states; a ^{3}n-π^*, a diene $^3\pi$-π^*, and a charge-transfer "^{3}CT" state involving transfer of charge into the diene. It is felt that in the polar solvents the ^{3}n-π^* or ^{3}CT is lowest in what is an unusual solvent effect for an n-π^* state. Intersystem

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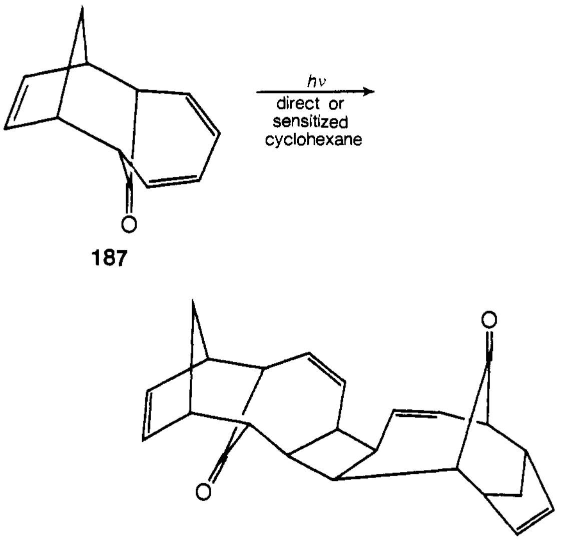
[84] D. O. Cowan and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 1153 (1971). See also ref 76b.

[85] K. G. Hancock and R. O. Grider, *J. Chem. Soc., Chem. Commun.*, 580 (1972).

[86] G. Marsh, D. R. Kearns, and K. Schaffner, *J. Amer. Chem. Soc.*, **93**, 3129 (1971).

crossing from the ^{1}n–π* state occurs rapidly. The oxa-di-π-methane reaction then occurs from the lowest triplet. In the less polar cyclohexane, the lowest triplet is the diene π–π* one which is said to twist and then attack another molecule of **187**.[87] A similar explanation is offered for the difference in reactivity between cycloheptadienones **206** and **208** (note eq 54).

The difference between the cyclic monoolefinic β,γ-unsaturated ketones where the triplet undergoes the oxa-di-π-methane rearrangement and the diene cases **187**, **206**, and **208**, in which the keto-diene triplet does not rearrange, may lie in part in the greater localization of triplet energy in the latter cases in the diene moiety.



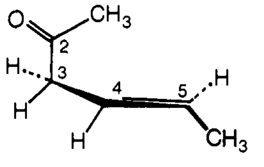
187

(59)

222 (70%)

D. Explanation for the Difference in Behavior of Singlets and Triplets

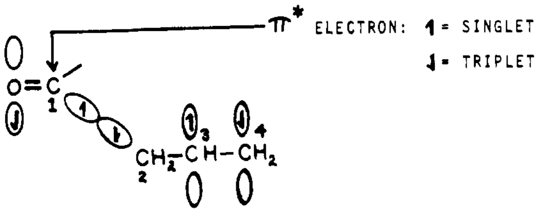
Houk[88] has also provided an interesting rationale for the diverging behavior of β,γ-unsaturated ketone singlets and triplets noted previously: singlets generally (though not always) undergo a 1,3-acyl shift while triplets generally (though not always) undergo a formal 1,2 shift, the oxa-di-π-methane rearrangement, no case of a singlet 1,2 shift or a triplet 1,3 shift being reported.[59] CNDO-MO calculations of **223** in the geometry shown indicate that the lowest singlet is composed primarily of n–π* (54%) and alkene-carbonyl charge transfer (32%) configurations, in agreement with the usual explanation for the enhanced n–π* absorption of β,γ-unsaturated ketones.[89] The lowest triplet is calculated to be predominantly π–π* (76%), this latter result being in nice agreement with the experimental work of Hancock[85] noted above.



223

The calculations also show that in the lowest singlet, taken as n–π*, an electron has been removed from an orbital which is C-2–C-3 bonding (note structure **223**) and placed in one which is C-2–C-3 nonbonding, C-2–C-4 antibonding, and weakly C-2–C-5 bonding. From this one would predict, as commonly observed, that singlet β,γ-unsaturated ketones would undergo α-cleavage and 1,3-acyl migration but not 1,2-acyl migration. On the other hand, in the triplet state, which was taken as π–π*, an electron has been promoted to an orbital which is C-2–C-4 bonding and C-2–C-5 and C-4–C-5 antibonding. The reactions predicted, 1,2-acyl migration and cis–trans isomerization, are those observed.

