Synthetic Aspects of the Di-π-methane Rearrangement

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Contents

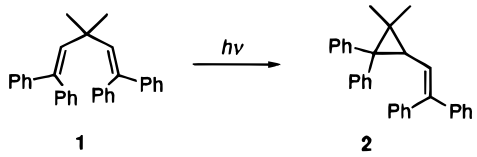
I. Introduction

The present review deals with the synthetic aspects of the most important types of di-π-methane rearrangements. The survey is limited to the all-carbon di-π-methane, the oxa-di-π-methane, and the aza-di-π-methane versions of the reaction. Mechanistic aspects are covered in depth in other reviews[1] and are discussed here to the extent required for synthetic purposes.

II. The All-Carbon Di-π-methane Rearrangement

The di-π-methane rearrangement was discovered in 1967 when we realized that the photolysis of reactants having two vinyl moieties bonded to an sp^3-hybridized carbon led to formation of a vinylcyclopropane.[2] The reaction was then termed a "divinyl methane rearrangement".[2] A very typical, but later, example is the photochemical rearrangement of 3,3-dimethyl-1,1,5,5-tetraphenyl-1,4-pentadiene (**1**)[3] that affords the cyclopropane **2** as depicted in Scheme 1.

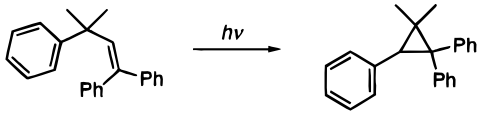
Scheme 1



1 **2**

However, shortly after our initial report we recognized[3,4] that the same basic rearrangement would take place when the "methane carbon" bore an aryl group in place of a vinyl. Note the example[5] in Scheme 2. At that point the reaction name of "di-π-methane" seemed more appropriate.

Scheme 2



The main requirement then is that a carbon bears two π-moieties. The rearrangement product therefore, more generally, is a π-substituted cyclopropane. The very broad spectrum of types of organic molecules obtainable by the di-π-methane rearrangement is remarkable and makes it particularly synthetically useful. More often than not, the photoproducts are not available by alternative routes.

The discovery of the di-π-methane rearrangement was serendipitous. Barrelene (**3**) had just recently been synthesized,[6] and in exploration of its chemistry it was found that a C_8H_8 isomer was formed on photolysis in the presence of acetone as a sensitizer. Having elucidated its structure as **4** (note Scheme 3), we named it semibullvalene[7] and provided a

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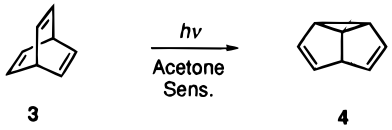
A native of Connecticut, Howard E. Zimmerman received his B.S. and Ph.D. are from Yale (1950 and 1953). After a NRC Postdoctoral Fellowship with R. B. Woodward at Harvard, he began at Northwestern University (1954–1960). He moved to Wisconsin in 1960. He holds the Arthur C. Cope (1975) and the Hilldale (1990) Chairs. His research has been in organic, physical-organic, quantum chemistry, and photochemistry. He has written one book, eight chapters, and over 200 publications. Seventy-four of his research students have entered academia. He received the First Northeast ACS Award for Photochemistry (1971), the ACS James Flack Norris Award in Physical Organic Chemistry (1976), the Halpern Award of the New York Academy of Sciences (1980), the Chemical Pioneer Award of the American Institute of Chemists (1986), Senior Humboldt Fellowship (1988), Hilldale Award in the Physical Sciences (University of Wisconsin, 1990), the ACS Cope Scholar Award (1990). He was elected to the National Academy of Sciences in 1980. Selected Research: (1) The stereochemistry of ketonization of enols and kinetic protonation; (2) 1,2-carbanion rearrangements ("Grovenstein–Zimmerman Rearrangement"); (3) Barrelene—original synthesis, nonaromaticity, and chemistry; (4) Möbius–Hückel Concept for reaction allowedness–forbiddeness; (5) the first correlation diagram for an organic reaction and relation to reactivity; (6) a general theoretical treatment of organic photochemical reactions relating three-dimensional excited-state structure to reactions observed; (7) a theoretical and experimental treatment of the Birch Reduction; (8) the di-π-methane rearrangement—discovery and development; (9) the 4-arylcyclohexenone to bicyclo[3.1.0]-2-hexanone rearrangement; (10) the α,β-epoxy ketone to β-diketone reaction; (11) the triplet vinylcyclopropene to cyclopentadiene conversion; (12) the reaction of cyclohexenones giving vinylcyclobutanones; (13) the mechanism of the Type-A (Lumi) rearrangement; (14) unusual rearrangements of S_1 1,3-diradicals; (15) mechanisms of radiationless decay via conical intersections for singlets and by free-rotor effects for triplets; (16) theoretical and experimental contributions to photochemistry in confined media; (17) moiety–moiety polarizability permitting prediction of organic reactions; (18) new theory on dissection of triplet–singlet spin–orbit coupling into hybrid pair contributions.

plausible but incorrect mechanism. However, within a year we arrived at not only the correct mechanism but also the realization that the reaction should be general.[2]

Scheme 3



3 **4**

The ensuing two decades have confirmed this observation by providing numerous examples of the rearrangement. Interestingly, the literature contains many superficially different reactions which, when analyzed in detail, proceed via the precise di-π-methane reaction mechanism. Finally, it needs to be noted that, in addition to the basic di-π-methane rearrangement (DPM), there are variations in which

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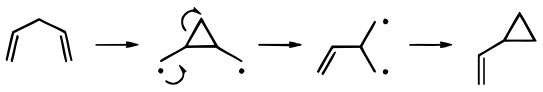
a carbon atom has been replaced by some other atom. The most common is the oxa-di-π-methane rearrangement (ODPM) in which one of the two π-moieties is a carbonyl group. Similarly the aza-di-π-methane rearrangement (ADPM) has a C−N double bond function as one of the π groups. These two variants of the basic di-π-methane reaction are discussed in sections III and IV, respectively.

A. Mechanism

1. Basic Skeletal Transformation Common to Di-π-methane Rearrangements

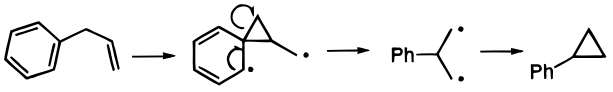
It is intriguing that one basic mechanism is capable of accounting for so many transformations which on first glance do not appear to be related. However, the Schemes 4 and 5 do indeed permit one to predict di-π-methane photochemistry in a very large spectrum of organic photochemistry. Scheme 4 portrays

Scheme 4



the behavior of reactants having two vinyl groups as π-moities while Scheme 5 describes the skeletal rearrangement where one of the two π-substituents is an aryl group. The same basic mechanism applies

Scheme 5

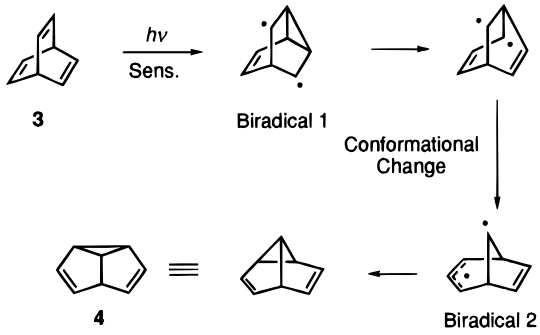


equally to those di-π-methane rearrangements which proceed by way of singlet excited states and to those proceeding via triplet counterparts. The singlet rearrangements are found among those occurring upon direct irradiation without the use of an added sensitizer, while the triplet rearrangements are effected by addition of a sensitizer which absorbs light, is itself converted to a triplet species, and then collides with the reactant, exciting that molecule to the triplet state.

2. The Reaction Mechanism Applied to Three Representative Examples

The example of the photochemical conversion of barrelene (**3**) to semibullvalene (**4**, Scheme 3) at first glance seems less straightforward; yet it was this case which alerted one of us to the reaction mechanism and to the potential generality of the reaction. One notes that barrelene does have the requirement of two π-bonds attached to an sp^3-hybridized carbon. That there are more than two vinyl groups bonded to a bridgehead poses no problem, nor does the availability of two bridgehead carbons, either of which may be considered to be the "methane carbon". The basic mechanism in Scheme 4 is applied to the barrelene (**3**) in Scheme 6.[2]

Scheme 6

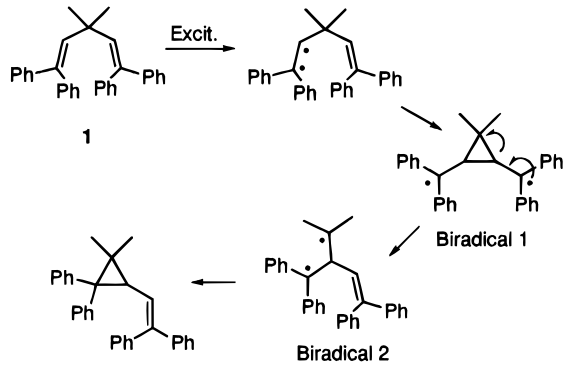


Here the reaction is depicted in standard organic notation. The biradical species (1 and 2) are drawn since they help understand and predict reaction courses, regioselectivity, and general reaction trends. However, in general, such biradical entities may be real reaction intermediates or, instead, may be transition states. In the particular case of barrelene there was early experimental evidence that triplet "Biradical 2" is an intermediate[2] and subsequent theoretical efforts[8] show this to be the case for triplet "biradical 1" as well. Also it needs to be noted that the barrelene to semibullvalene rearrangement is a triplet reaction.

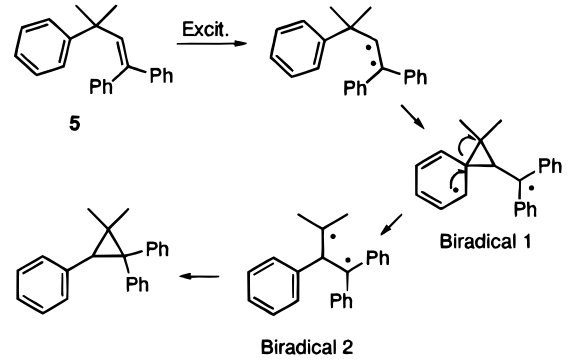
A similar detailed mechanism is outlined for diene **1** as an example of an acyclic di-π-methane rearrangement (Scheme 7).[3] This, however, proceeds without addition of a sensitizer and is known to be a singlet process. Again, "biradical 1" and "biradical 2" are species along the mechanistic pathway.

A third example, compound **5**, is acyclic but has an aryl group as one of the π-components.[5] This proceeds by a perfectly similar mechanism except that the aromatic ring is involved in the bridging process (Scheme 8). Again, it is the singlet excited state which rearranges.

Scheme 7



Scheme 8



The three examples given above typify the rearrangements of bicyclic and acyclic di-π-methane systems. Additionally, they illustrate reactions which proceed via triplet excited states on sensitization and as well as reactions which occur on direct irradiation (i.e. without use of a sensitizer). However, not all reactions proceeding without use of a sensitizer occur by way of the singlet excited state, since the initially formed singlet (S_1) in some instances will convert itself to the triplet by "intersystem crossing" to give the triplet which then rearranges.

The matters of reaction regioselectivity, reaction multiplicity, stereochemistry, and dependence on structure are certainly related to reaction mechanism. Nevertheless, they are intimately entwined with the scope of the reaction and are therefore considered in the following section. Thus, for example, where there is a question of which of two alternative products will result because, a priori, one sees two potential regiochemical reaction courses, or where there is a possibility of energy dissipation and thus no reactivity, consideration of mechanism is necessary.

B. Scope and Limitations

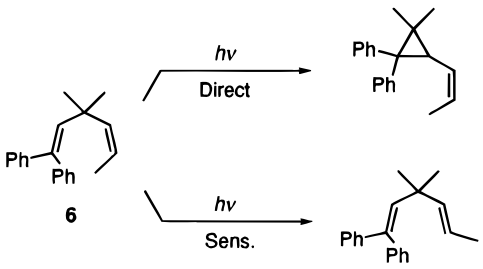
1. Reaction Multiplicity

The subject of reaction multiplicity is a practical matter in the di-π-methane rearrangement. Thus, some molecules are unreactive when a sensitizer is used while others require a sensitizer. The most common sensitizers employed are ketones such as acetophenone, benzophenone, and xanthone. The role of the sensitizer is to generate the triplet excited state of the di-π-methane reactant with certainty. Without the use of a sensitizer one is more likely to

observe the reaction of the singlet excited state but sometimes the initially generated excited singlet will convert to its triplet faster than it reacts; this is a point which may be checked experimentally.