A different rationale based on spin distribution has been proposed by Schuster and Underwood.[90a] Starting with an assumed n–π* excited state with a geometry as in **223**, it is concluded that the spin polarization of the σ framework in the excited state is primarily a result of interaction with the lone p_y electron. The spin of the π* electron, in an orbital assumed orthogonal to the σ framework, is fixed relative to the p_y electron by multiplicity. The vinyl portion of the molecule is spin polarized, in turn by the α bond as shown in **224**. The relative spin of the π* electron and the vinyl electrons are thus fixed. It is now assumed that the path of reaction is dictated by the initial interaction of the π* electron with an electron of the olefin moiety of the opposite spin. A triplet state therefore gives a 1,2 shift (C-1–C-3 bonding); a singlet, a 1,3 shift (C-1–C-4 bonding). Thus the Schuster[90a] rationale for the triplet differs from Houk's[88] in assuming an n–π* triplet *vs.* Houk's preference for π–π*.



224

Finally, Fukui[90b] has noted that the singlet–triplet reactivity differences are consistent with the general tendency for triplet states to bond in such a manner that the intermediates produced have their odd electrons separated maximally from each other. Such is not necessarily expected of singlet states. Thus, the preferred orbital interactions are as shown (p 550). This rationale does not utilize the carbonyl π system and differs from Houk and Schuster explanations.

E. Reaction Mechanism

The detailed mechanism by which the enone triplets rearrange to cyclopropyl ketones is a matter of current debate. Pathways postulated are (i) initial α-cleavage to a radical pair which combines to form

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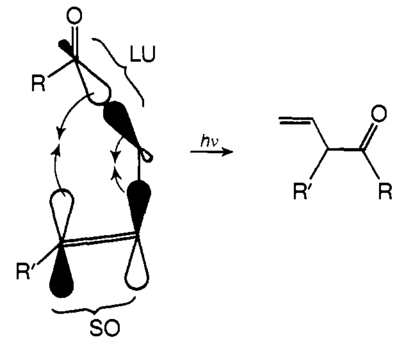
(87) T. Mukai, *et al.* [*J. Amer. Chem. Soc.*, **94**, 675 (1972)] have likewise studied the photochemistry of **187**. Upon sensitized irradiation of **187** in ether or benzene they observe only **222** and no **188**, whereas direct irradiation in hexane afforded substantial amounts of decarbonylation and electrocyclic ring closure products in addition to **222**. Differences between these results and those of Houk[65] appear to be due to solvent polarity and enone concentration differences.

(88) K. N. Houk, D. J. Northington, and R. E. Duke, Jr., *J. Amer. Chem. Soc.*, **94**, 6233 (1972).

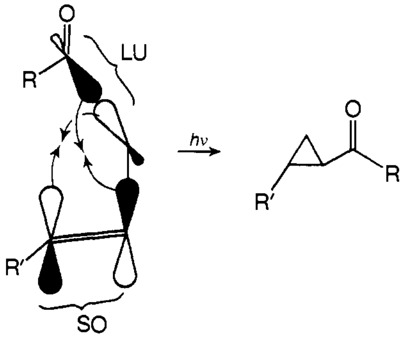
(89) D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc. B*, 215 (1967); D. E. Bays and R. C. Cookson, *ibid.*, 226 (1967); A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Amer. Chem. Soc.*, **84**, 1945 (1962), and references in these articles.

(90) (a) D. I. Schuster, G. R. Underwood, and T. P. Knudsen, *J. Amer. Chem. Soc.*, **93**, 4304 (1971); (b) K. Fukui, *Accounts Chem. Res.*, **4**, 57 (1971).

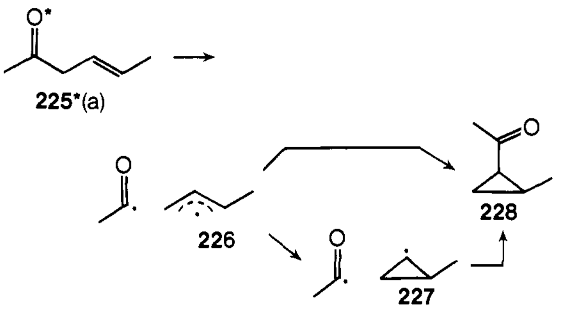
Singlet



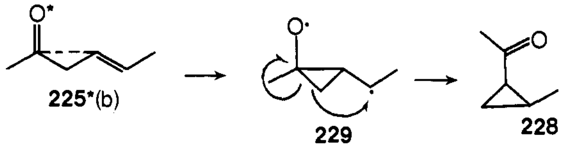
Triplet



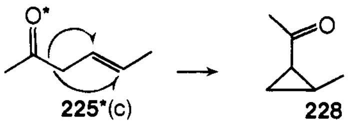
LU = lowest unoccupied molecular orbital
SO = singly occupied molecular orbital



(60a)



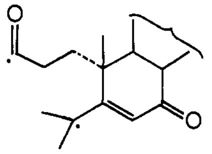
(60b)



(60c)

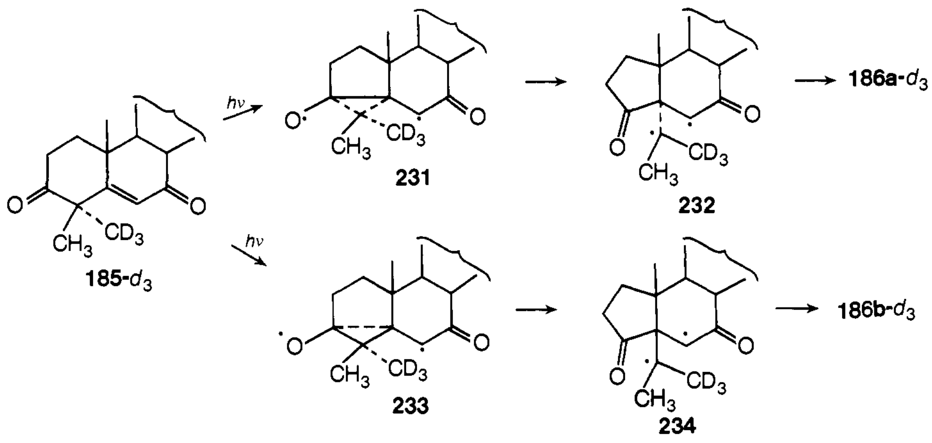
product,$^{50-52,54,66,69,83}$ (ii) initial bonding between the carbonyl and the β carbon followed by rearrangement or a concerted variation of this (the oxa-di-π-methane mechanism),^{48,49,62,63,68,76d,91} and (iii) a concerted ${}_{\sigma}2_a + {}_{\pi}2_a$ cycloaddition of the carbonyl α-carbon bond across the β,γ-olefinic bond.^{56,63,76,92}

Mechanism i appears to be the least likely,^{49,56,76d,91} for bonding at C-2 of the allyl moiety or closure of the latter to a cyclopropyl radical is not what one would predict would be the most likely reaction paths of the initially formed radical pair. Bonding at C-1 and C-3 of the allyl group, as in the singlet reaction, should predominate. In addition it is noted^{91} that irradiation of steroid enedione **185** (note eq 50b and 61a,b) gives predominantly **186a** with lesser amounts of **186b** whereas molecular models indicate cyclization of diradical **230** to **186a** is clearly less favorable. Thus mechanisms ii and iii appear more probable.



230

The only case where a clear choice between (ii) and (iii) can be made is in this special case of **185**^{91} (special because the olefin forms part of an α,β-unsaturated ketone group). Irradiation of **185**-d_3 gives **186a**-d_3 and **186b**-d_3 in which the CD_3 and CH_3 groups are completely scrambled. This is not consistent with a concerted ${}_{\sigma}2_a + {}_{\pi}2_a$ mechanism. The authors^{91} favor the stepwise version of the oxa-di-π-methane mechanism ii.



(61a)

(61b)

Givens^{67,68} has presented some evidence also bearing on the mechanism.