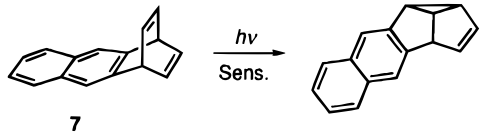
One particularly relevant reason for deciding whether to use a sensitizer or not derives from the oft-observed rapid decay of triplets to reactant ground state without reaction. Clearly one wants to avoid this. The most common mode of decay of triplet excited states to ground state is via the "free rotor" effect.[9a−c] It has been observed that di-π-methane triplets which have double bonds not incorporated in a ring structure or not inhibited from free rotation in some other manner, are commonly unreactive. Thus triplet excited π-bonds in acyclic systems have very low bond orders and tend to twist toward perpendicularity. Such a twisted triplet has a geometry ideally suited to convert to ground state. For example the tetraphenyl 1,4-diene **1** in Scheme 1 does not react when a sensitizer is utilized, in contrast to its reactivity on direct irradiation. Still another example is found in the case of the unsymmetrically substituted diene, 3,3-dimethyl-1,1-diphenyl-1,4-hexadiene (**6**) (Scheme 9).[9d]

Scheme 9



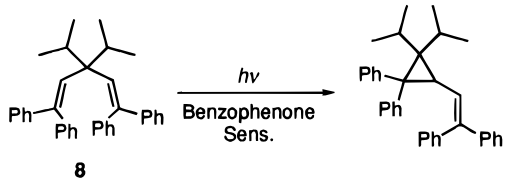
In contrast, cyclic dienes tend to be perfectly reactive as triplets, and this can be ascribed to their inability to undergo free rotation in the excited state. One example is that of the barrelene (**3**) to semibullvalene (**4**) transformation depicted in Scheme 3 and another is that of 2,3-naphthobarrelene (**7**) as outlined in Scheme 10.[10]

Scheme 10



Of course there are exceptions to any generalization. Thus, one is dealing with the rate of radiationless conversion of the triplet reactant to ground state compared with the rate of reaction. If the rate of reaction is exceptionally rapid despite the presence of a free-rotor group, one may well observe triplet reactivity in an acyclic system. For example, if free rotation is inhibited by effects such as steric hindrance, the triplet may be reactive. The case of 3,3-diisopropyl-1,1,5,5-tetraphenyl-1,4-pentadiene (**8**)[8d] is one where the bulky isopropyl groups inhibit free rotation, and this acyclic diene is reactive despite its similarity to diene **1** which is quite unreactive as a triplet (Scheme 11).

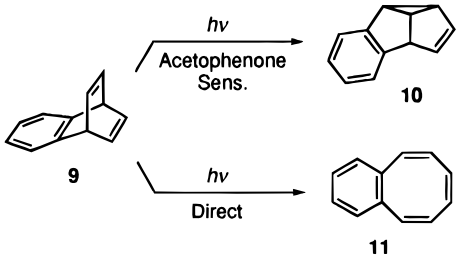
Scheme 11



Having discussed examples where sensitization leads to unreactive triplets, we need to consider when direct irradiation may give rise to problems. The original generalization[3] was that cyclic molecules are more likely to react successfully from the triplet excited state via sensitization while acyclic molecules tend to perform better as singlets. In the case of triplet reactivity this has been noted to relate better to the absence or presence of a free rotor. Now we are left with the fact that for many cyclic molecules, direct irradiation with formation of the singlet excited state does not lead to a successful di-π-methane rearrangement.

This behavior arises not because the singlet excited state is incapable of a di-π-methane rearrangement but rather because many cyclic systems have potentially available facile alternative pericyclic processes which compete all too successfully. Just one example[11] is given in the following where benzobarrelene (**9**) is shown on sensitization to afford benzosemibullvalene (**10**). However, on direct irradiation, benzocyclooctatetraene (**11**) is formed by an electrocyclic [$2\pi + 2\pi$] addition of the benzo group to double bond, followed by a retrocycloaddition (Scheme 12).

Scheme 12

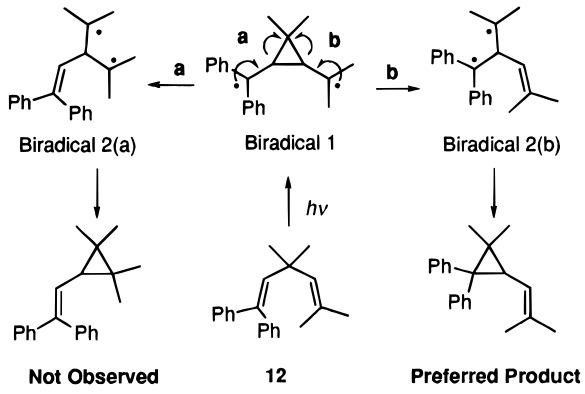


Such electrocyclic processes tend to occur preferentially from the singlet excited state and, in addition, tend to be exceptionally rapid. This example is just one of many which arise from the fact that cyclic di-π-methane systems have available competing pericyclic processes more often than acyclic ones. However, not all cyclic di-π-methane systems have such potentially competing processes, and each example needs to be considered on its own merits.

2. Reaction Regioselectivity

One encounters a number of examples of di-π-methane reactants which are unsymmetrically substituted. Here one needs to predict which of the two π-systems will survive in the photoproduct. Fortunately, from mechanistic reasoning one is able to predict the reaction regioselectivity. One example is found in the direct irradiation of 3,3,5-trimethyl-1,1-diphenyl-1,4-hexadiene (**12**)[9c] as outlined in Scheme 13.

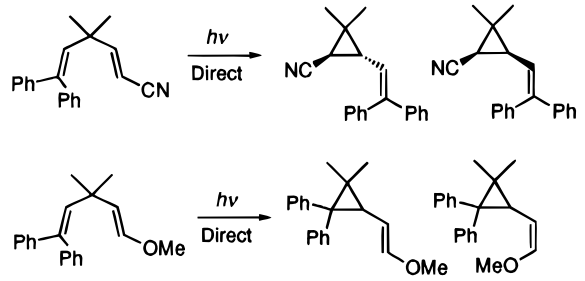
Scheme 13



The observed regioselectivity is understood on the basis of "biradical 1" undergoing three-ring opening preferentially by process b rather than a. One can predict this on the basis that the less delocalized odd-electron center, with dimethyl substitution, is utilized in the ring opening. This is basically equivalent to saying that the opening occurs to afford the more stable of two, alternative 1,3-biradicals, the one with benzhydryl delocalization. In summary, in such cases one obtains that regioisomer which has the less delocalizing group on the residual double bond. The regioselectivity of aryl−vinyl di-π-methane systems is even easier to understand and predict. In this case, the odd-electron center which is involved in the three-membered ring opening is the one which restores aromaticity. This is illustrated in the mechanism for the reaction of 3-methyl-1,1,3-triphenyl-1-butene (**5**) given earlier (Scheme 8). In biradical 1, it is seen that the three-membered ring opening occurs utilizing the odd electron which is in the six-membered ring with restoration of that ring's aromaticity. If the benzhydryl odd electron were involved in the three-membered ring opening, not only would the benzhydryl delocalization be lost, but also the driving force of aromatization would not be gained.

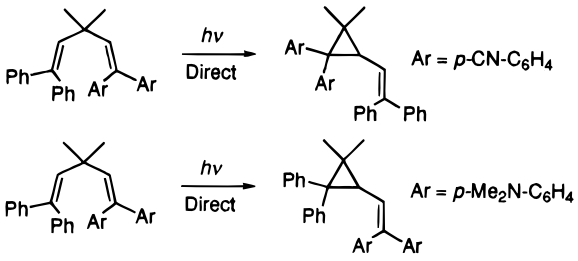
Still another kind of situation arises. This results from the presence of electron donors and/or acceptors on one of both of the π-moieties. Here a general rule may be formulated. This is that there is a strong tendency for electron donors to appear on the residual π-bond of the photoproduct and for electron-withdrawing groups to be found on the product three-membered ring. Four representative examples are found in the Schemes 14 and 15. It is seen that the generalization[12] operates both where the electron donating group is directly on one of the double bonds and also where it is a para substitutent on an aryl

Scheme 14



group. In Scheme 14, the double bond bearing the cyano substituent is dissipated and this electron-withdrawing group appears on the cyclopropyl ring of product.[12] Conversely, in Scheme 14, the enol ether methoxyl group is found on the surviving double bond of photoproduct.[12] In Scheme 15 the

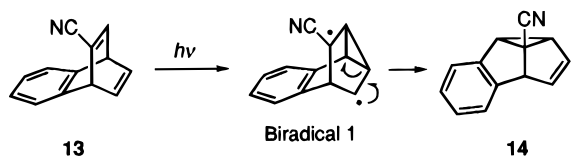
Scheme 15



p-cyanophenyl groups are found on the three-membered ring of photoproduct[13] while the (*N*,*N*-dimethylamino)phenyl groups remain on the double bond of product.[14]

A further question occurs when there are three π-systems bonded to a single "methane carbon". One might term these "tri-π-methane" reactants. When the three bridges are nonequivalent, there is the question of which two π-systems will bond. In the cases of benzobarrelene (**9**),[11] 2,3-naphthobarrelene (**7**),[10] 2,3-anthracenobarrelene,[15] and related examples, there is a preferential bonding between the two vinyl bridges rather than between the benzo and vinyl bridges. One exception is that of 1,2-naphthobarrelene where α-naphtho−vinyl bridging is preferred.[10] For all these reactions there is considerable mechanistic detail known[10,11,15,16] but this will not be discussed here. A related but still different variation in regioselectivity is encountered in systems where the two π-moieties are bonded to "methane carbons" at both ends. Here there is a choice of at which end of the molecule the π−π bridging will occur. This situation occurs in bicyclic systems such as in the rearrangement of 2-cyanobarrelene (**13**) studied by Bender.[17] The regiochemistry can be predicted by writing the more delocalized of the cyclopropyldicarbinyl biradicals (i.e. "biradical 1") which can be formed on π−π bridging. This is outlined in Scheme 16. It is noted that the initial

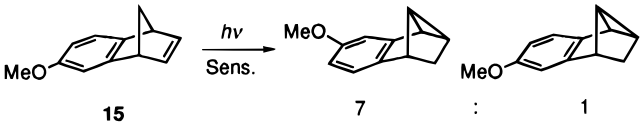
Scheme 16



bridging occurs between two vinyl groups to leave the cyano group at an odd-electron center. While benzo−vinyl bridging could also afford a cyano-stabilized biradical, Bender has ruled this out using isotopic labeling, and in any case such bridging would lead to the same product in the unlabeled example here. Furthermore, of the two three-membered ring-opening possibilities, the odd-electron not stabilized by the cyano group is the one utilized. This reasoning permits us to predict the observed photoproduct **14**.

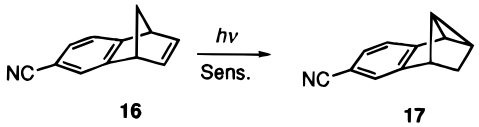
Further examples of this general type occur in the photochemistry of substituted benzonorbornadienes.

Scheme 17



Paquette[18] has shown that the regiochemistry is governed in similar fashion. Thus in the methoxybenzonorbornadiene (**15**) in Scheme 17 benzo−vinyl bridging occurs distal to the methoxy group while in the cyanobenzonorbornadiene (**16**) in Scheme 18,

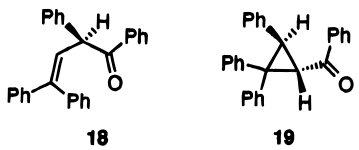
Scheme 18



benzo−vinyl bridging takes place proximate to the cyano group to give the observed product **17**. The regioselectivity is similar to that observed with electron-donating and -withdrawing substituents on acyclic di-π-methane systems. Thus, one draws the generalization that electron donors avoid positioning themselves in conjugation with the carbinyl centers of the cyclopropyidicarbinyl biradicals (i.e. "biradical 1") and electron-withdrawing groups lead to stabilization when so situated. Examples of DPM rearrangements of acyclic, cyclic, and bicyclic 1,4-dienes are collected in Tables 1−9.[2,3,5,7,8,9a,11−53]

III. The Oxa-di-π-methane Rearrangement

As has been mentioned above, the di-π-methane processes are not restricted to 1,4-dienes. Other 1,4-unsaturated systems, such as β,γ-unsaturated ketones and 1-aza-1,4-dienes, undergo similar rearrangements. The first example of a reaction of this type in a β,γ-unsaturated ketone was reported as far back as 1966 in the direct irradiation of compound **18** that affords the cyclopropyl ketone **19** by an oxa-di-π-methane (ODPM) rearrangement, in 7% yield.[54] Since then a large number of studies have been carried out on the photochemistry of β,γ-unsaturated ketones and there are many examples of compounds of this type that undergo synthetically useful ODPM rearrangements. Some comprehensive reviews have been published in the last 25 years or so on this subject.[1c−f]

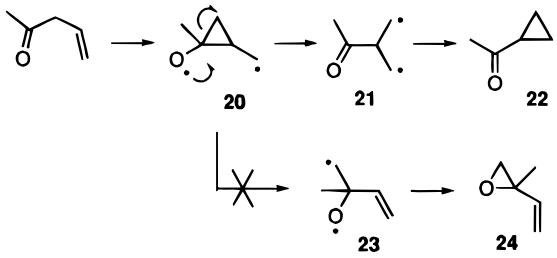


The large number of studies carried out on the photoreactivity of β,γ-unsaturated ketones have demonstrated that these compounds may undergo several different photochemical reactions. The two main reaction paths are the 1,3-acyl migration and the oxa-di-π-methane rearrangement. However, other alternative reaction routes such as decarbonylation, ketene formation, epimerization, 2 + 2 intramolecular cycloadditions, Norrish type I and Norrish type II reactions, cis−trans isomerizations, and reductions of the C−C double bond, have also been described in some instances depending on some particular structural features that are present in the β,γ-unsaturated ketone.[1c] Nevertheless, the reactivity of β,γ-unsaturated ketones is dominated by the two main processes mentioned above. Speaking in general terms, the 1,3-acyl migration is the normal photochemical behavior of β,γ-unsaturated ketones on direct irradiation while the ODPM rearrangement is expected on triplet sensitized irradiation.[1c−f] This simplification applies to most of the cases studied although there are exceptions that will be discussed later. From a synthetic point of view the ODPM rearrangement has proved to be a useful tool in organic synthesis. The synthetic utility of the ODPM rearrangement can be summarized in the following general features: very often the reaction takes place in high chemical yield, the quantum yield is also high in many instances, it is very general for many cyclic β,γ-unsaturated ketones, and it shows a high degree of stereoselectivity or even enantioselectivity in some instances. Therefore, it is not surprising that it has been applied as the key step in the synthesis of some natural products and other highly complicated molecules that are difficult to obtain by alternative reaction routes. Finally, the reaction can be carried out in the presence of other functional groups that are not affected under sensitized irradiation. This is a characteristic of most of the photochemical reactions, and it is an advantage that increases the synthetic potential of the reaction.

A. The Mechanism

The ODPM rearrangement consists formally of a 1,2-acyl migration followed, or accompanied, by cyclization. A formal mechanism, analogous to that shown in Scheme 4 for the DPM reaction, is given in Scheme 19. This was first postulated by Givens and

Scheme 19

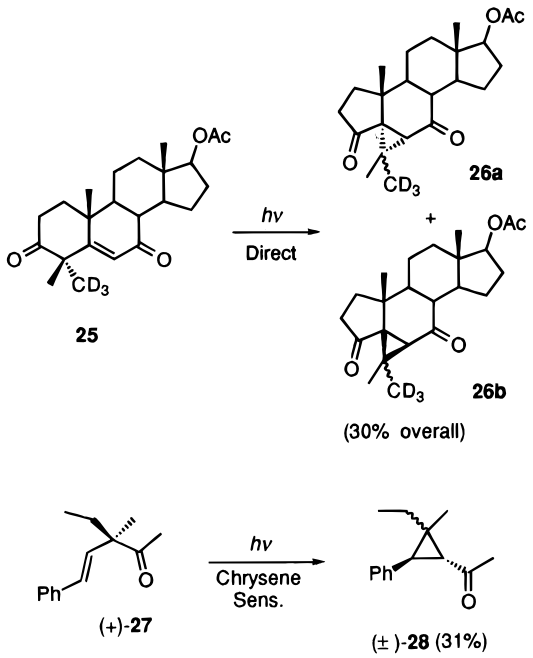


Oettle to account for the photochemical conversion of benzobicyclo[2.2.2]octadienone into 3,4-benzotricyclo-[3.3.0.0^{2,8}]octan-7-one.[55] The mechanism explains the regioselectivity encountered in the rearrangement. In all the cases studied the ODPM reaction yields the corresponding cyclopropyl ketone **22**. The alternative ring opening of the biradical intermediate **20** that would yield the oxirane **24** has never been observed. This regioselectivity can be understood, considering that the opening of the cyclopropyl biradical intermediate **20** occurs to afford the 1,3-biradical **21** which is more stable than the alternative 1,3-biradical **23**. As a result, the C−O double bond is always restored.

The biradical structures represented in Scheme 19 could be considered as true intermediates or simply

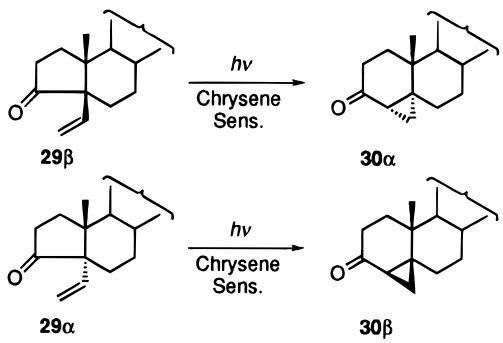
points of low energy along the reaction coordinate in a concerted rearrangement pathway. Efforts have been made in order to determine whether the reaction takes place by a stepwise mechanism or by alternative concerted processes. Most of the studies on this subject have concentrated on establishing the stereochemistry of the process. The results obtained show that the three possible alternatives—loss of stereochemistry,[56−60] retention of configuration,[61] and inversion of configuration[62−71]—can occur. Among the three possibilities the latter process is the one that has been observed more frequently. Two examples of loss of stereochemistry are shown in Scheme 20 for compounds **25**[56] and **27**.[59,60]

Scheme 20



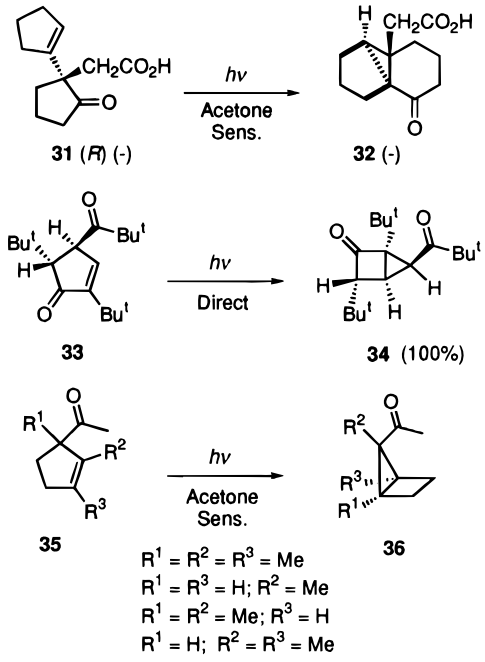
Thus, the direct irradiation of **25** gives a mixture of **26a** and **26b** in which a complete scrambling of the methyl and trideuteromethyl groups has taken place.[56] Similarly chrysene-sensitized irradiation of the optically active acyclic ketone **27** yields a mixture of largely racemized products **28**.[59,60] These results are in support of a stepwise mechanism via biradical intermediates. However, sensitized irradiation of the β-enone **29*β*** yields the α-methane ODPM product **30α** while the corresponding α-enone **29α** gives the β-methane ODPM product **30*β***; here retention of configuration at the methane carbon is observed[61] (Scheme 21).

Scheme 21



Finally, Scheme 22 shows examples of ODPM rearrangements that proceed with preferential inversion of configuration at the methane carbon, a situation frequently observed. The acetone-sensitized

Scheme 22



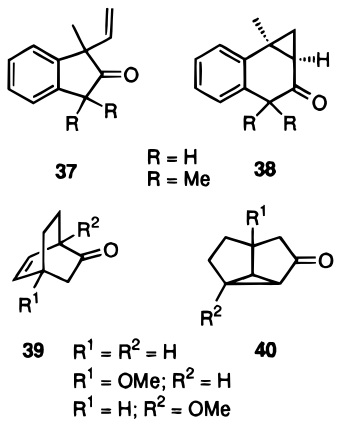
irradiation of the enantiomerically pure cyclic ketone **31** gives **32**, in high chemical yield, and with 95% optical purity.[69,70] The direct irradiation of **33** brings about the formation of the endo isomer **34** in quantitative yield.[71] A series of studies on the ODPM rearrangement of cyclopentenyl ketones **35** show that all of them yield preferentially the endo product **36**.[64−66] The stereochemical results observed for the compounds collected in Scheme 22 suggest concertedness or slow conformational equilibration of intermediates.

However, the high stereochemical control often observed in many ODPM rearrangements does not necessarily imply that the reaction is taking place via concerted mechanisms. A stepwise process is also consistent with the stereochemical outcome of the reaction, where there are conformational or configurational restrictions to rapid C−C rotation. This subject has been extensively discussed and reviewed by Schuster.[1e]

B. The Nature of the Excited State Involved in the ODPM Rearrangement

The problem of the nature of the excited states involved in the ODPM rearrangement has also deserved a lot of attention. The first examples reported on the photochemical reactivity of β,γ-unsaturated ketones fit a pattern in which direct irradiation yielded products resulting from 1,3-acyl migration while the triplet-sensitized irradiation brought about the formation of ODPM products.[1c−f] On the basis of these results, together to CNDO-MO calculations,[72] phosphorescence studies,[66,74−76] quenching and sensitization experiments,[53,62,73,77,78] the excited state responsible for the rearrangement was

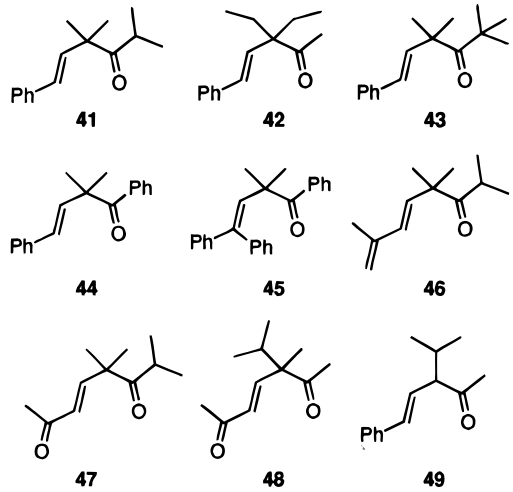
considered to be the alkene T_1 state. The fact that the 1,3-acyl shift was not observed on triplet-sensitized irradiation and was not quenched by triplet quenchers,[77,78] in addition to nuclear polarization effects (photo-CIDNP)[79a,b] favored the assignment of a keto S_1 (n,π*) excited state for the 1,3-acyl shift reaction. However, later results have shown this not to be general. Thus, independent studies by Schuster[80] and Schaffner[79] have provided evidence suggesting that the 1,3-acyl shift can take place from both S_1 (n,π*) and T_2 (n,π*) excited states. Other authors have also concurred in the involvement of the T_2 (n,π*) state in the 1,3-acyl shift.[81,82] On the other hand, a study of Koppes and Cerfontian[83] has demonstrated that ketones **37** undergo the ODPM rearrangement on direct irradiation yielding compounds **38**, in a reaction thought to take place from the S_2 (π,π*) state. In another study Rogers et al.[84b,c] have reported that direct irradiation of ketones **39** give **40**, by the ODPM rearrangement, in a reaction that was said to originate from some excited state other than the T_1 (π,π*) state. An extensive discussion can be found in Schuster's review.[1e]