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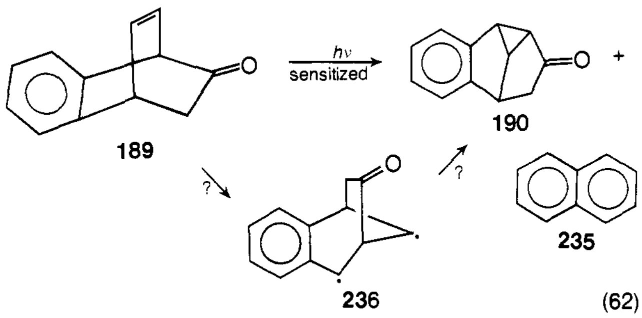
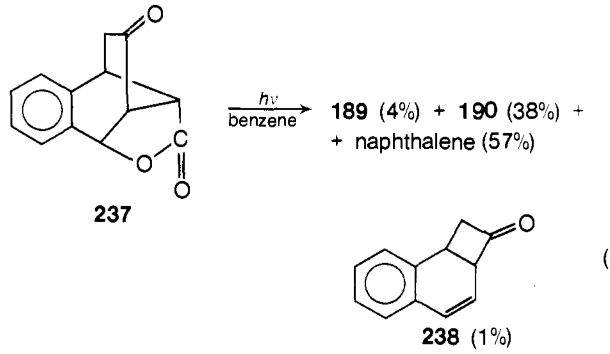
(91) S. Domb and K. Schaffner, *Helv. Chim. Acta*, **53**, 677 (1970).

(92) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.



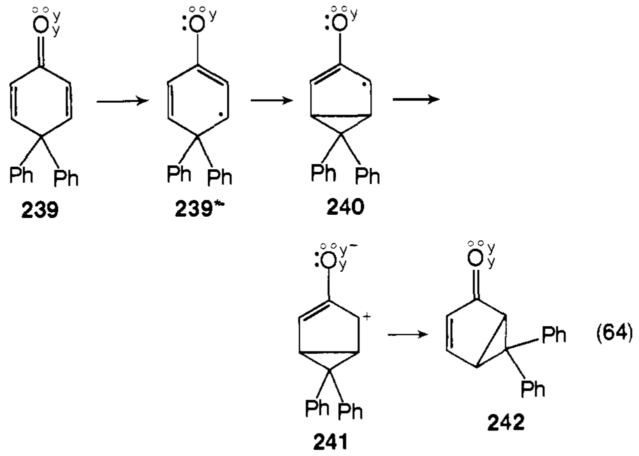
(62)

In a very pretty study designed to test if the triplet diradical **236** lay on the reaction route from **189** to **190**, **236** was independently generated by photolysis of lactone **237**, utilizing a triplet-state process which proceeds as shown in eq 63. It was observed that the oxa-di-π-methane reaction product **190** of the triplet reaction of enone **189** was indeed formed starting with this lactone. This is shown in eq 63. One might conclude that if a discrete biradical such as **236** is not actually on the ordinary reaction pathway from enone **189**, it nevertheless must be close to this pathway on the hypersurface used for reaction.

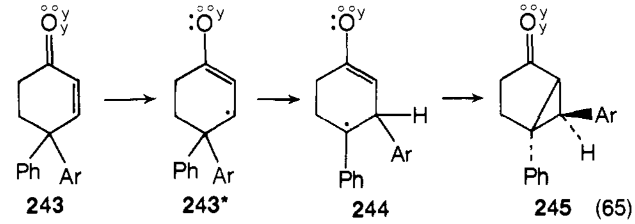


(63)

A final interesting point is that both the type A rearrangement of 2,5-cyclohexadienones and the aryl migration reaction of 4-arylcyclohexenones are formally vinylogs of the oxa-di-π-methane rearrangement. Thus, the type A rearrangement of 4,4-diphenylcyclohexadienone (**239**) has been shown to proceed *via* the Zimmerman–Schuster zwitterionic intermediate[93] **241** in a reaction initiated by β–β bonding. However, this reaction proceeds by way of the n–π* triplet and thus is somewhat different from processes involving π–π* excitation. In the case of the 4,4-diarylcyclohexenones,[94] again the n–π* triplet was shown to be utilized. Thus these two reactions have not been included in the present survey.



(64)



(65)

IV. Conclusion

It can be seen that, even excluding the vast literature on cyclohexenone and cyclohexadienone photochemistry, the di-π-methane rearrangement is already one of the most general of photochemical reactions. One might jocularly conclude that the challenge in photochemistry is to find a reaction which does not add another di-π-methane example. Nevertheless, it is obvious that despite the considerable information on reaction multiplicity, regiospecificity, stereochemistry, and substituent effects, there is still a real challenge in exploring the di-π-methane and oxa-di-π-methane reactions.

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(93) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962).

(94) H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *J. Amer. Chem. Soc.*, **89**, 2033 (1967), and earlier studies.

(95) (a) J. Gloor, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **54**, 1864 (1971); (b) H. Hart, R. K. Murray, and G. D. Appleyard, *Tetrahedron Lett.*, 4785 (1969); (c) K. Kurabayashi, *ibid.*, 1049 (1972).