37 38 39 40

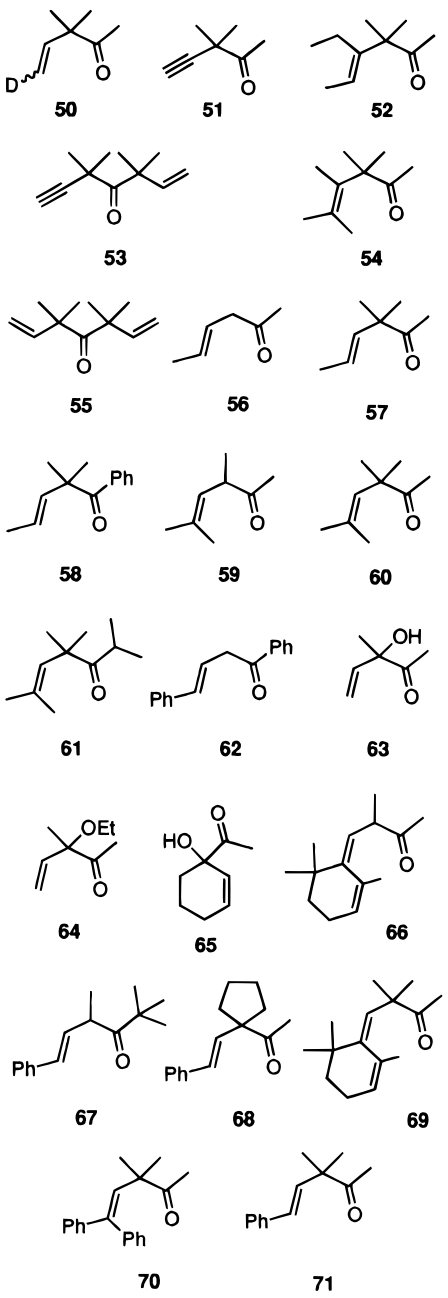
C. The ODPM Rearrangement of Acyclic β,γ-Unsaturated Ketones

As has been mentioned above, the ODPM rearrangement has proved to be very general for a large number of cyclic and polycyclic β,γ-unsaturated ketones. However, there are only a few examples of acyclic β,γ-unsaturated ketones that undergo this reaction. In most acyclic and medium- and large-ring cycloalkenyl ketones the triplet excited state normally undergo free-rotor deactivation with E/Z C−C double-bond isomerization. This situation contrasts with the DPM process in which many acyclic 1,4-dienes undergo efficient rearrangement in the singlet excited state, affording the corresponding cyclopropane derivatives in high yield. The difference between the two reactions may be understood as a consequence of the more efficient deactivation of the triplet excited state in the β,γ-unsaturated ketone by the "free rotor effect". This interpretation also is in accord with the lack of DPM reactivity of acyclic 1,4-dienes in the triplet state.[9] The central carbon of the β,γ-unsaturated ketone is usually dialkyl substituted. However, examination of the photoreactivity described in the literature for acyclic β,γ-unsaturated ketones, in the triplet excited state, shows that other factors should be taken into account as well. In the majority of the cases in which the ODPM rearrangement of acyclic systems is operative, not only is there methane carbon substitution but also the C−C double bond is conjugated with one or two phenyl groups at the γ-position of the enone. The compounds that fall in these groups are illustrated in structures **27** (Scheme 20),[58] **41**,[85] and **42**−**45**.[86] All of them undergo the ODPM rearrangement to the corresponding cyclopropyl derivatives in reasonable yields (Table 10). Compound **46**, in which the alkene moiety is conjugated with a vinyl group also undergoes the rearrangement, on benzophenone-sensitized irradiation.[87] The ODPM reaction is also observed, although in low yield, on direct irradiation of compounds **47** and **48**, in which the alkene is part of a conjugated enone system.[87]



41 42 43 44 45 46 47 48 49

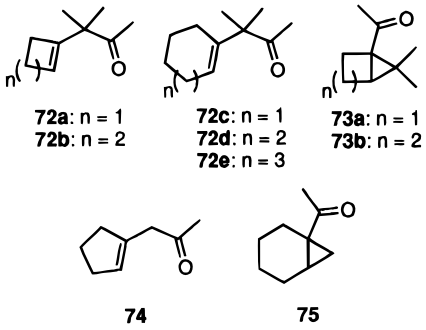
However, there are two cases in which the ODPM rearrangement takes place in the absence of disubstitution at the central carbon. As mentioned above, the cyclopropyl ketone **19** is obtained in 7% yield on the direct irradiation of compound **18** with monophenyl substitution at C2.[54] Another example of this situation is found in ketone **49** that on sensitized irradiation, using *p*-benzoylbiphenyl, gives the corresponding cyclopropyl derivative in 70% yield.[86] The reactivity observed in these two cases could be due to the bulk of the substituents at C-2 (phenyl and isopropyl) that overcomes the absence of disubstitution at that position. It seems that the key structural features favoring the ODPM rearrangement of β,γ-unsaturated acyclic ketones are (i) conjugation of the alkene moiety with phenyl, vinyl, or oxo groups and (ii) disubstitution or, alternatively, mosubstitution by bulky substituents at the central carbon. The former requirement ensures that the triplet energy from the sensitizer will be concentrated in the vinyl group of the enone. Also, this type of substitution stabilizes the biradical intermediates **20** and **21** (Scheme 19) favoring the ODPM process relative to alternative reaction paths. The lack of ODPM reactivity is encountered in many other acyclic β,γ-unsaturated ketones. Thus, none of the ketones **50**−**52**,[81,88] **53**−**55**,[88] **56**−**58**,[89a] **59**−**61**,[89b] **62**,[90] **63**−**65**,[91] **66**,[89c] and **67**[86] undergo the rearrangement on triplet sensitization. In most cases the only reactivity observed was E/Z isomerization around the C−C double bond. Some of them (**56**, **59**, **62**, **66**, and **67**) do not have



methane disubstitution or, alternatively monosubstitution by bulky substituents, at the central carbon. Thus, these compounds lack the substitution pattern insuring both efficient energy transfer from the triplet sensitizer, slow radiationless decay to reactant, and the necessary stabilization of the biradical intermediates. Interestingly, ketones **68**,[86] **69**,[89c] **70**[92] and **71**[86] having disubstitution at the central carbon, and phenyl or vinyl substituents at the γ-position have been reported as unreactive. Examples of ODPM rearrangement of acyclic ketones, including yields and references, are collected in Table 10.

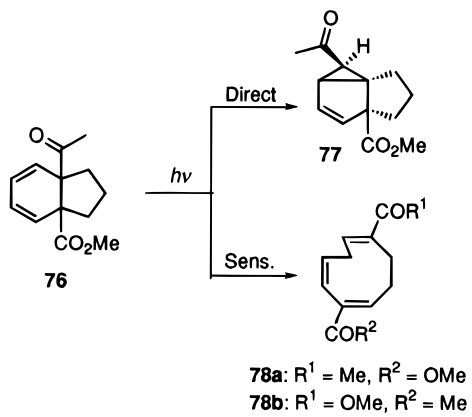
D. The ODPM Rearrangement of Cycloalkenyl β,γ-Unsaturated Ketones

Contrary to the lack of reactivity observed so far in the studies on the ODPM reactivity of many acyclic β,γ-unsaturated ketones, the majority of cyclic systems undergo the rearrangement very efficiently. Incorporation of the alkene moiety into a four- or five-membered ring allows one to observe the ODPM rearrangement in high yield. Engel and Schexnayder,[93] published a study on the influence of ring size on the ODPM rearrangement of cycloalkenyl ketones **72** showing that an increase in the size of the ring is detrimental for the reaction. Thus, cyclobutenyl and cyclopentenyl ketones **72a** and **72b** undergo the ODPM rearrangement to the corresponding bicyclic derivatives **73** on acetone-sensitized irradiation. However, when the size of the ring is increased to six, seven, and eight, as in ketones **72c**−**e**, the rearrangement does not take place. These results demonstrate that the triplet-state photochemistry of ketones **72** depends on the rigidity of the C−C double bond and absence of the free rotor effect. Surprisingly, ketone **74** without alkyl substitution at the methane carbon undergoes the ODPM rearrangement to **75**, both on direct and sensitized irradiations. However, no isolated yields of products are given in this study.[93]



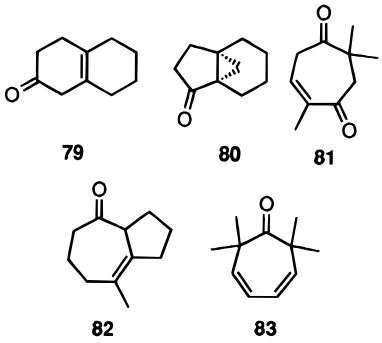
Other examples of this class of compound that undergo the rearrangement in high yield are collected in Table 11.[66,71,87,94] In some cases a high degree of stereochemical control is observed.[66,71,94] This feature has been considered before for ketones **33**[71] and **35**.[66] In this context it is worth mentioning the unusual photochemical reactivity of the keto ester **76**.[94] This compound undergoes diastereoselective ODPM rearrangement, on direct irradiation at 350 nm, affording **77** in 32% yield. However, triplet sensitization of **76** brings about the formation of a mixture of *all-cis*-cyclononatrienes **78**, resulting from a ring-opening process. Quenching experiments indicated that both products **77** and **78** are formed via different triplet excited states.[94] See Scheme 23.

Scheme 23



E. The ODPM Rearrangements of Monocyclic and Condensed Polycyclic β,γ-Unsaturated Ketones

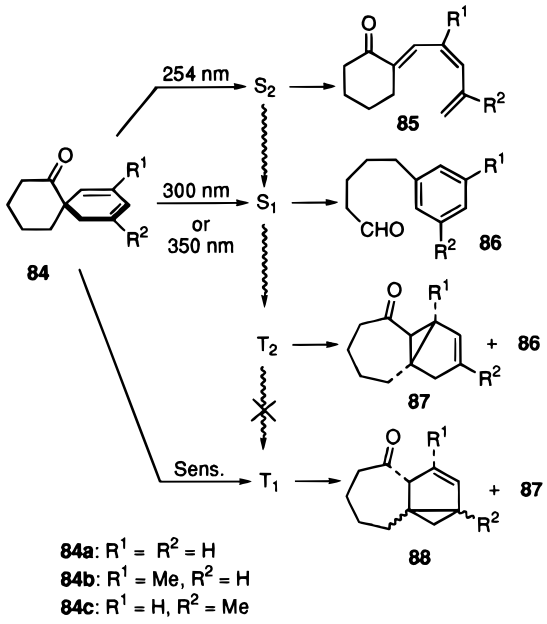
The ODPM rearrangement of β,γ-unsaturated ketones in which both the carbonyl group and the alkene moiety are part of a cyclic system usually takes place very efficiently. Quite a few cases of this type of compound have been described and representative examples are collected in Table 12. The second example of an ODPM rearrangement was described by Ziffer and Williams[95] in the direct irradiation of the hexahydronaphthalene **79** that gives more than 50% yield of the corresponding tricyclic derivative **80**.[78,95] Even in cases in which the alkene unit is part of a medium size ring, as in **81**, the reaction still takes place.[87] This is in contrast to the results obtained for the cycloalkenyl ketones **72c**−**e** in which the presence of the double bond in a six-, seven-, or eight-membered ring suppresses the ODPM rearrangement.[93] Still further examples of ODPM reactivity in cycloheptenone derivatives have been reported for ketones **82**[96] and **83**[97] although in these cases the flexibility of the double bond is much more restricted than in **81**.



The incorporation of the carbonyl group to a small ring system seems to facilitate the rearrangement even in cases in which the alkene moiety is free to rotate. This is the case of ketones **29**[61] (Scheme 21) and **37**[83] that yield the corresponding ODPM products on chrysene sensitization and direct irradiation respectively. Many of the studies in this area have been dedicated to steroidal compounds such as **25**[56] (Scheme 20) and **29**[61] (Scheme 21). In some of the cases reported, the reaction takes place with a high degree of stereochemical control as mentioned before for ketone **29** although in other cases, such as **25**, loss of stereochemistry is observed. Examples of ODPM rearrangement of cyclic ketones, with yields and references, are collected in Table 12.[56,57,69,70,78,87,95,97−102]

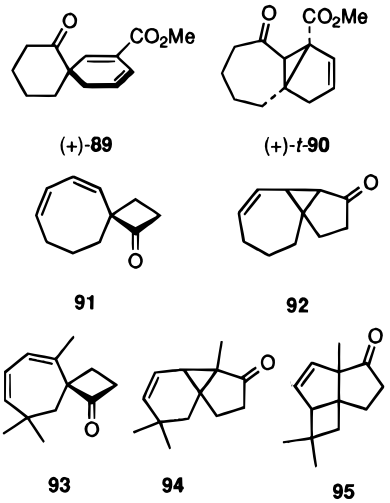
The photochemistry of $\beta,\gamma,\delta,\epsilon$-unsaturated spiroketones is very interesting. These compounds undergo regioselective and diastereoselective ODPM rearrangements. Furthermore, and of considerable mechanistic interest, the studies carried out have shown a wavelength selectivity in their reactivity.[103] Thus, irradiation of ketones **84**, at 254 nm, brings about an electrocyclic ring opening of the cyclohexadiene ring to the corresponding conjugated trienone **85** via an S_2 (π,π^* excited state, Scheme 24). At 300 nm α-cleavage takes place giving aldehyde **86** from an S_1 (n,π^*) state. On irradiation at 350 nm the transfused ODPM product **87** is obtained, in addition to

Scheme 24



86, in a reaction that is highly regio- and diastereoselective. The rearrangement to **87** is proposed to occur from the T_2 (π,π^*) excited state populated by intersystem crossing from S_1 (n,π^*). Finally acetone-sensitized irradiation of **84** yields **88** resulting from a vinylogous oxa-di-π-methane rearrangement, in both the trans and cis configurations, in addition to **87**. A T_1 (π,π^*) state was proposed to account for the latter result (Scheme 24).[103]

Within this area of research an example of enantiospecific ODPM rearrangement has been described for the spiro compound **89** that yields quantitatively the tricyclic derivative **90** both on direct, at wavelengths above 340 nm, and on acetone-sensitized irradiations. The formation of **90** is proposed to take place from the T_1 (π,π^*) excited state.[104] A similar study has been carried out on homoconjugated spirocyclobutanones.[105] In this instance a dependence of methyl substitution in the starting enone on the photoproduct distribution was observed. Thus, on sensitized irradiation using Michler's ketone, unsubstituted ketone **91** yields the ODPM product **92**. However, under the same conditions, trimethyl-substituted ketone **93** gives a mixture of products **94**

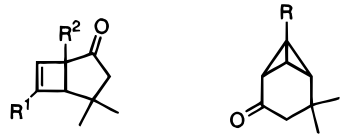


and **95** resulting from a normal oxa-di-π-methane rearrangement and the vinylogous ODPM reaction, respectively.[105] The results of these studies on spirohomoconjugated ketones, including yields and references, are collected in Table 13.[103−105]

F. The ODPM Rearrangement of Bridged Cyclic β,γ-Unsaturated Ketones

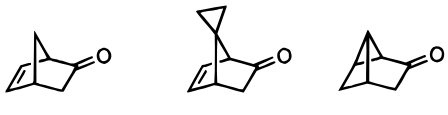
The studies carried out on the photoreactivity of bridged bicyclic ketones have probably been the most rewarding area of research within the ODPM rearrangement. In fact the majority of ODPM reactions reported in the literature deals with β,γ-unsaturated ketones in which both the alkene moiety and the keto group are part of a constrained bicyclic system. The rearrangement of these ketones allows the synthesis of tricyclic compounds that, in most cases, are difficult to obtain by alternative methods. Many of the reactions described in this class of compound give high isolated yields of products and, furthermore, the reactions are highly stereospecific and in some cases enantiospecific. Therefore, it is not surprising that the ODPM rearrangement of these compounds has been used as the key step in the synthesis of quite a few natural products. The potential of the ODPM in this area should be realized by the more conventional organic synthetic chemist.

Early work in this area by Ipaktschi showed that bicyclo[3.2.0]hept-6-en-2-ones **96** undergo the ODPM rearrangement to the corresponding bicyclo[1.1.0] derivatives **97** on sensitized irradiation (Table 14).[50,106] In another study by the same author the reaction was extended to bicyclo[2.2.1]hept-5-en-2-ones **98** and **99** that gave, under the same experimental conditions, the corresponding tricyclic derivatives **100** and **101** in high yield (Table 15).[53,62]

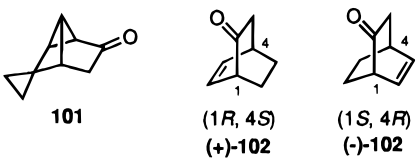


96a: R^1 = Me, R^2 = H
96b: R^1 = H, R^2 = Me
96c: R^1 = R^2 = H

97a: R = Me
97b: R = H



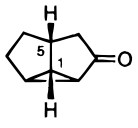
98 **99** **100**



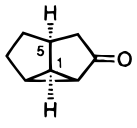
101

(1*R*, 4*S*) **(+)-102**

(1*S*, 4*R*) **(-)-102**



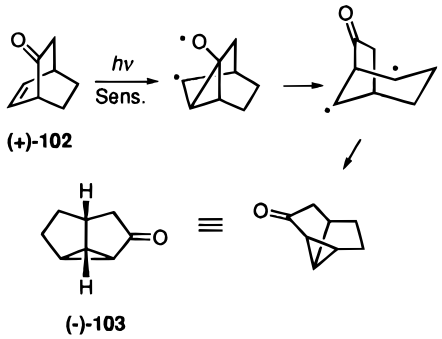
(1*S*, 5*R*) **(-)-103**



(1*R*, 5*S*) **(+)-103**

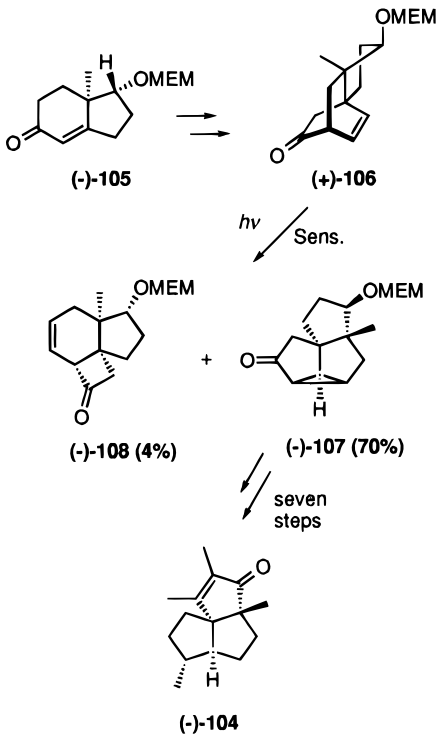
However, the largest amount of work in the area of the photochemistry of bridged bicyclic ketones has been in the study of bicyclo[2.2.2]octenone derivatives. The ODPM reactivity of these compounds has proved to be very general. Furthermore, the reactions take place with a high degree of stereochemical control and in high yield. Early work by Givens et al. demonstrated that acetone-sensitized irradiation of the racemic parent compound **102** gave the corresponding tricyclic derivative **103**, resulting from an ODPM rearrangement.[68] Many years later Demuth, Schaffner, et al. showed that the optical active compounds (1*R*,4*S*)-(+)-**102** and (1*S*,4*R*)-(−)-102 undergo enantiospecific rearrangements, on acetophenone-sensitized irradiation, to the corresponding products (1*S*,5*R*)-(−)-**103** and (1*R*,5*S*)-(+)-**103**, respectively, in 84−85% yield.[107] A stepwise mechanism, as shown in Scheme 25, with conformational restrictions was proposed.[107]

Scheme 25



Due to the above-mentioned features the ODPM rearrangement of bicyclo[2.2.2]octenones has been used as the key step in the synthesis of some natural products. Demuth and Schaffner have used the tricyclooctanones resulting from the ODPM reaction of bicyclo[2.2.2]octenones as building blocks that provided enantiospecific access to diverse cyclopentanoid derivatives.[108] The total synthesis of boschnialactone, allodolicholactone, irido- and isoiridomyrmecin, loganin aglucone 6-acetate, forsythide aglucone dimethyl ester, and (−)-coriolin have been achieved by this method. First steps toward the enantiospecific total synthesis of carbaprostacyclins and 9,11-dehydroestrone have also been made. This synthetic approach has been reviewed.[108] The synthesis of polycyclopentanoids and related compounds by this photochemical method has some advantages over ground-state alternatives; namely: (a) it is enantiospecific, (b) it allows incorporation of different substitution patterns, and (c) the starting materials are readily accessible from commercially available aromatic compounds. Furthermore, the ODPM rearrangement of bicyclo[2.2.2]octenones can be carried out in some cases at exceptionally high concentrations (>20%). A variant of this synthetic approach has been used by Demuth and Hinsken[109] to carry out the first synthesis, in enantiomerically pure form, of the angular triquinane (−)-silphiperfol-6-en-5-one (**104**) as shown in Scheme 26. The synthesis starts from the ketone (−)-**105** which is transformed in two steps into the bicyclo[2.2.2]octenone (+)-**106**. The acetone-sensitized irradiation of **106** gives (−)-**107** in

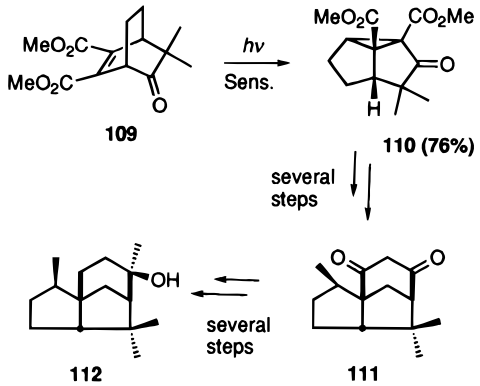
Scheme 26



70% yield, resulting from the ODPM rearrangement, and 4% of compound **108** which is formed by a competing 1,3-acyl shift due to residual light absorption by **106**. The tricyclooctanone **107** is converted into the angular triquinane **104**, in >97% enantiomerical excess, in seven steps.[109]

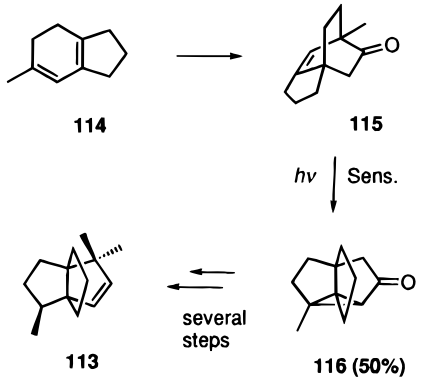
Other authors have also used the ODPM rearrangement of bicyclo[2.2.2]octenone derivatives in the synthesis of cedranoid sesquiterpenes.[110] Thus, the acetophenone-sensitized ODPM rearrangement of **109** gives **110** in 76% yield. Compound **110** was transformed in several steps into the β-diketone **111**, a key intermediate in the synthesis of cedrol (**112**, Scheme 27).[110a]

Scheme 27



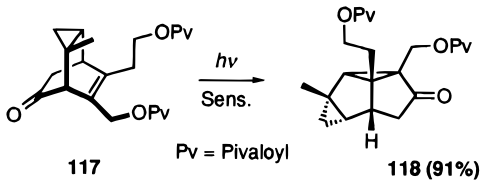
A photochemical approach to [3.3.3]propellanes by the ODPM rearrangement has allowed the synthesis of the sesquiterpene hydrocarbon (±)-modhephene (**113**).[111] In this instance the synthesis starts from the readily available diene **114** that is transformed into the bicyclo[2.2.2]octenone (**115**) through a Diels–Alder cycloaddition using α-chloroacrylonitrile as the ketene equivalent. Acetone-sensitized irradiation of **115** brings about the formation of the tetracyclic ketone **116** in 50% yield. This was converted by conventional procedures into the propellane (±)-modhephene (**113**,[111] Scheme 28).

Scheme 28



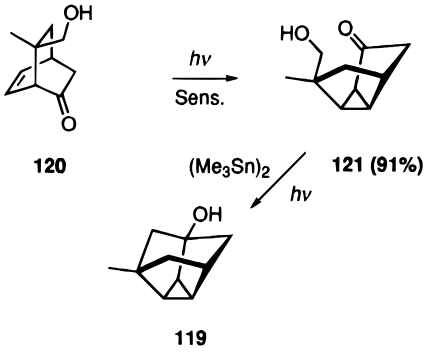
In a synthesis of pentalenolactone P methyl ester, the most highly condensed pentalenolactone antibiotic, Paquette et al.[112] have also made use of the ODPM rearrangement. One of the key steps in this synthesis is the very efficient conversion (91% yield) of the bicyclo[2.2.2]octenone derivative **117** into **118** by acetone-sensitized irradiation (Scheme 29).

Scheme 29



The synthetic utility of the ODPM rearrangement has also been demonstrated in its application to the synthesis of special molecules such as peristylanes. Thus, a key step in the synthesis of the hydroxyl-substituted [3]peristylane **119** is the ODPM rearrangement of the bicyclo[2.2.2]octenone **120** that gives **121** in 91% yield (Scheme 30).[113]

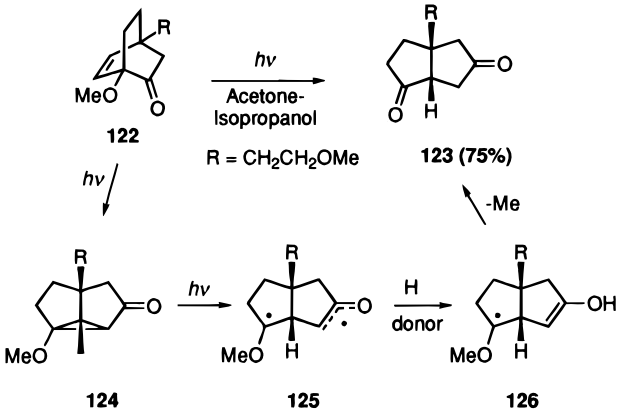
Scheme 30



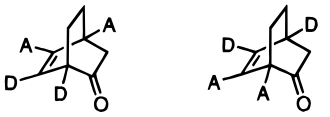
A variant of the ODPM rearrangement of bicyclo-[2.2.2]octenones is observed in the sensitized irradiation of 1-methoxybicyclo[2.2.2]octenones in the presence of isopropyl alcohol.[114,115] Thus, under these conditions, compound **122** gives the 1,4-diketone **123** in 75% yield.[115] To account for this result, a mechanism has been proposed consisting in the ODPM rearrangement of **122** to **124**, followed by photolytic

cleavage of the three membered ring that gives the biradical **125**. This intermediate transforms into **126** by hydrogen abstraction from the solvent. Loss of a methyl radical from **126** affords the observed product **123** (Scheme 31).[114,115]

Scheme 31

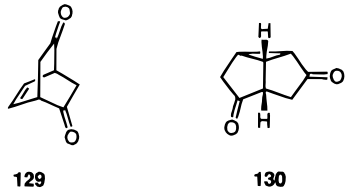


The synthetic utility and generality of the ODPM reaction of bicyclo[2.2.2]octenone is illustrated by the examples collected in Table 16, including yields and references.[67,68,107−113,115−122] However, it should be pointed out that there are limitations in the type of substitution that can be present in the bicyclo[2.2.2]-octenone skeleton. Demuth has summarized the influence of substitution by electron-acceptor and electron-donor groups on the outcome of the reaction. According to this generalization, compounds of the type represented by structure **127** undergo the ODPM reaction while those with a substitution pattern as in **128** are unreactive. A detailed discussion of this influence of substitution can be found in the Demuth review.[1f]

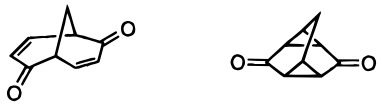


A = electron acceptor: CO_2Me, CO_2H or CO_2^-
D = electron donor: OMe, Me or H

Bicyclo[2.2.2]octenediones (**129**) are another type of compounds that undergo efficient ODPM rearrangement to tricyclooctadiones (**130**). These reactions have found interesting applications in the synthesis of natural products such as (−)-coriolin[123] and cedranoid sesquiterpenes.[110] An attractive feature of the photoreactivity of these compounds is that the reaction can be carried out at high concentration (greater than 20%) without the formation of side products. Examples of the ODPM rearrangement of bicyclo[2.2.2]octendiones showing the carbonyl group involved in the rearrangement, the yields of the reactions, and the references are collected in Table 17.[110,123]

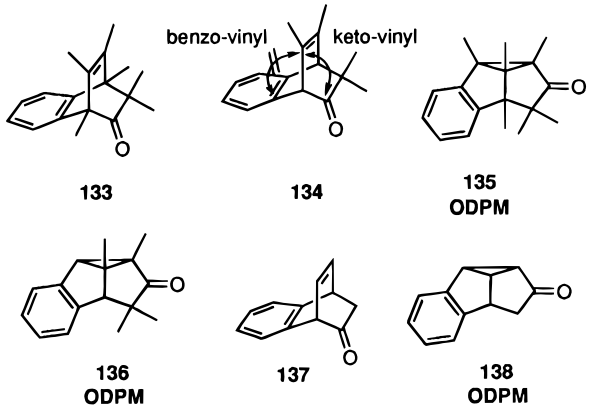


The ODPM rearrangement of bridged bicyclic ketones has also been extended to less constrained molecules such as bicyclo[3.2.1]octenones,[124,125] bicyclo-[3.3.1]nonadiendiones,[126] and bicyclo[4.2.1]nonatrienones.[127] An interesting observation has been described in the photoreactivity of bicyclo[3.3.1]nona-3,7-dien-2,6-diones.[126] These compounds undergo two successive ODPM rearrangements to give triasterandione derivatives in reasonable yields. Thus, for example, direct irradiation of compound **131** affords **132** in 58% isolated yield. These and other related examples, including yields and references, are collected in Table 18.[124−129]



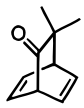
G. Competition between the All-Carbon DPM and the ODPM Processes

The intramolecular competition between the DPM and ODPM rearrangements in compounds that have both the 1,4-diene and the β,γ-unsaturated ketone moieties has been studied. Early work in this area by Hart and Murray[130] showed that benzobicyclo-[2.2.2]octadienones **133** and **134** undergo the regioselective ODPM rearrangement on acetone-sensitized irradiation giving compounds **135** (26%) and **136** (9%) respectively. These results indicated that keto−vinyl bridging takes preference over the alternative benzo−vinyl bonding, as shown for structure **134**. A similar result was obtained in another study by Givens and Oettle[55,67,68] of the triplet reactivity of benzobicyclo-[2.2.2]octadienone **137**. Again in this instance the ODPM product **138** was obtained in 21% yield. On the basis of deuterium-labeling experiments a concerted mechanism was proposed for the reaction.

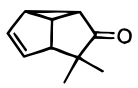


In a study by Luibrand et al.,[131] acetone-sensitized irradiation of dimethyl[2.2.2]octenone **139** gives **140**. Results with deuterium-labeled starting material indicate that **140** is formed in a DPM rearrangement and not in an ODPM reaction. These authors have made an attempt to rationalize the intramolecular competition between the two processes. Their con-

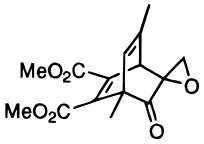
clusion is that in the competition between different DPM paths the relative rates follow a sequence determined by the type of bridging obtained in the reaction. The order of preference proposed by the authors is vinyl−vinyl bridging > keto−vinyl bridging > benzo−vinyl bridging.[131] This preference is in agreement with the order suggested[16] for the ordinary DPM, the results obtained for the compounds mentioned above and also with the energy requirements involved in breaking vinyl, carbonyl, and aromatic π-bonds. Other studies are also in good accordance with this generalization. Thus, in the acetophenone-sensitized irradiation of a series of spirooxirano-substituted bicyclo[2.2.2]octadienones, a total regiospecific DPM rearrangement was observed.[132] As an example, compound **141** gives the tricyclic derivative **142**, in 53% yield, exclusively. The absence of the other possible regioisomer **143**, that could have also been formed by the DPM path, was explained as a consequence of the differences in the stability of the two alternative 1,3-biradical intermediates that could result from the ring opening of the 1,4-cyclopropyl biradical formed in first place. The results obtained in this study corroborate Luibrand's postulate showing that vinyl−vinyl bridging takes preference over keto−vinyl bridging.



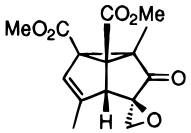
139



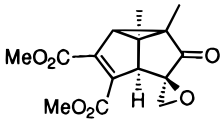
DPM
140



141

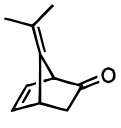


142 (53%)
DPM

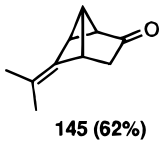


143
Not Observed

However, this situation is not general and other factors, apart from the bond strength, should be taken into account to explain the results obtained in other cases. Thus, for instance, sensitized irradiation of the bicyclo[2.2.1]heptenone derivative **144** was reported to give the ODPM product **145** in 62% isolated yield, showing that keto−vinyl bridging takes preference over vinyl−vinyl bridging in this instance.[53] In another study, the direct or sensitized

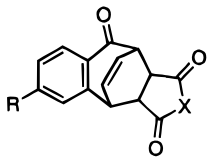


144

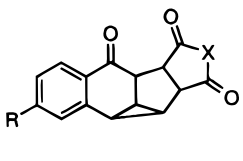


145 (62%)
ODPM

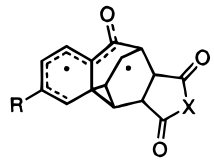
irradiation of ethenobenzocycloheptenones **146** brings about the formation of the corresponding DPM products **147** exclusively.[133] This result shows that for compounds **146** aryl−vinyl bridging is preferred to keto−vinyl bridging. The greater stability of the biradical intermediate **148**, resulting from benzo−vinyl bridging, compared to biradical **149**, which would



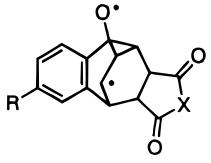
146



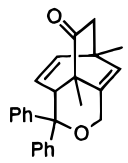
147
DPM



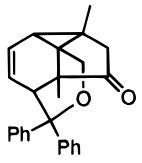
148



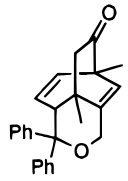
149



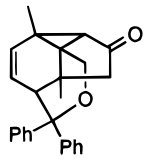
150



151 (80%)
DPM



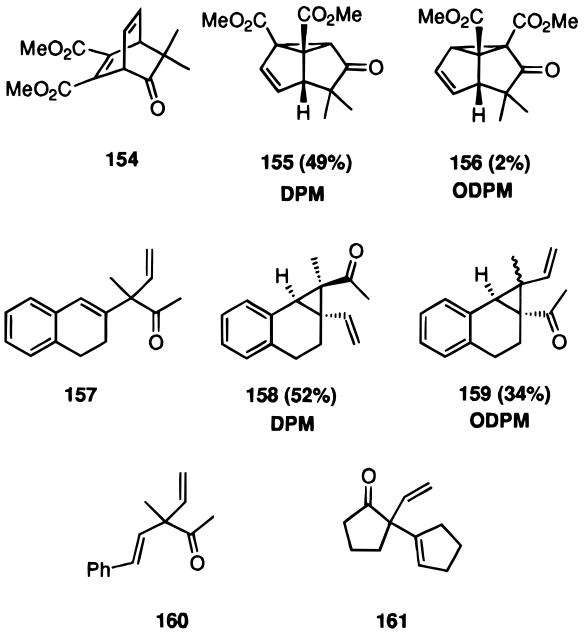
152



153 (69%)
ODPM

have been formed in a keto−vinyl bridging, could explain the results obtained in this study. Nevertheless, other factors, apart from the bond energy and the stability of the intermediates, may also be important in the outcome of the competition. Thus, benzophenone-sensitized irradiation of compound **150** gives the DPM product **151** in 80% yield.[134] However, under the same experimental conditions, compound **152** rearranges to **153**, in 69% yield, by the ODPM path.[134] Structural factors such as ring constraint and different interactions between the carbonyl group and the vinyl groups are postulated to explain the regioselectivity observed in these two cases.

Other studies have shown that the two processes, DPM and ODPM, can be operative in the same substrate. Thus, acetophenone-sensitized irradiation of **154** gives 49% of the DPM product **155** in addition to **156** (2%) resulting from an ODPM rearrangement.[135] This result shows that the presence of substituents at the vinyl moiety can make the competition possible. In a study by Cerfontain et al.[136] sensitized irradiation of dienone **157** yields the DPM product **158**, in 52% yield, and the ODPM products **159**, in 35% yield, as a mixture of two stereoisomers. The preference for the DPM over the ODPM rearrangement is explained in terms of lower bond strength of the vinyl unit compared to the carbonyl π-bond (Table 19). However, dienones **160** and **161** under similar reaction conditions give *E*/*Z* isomerization and decomposition, respectively.[136] The results of these studies on the competition between the ODPM and the DPM rearrangements, including yields, are collected in Tables 19,[53,55,67,68,130,134−136]

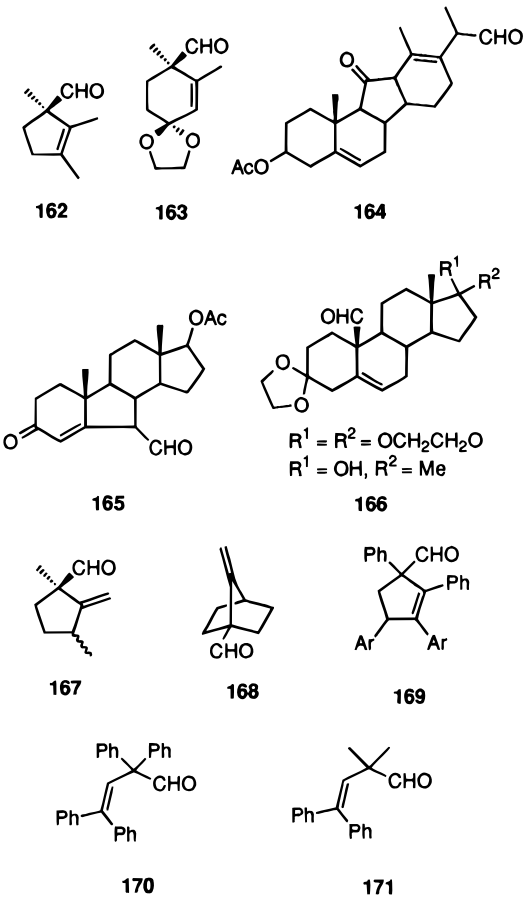


20,[132] and 21.[133] Examples of competition between the DPM and ODPM processes in β,γ-unsaturated aldehydes, as well as competition between the DPM and the aza-di-π-methane (ADPM) rearrangements will be discussed in the following sections.

H. The ODPM Rearrangement of β,γ-Unsaturated Aldehydes

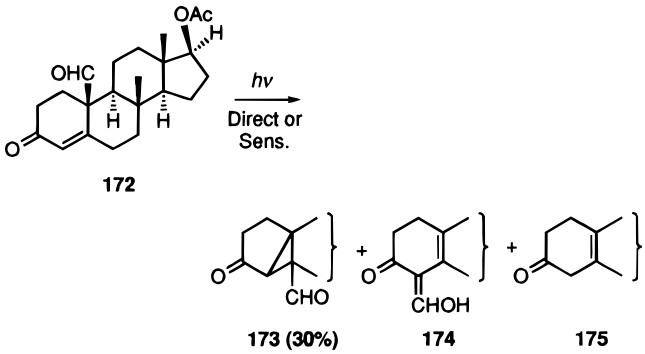
The results discussed above on the photoreactivity of β,γ-unsaturated ketones demonstrate clearly that the ODPM rearrangement is the normal photochemical behavior of these compounds in the triplet excited state. However, the usual photoreactivity reported for the majority of β,γ-unsaturated aldehydes, until very recently, was decarbonylation. Thus, Schaffner et al. demonstrated in a series of reports, published almost 20 years ago, that β,γ-unsaturated cycloalkenyl aldehydes **162**[137] and **163**,[137b] steroidal β,γ-unsaturated aldehydes **164**,[138] **165**,[139] and **166**[140] and the β,γ-unsaturated aldehyde with an exocyclic double bond **167**[137b] underwent decarbonylation on direct irradiation. The triplet-sensitized reactivity of aldehyde **163** was also investigated. Again, under these conditions, decarbonylation took place. Triplet-state photoreduction to alcohol and homologization to the corresponding methyl and ethyl ketones were observed on direct irradiation of aldehyde **168**.[137b] In another study by Dürr et al.[141] direct or acetophenone-sensitized irradiation of aldehydes **169** gave two products resulting from decarbonylation and 6-electron cyclization of the *cis*-stilbene type. The photoreactivity of acyclic aldehydes **170**[142] and **171**[143] was also investigated. These aldehydes undergo decarbonylation on direct irradiation. Ambiguous results were obtained on acetophenone sensitization of aldehyde **171**.

However, two examples of aldehydes that do not follow this general rule have been described in early studies. The first example of an ODPM rearrangement in a β,γ-unsaturated aldehyde was reported by Schaffner et al.[144] in the direct or acetophenone-sensitized irradiations of the steroidal aldehyde **172**. Under these conditions **172** gives the ODPM product

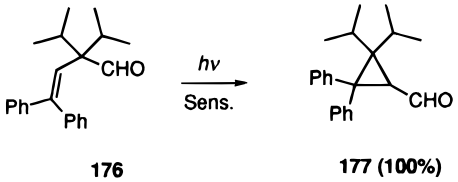


173 and two other compounds **174** and **175** derived from 1,3-formyl migration and decarbonylation, respectively (Scheme 32). Many years later Zimmerman and Cassel[145] reported the ODPM reactivity of the sterically hindered aldehyde **176** that afforded the cyclopropyl aldehyde **177**, in quantitative yield, on acetophenone-sensitized irradiation (Scheme 33). From all these precedents a general conclusion, which is reflected in all the reviews and monographs, was that decarbonylation is the normal photoreactivity of β,γ-unsaturated aldehydes. The ODPM

Scheme 32

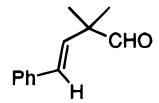


Scheme 33

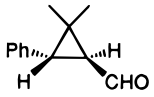


reaction was considered to be an exception with only two precedents. The 1,3-acyl migration, which is the normal photochemical reactivity of β,γ-unsaturated ketones in the S_1 (n,π^*) excited state, was also observed in the irradiation of aldehyde **172**.[144]

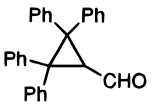
On the basis of these results a general consensus on the lack of ODPM reactivity of β,γ-unsaturated aldehydes resulted.[1c−f] However, this situation has changed recently. Armesto et al.[146] have reported the ODPM rearrangement of a series of acyclic and cyclic β,γ-unsaturated aldehydes on triplet-sensitized irradiation. In most cases the reaction gives the corresponding cyclopropyl aldehydes in high yield after a short irradiation time. Thus, acetophenone-sensitized irradiation of aldehyde **178**, for 15 min, affords the ODPM product **179** in 90% yield as the trans isomer. Under similar conditions aldehyde **170** gives the cyclopropyl derivative **181** in 82% yield, after 10 min of irradiation. It seems that decarbonylation product 1,1,3,3-tetraphenylcyclopropane **180** results from longer irradiation.



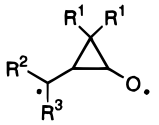
178



179 (90%)



181 (82%)



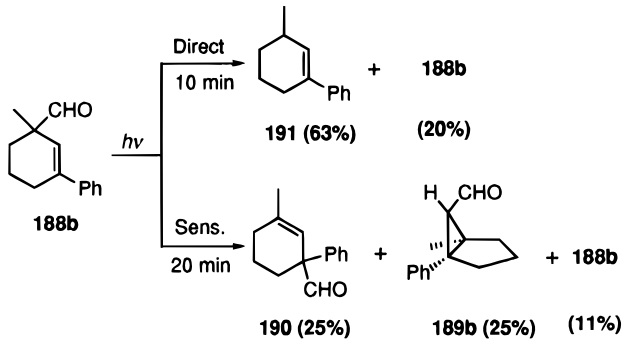
182

R^1 = Me or Ph
R^2 = Ph
R^3 = H or Ph

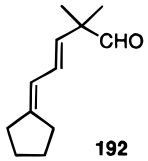
Two factors were considered to be responsible for the efficient ODPM reactivity of aldehydes **178** and **170**; namely (a) the excitation of the molecule to the T_1 (π,π^*) excited state and (b) the stabilizing influence of the phenyl group on the bridging 1,4-biradical reaction intermediates **182**. To confirm this hypothesis the photoreactivity of aldehyde **171** was reinvestigated.[146] The result obtained in this study shows that *m*-methoxyacetophenone-sensitized irradiation of **171** (2 h) brings about the formation of the cyclopropyl aldehyde **183**, resulting from an ODPM rearrangement, in 57% isolated yield. Further support for the above postulates was obtained in the acetophenone-sensitized irradiation of aldehydes **184** and **185** that undergo the ODPM rearrangement to the corresponding cyclopropyl aldehydes **186** (83%) and **187** (96%), respectively.

Cycloalkenyl aldehydes **188** also undergo the rearrangement to the corresponding ODPM products **189**. In one case (**188b**) the 1,3-migration product **190** (25%) was obtained in addition to the ODPM product **189b** (25%). Direct irradiation of **188b** affords the diene **191** resulting from decarbonylation (Scheme 34).

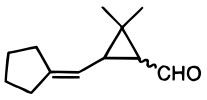
Scheme 34



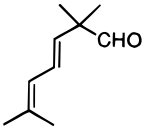
The ODPM reactivity of β,γ-unsaturated aldehydes is not restricted to γ-phenyl-substituted compounds but can also be extended to systems in which the intermediate biradicals are stabilized by conjugation with a vinyl group. Thus, *m*-methoxyacetophenone-sensitized irradiation of **192**, for 20 min, affords the cyclopropyl derivative **193** (47%) as a 1:8 mixture of cis−trans isomers. Similarly, irradiation of **194**, for 15 min, under the same conditions, yields **195** (52%) as the trans isomer exclusively. The synthesis of



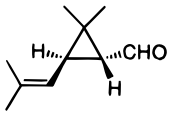
192



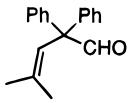
193 (47%)



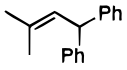
194



195 (52%)

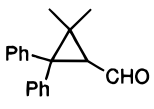


196

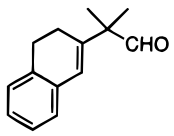


197 (14%)

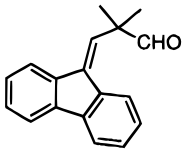
compounds **193** and **195** by the ODPM rearrangement opens a novel photochemical route to chrysanthemic acid and other cyclopropyl components present in pyrethrins and pyrethroids.[147] Even in the absence of phenyl or vinyl substituents at the γ-position of the β,γ-unsaturated aldehyde the rearrangement can take place although very inefficiently. Thus, acetone-sensitized irradiation of aldehyde **196**, for 30 min, gives the alkene **197** (14%) resulting from decarbonylation and the ODPM aldehyde **183** in 8% yield. The reactivity observed for **196** could be due to the facile ring opening of the 1,4-cyclopropyl biradical intermediate formed by vinyl−vinyl bridg-



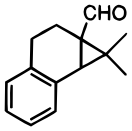
183 (57%)



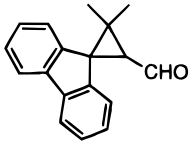
184



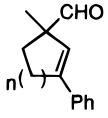
185



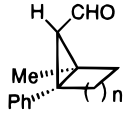
186 (83%)



187 (96%)



188a: n = 1
188b: n = 2
188c: n = 3

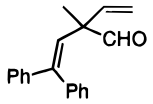


189a: n = 1 (90%)
189b: n = 2 (25%)
189c: n = 3 (25%)

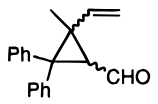
ing. This interpretation is in agreement with similar increases in efficiency and triplet reactivity promoted by phenyl substitution at the methane carbon, observed by Zimmerman in the DPM process.[19,43,145,148]

An intriguing observation in this study is that aldehyde **171** undergoes the ODPM rearrangement while the analogous methyl ketone **70** does not react in this mode. This is the first example of such a situation and, therefore, it opens the possibility of observing ODPM reactions in other aldehydes with substitution patterns similar to ketones that do not undergo the rearrangement.

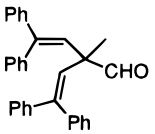
The possible competition between the ODPM and the DPM processes was also studied. Irradiation of **198** using *m*-methoxyacetophenone as sensitizer, for 10 min, affords the cyclopropyl aldehyde **199** (19%), as a 3:2 mixture of cis−trans (i.e. formyl−diph-vinyl) isomers, resulting from an ODPM rearrangement exclusively. However, under the same conditions, aldehyde **200** yields the cyclopropyl aldehyde **201** (48%), resulting from a DPM rearrangement, as a 1:1 mixture of cis−trans isomers. The selectivity observed was interpreted as being dependent on the relative stabilities of the 1,4-bridged biradicals for the two possible rearrangement paths.



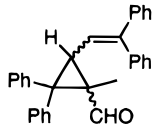
198



199 (19%)
ODPM



200



201 (48%)
DPM

The results obtained in this study indicate that the ODPM rearrangement of β,γ-unsaturated aldehydes occurs when the triplet energy from the sensitizer is efficiently transferred to the alkene moiety generating a T_1 (π,π*) excited state and, furthermore, when the biradical intermediates are stabilized by phenyl or vinyl substitution. Aldehydes that do not meet these two requirements, as in most of the cases previously reported, undergo decarbonylation. Examples of ODPM rearrangement of β,γ-unsaturated aldehydes, including yields and references, are collected in Table 22.[144−146]

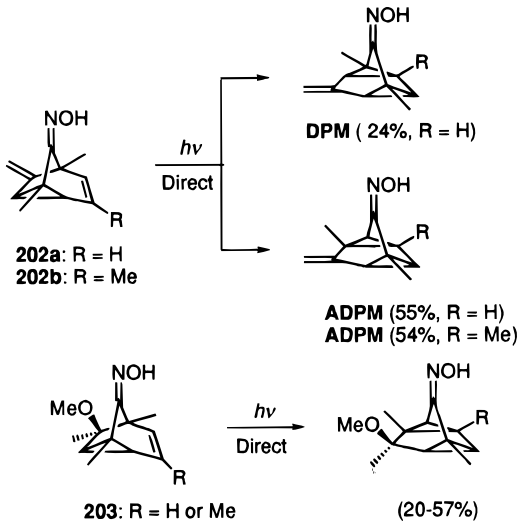
IV. The Aza-di-π-methane (ADPM) Rearrangement

The photochemistry of the C−N double bond has not been studied as extensively as the photoreactivity of other functional groups such as alkenes and ketones. As a consequence, the extension of the di-π-methane rearrangement to β,γ-unsaturated C−N double bond is relatively recent. However, in the last 15 years there has been an increasing interest in the photochemistry of nitrogen-containing compounds. Among the new reactions uncovered in the study of the photochemistry of imine derivatives, the aza-di-π-methane rearrangement has been most studied.

A. The ADPM Rearrangement of β,γ-Unsaturated Imines and Oxime Acetates

The first example of an aza-di-π-methane (ADPM) rearrangement was reported by Nitta et al. in a study on the photoreactivity of the tricyclic oximes **202**. Direct irradiation of compound **202a** brought about the formation of products resulting from the DPM and the ADPM rearrangements in the first example of competition between these two processes. Surprisingly, the methyl substituted derivative **202b** undergoes the ADPM reaction exclusively (Scheme 35).[149a]

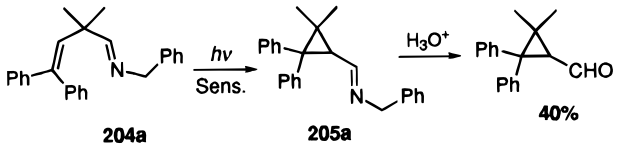
Scheme 35



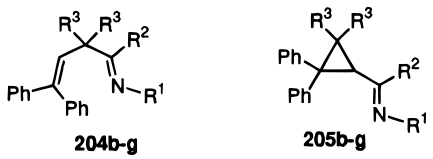
A few years later the study was extended to the related tricyclic oximes **203**. Direct irradiation of compounds **203** affords the corresponding products resulting from the ADPM rearrangement (Scheme 35).[149] These have been the only examples of ADPM reactivity in β,γ-unsaturated oximes until very recently.

The first ADPM rearrangement in an acyclic derivative was reported by Armesto et al. in the sensitized irradiation of the β,γ-unsaturated imine **204a** that yielded exclusively the corresponding cyclopropyl imine **205a** (Scheme 36).[150]

Scheme 36



Early studies in this area suggested that while the ADPM reactivity of β,γ-unsaturated imines was quite general, the corresponding rearrangement of oximes was limited to compounds **202** and **203** and closely related systems were unreactive.[149b] The ADPM rearrangement of **204a** was extended to other imines

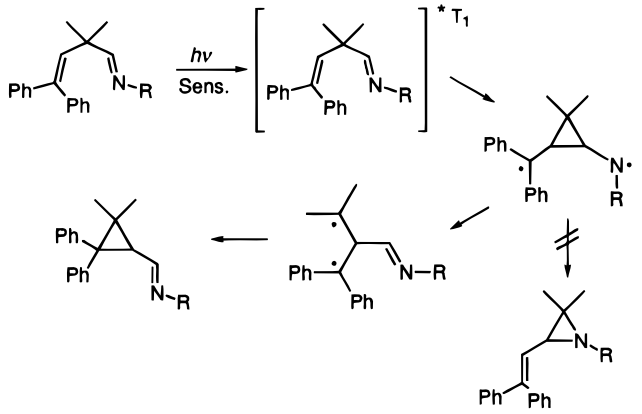


R^1 = $PhCH_2$, Ph, PhCHMe, $Ph(CH_2)_2$, Pr^i;
R^2 = H, Me; R^3 = Me, Ph

204b−**g**.[150,151] Acetophenone-sensitized irradiation of compounds **204** brought about the formation of the corresponding cyclopropyl imines **205**.

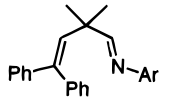
Quenching and sensitization experiments showed that the reaction was taking place via the triplet excited state.[150] A biradical mechanism similar to those shown in Schemes 4 and 19, for the DPM and ODPM rearrangements, was proposed for the ADPM reaction (Scheme 37). This mechanism explains the

Scheme 37

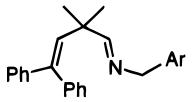


regioselectivity observed for the rearrangement. The reaction always yields cyclopropylimines. The corresponding aziridines that could have resulted from the alternative ring opening of the 1,4-cyclopropyl biradical intermediates have never been observed. This regioselectivity is analogous to that encountered in the ODPM rearrangement.

However, studies on the influence of substitution on the efficiency of the reaction, carried out in a series of *N*-aryl **206**[152] and *N*-benzyl **207**[153] β,γ-unsaturated imines, showed that the quantum yield of the cyclization increases with electron-withdrawing groups at the para position of the *N*-aryl or *N*-benzyl groups.



206a: Ar = Ph
206b: Ar = *p*-$MeOC_6H_4$
206c: Ar = *p*-ClC_6H_4
206d: Ar = *m*-$MeOC_6H_4$
206e: Ar = *p*-CNC_6H_4

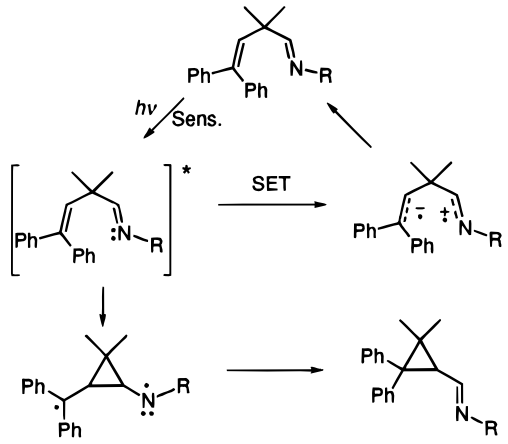


207a: Ar = Ph
207b: Ar = *p*-MeC_6H_4
207c: Ar = *p*-ClC_6H_4
207d: Ar = *m*-FC_6H_4
207e: Ar = *p*-$CF_3C_6H_4$

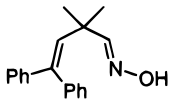
The excellent linear correlation between log ϕ and σ^+ obtained in both cases demonstrates the dependence of reactivity on the conjugative interaction between the aryl group and the nitrogen lone pair in **206** and also on the homoconjugative interaction between the benzyl group and the nitrogen lone pair in **207**. This is evidence in support of the postulate that an electron transfer from the imine nitrogen to the alkene group is detrimental to the cyclization. To account for these results a decay mechanism involving the electron transfer process, adversely affecting the efficiency of the reaction, was proposed (Scheme 38).[152,153]

This mechanism gives a reasonable explanation for the previously reported failure of oxime **208**[151] and

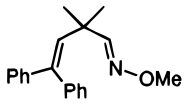
Scheme 38



oxime ether **209**[154] to undergo the aza-di-π-methane rearrangement.



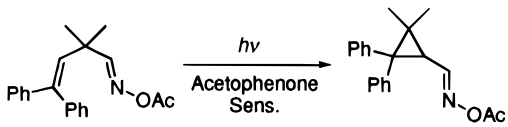
208



209

Thus, in these cases efficient SET from the nitrogen lone pair to the alkene moiety due to the low ionization potential of the oxime and oxime ether groups makes the rearrangement very inefficient, or failing. Thus, it was postulated that the rearrangement would be operative provided that the ionization potential of the oxime could be raised. This was easily achieved by incorporating an electron-withdrawing group by simple acetylation of the oxime. Acetophenone-sensitized irradiation of oxime acetate **210a** gave the ADPM product **211a** in 86% yield in agreement with the above postulate (Scheme 39).[155]

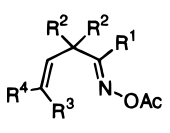
Scheme 39



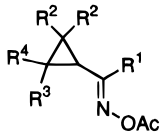
210a **211a (86%)**

This was the first example of an ADPM rearrangement in an acyclic C−N double-bond-stable derivative. The ADPM reaction has been extended to a series of acyclic and cyclic β,γ-unsaturated oxime acetates **210a**−**h**,[155−158] **212**,[159] **214**,[159] **216**,[159] **218**,[159] and **220a,b**.[160] All of them undergo the ADPM rearrangement to the corresponding cyclopropyl oxime acetates **211a**−**h**, **213**, **215**, **217**, **219**, **221a,b**, respectively. In most cases the reaction gives the corresponding ADPM products in high isolated yield.

The chemically efficient ADPM reactivity of oxime acetates **212**, **214**, **216**, and **218** has opened a new synthetic route to chrysanthemic acid and other cyclopropanecarboxylic acids present in pyrethroids of known insecticidal activity.[159] Quantum yield measurements show that the quantum efficiency for the formation of **210a** by acetophenone sensitization is 0.12, that is 10-fold better than the quantum yield for the cyclization of the *N*-aryl-substituted imines

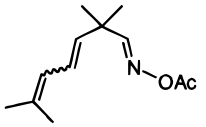


210



211

210a, **211a**: R^1 = H, R^2 = Me, R^3 = R^4 = Ph
210b, **211b**: R^1 = H, R^2 = R^3 = R^4 = Ph
210c, **211c**: R^1 = H, R^2 = R^3 = R^4 = Me
210d, **211d**: R^1 = R^2 = Me, R^3 = R^4 = Ph
210e, **211e**: R^1 = R^3 = H, R^2 = Me, R^4 = Ph
210f, **211f**: R^1 = H, R^2 = R^3 = Me, R^4 = CO_2Et
210g, **211g**: R^1 = H, R^2 = R^3 = Me, R^4 = CN
210h, **211h**: R^1 = H, R^2 = R^3 = Me, R^4 = CH_2OAc



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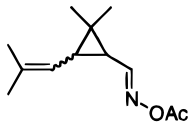

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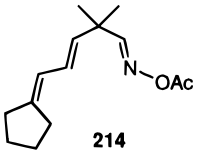

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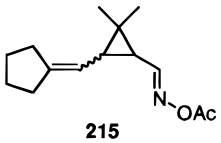

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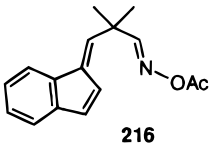

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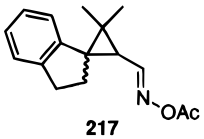

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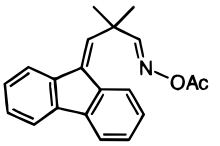

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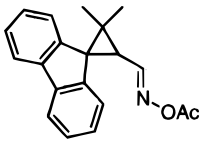

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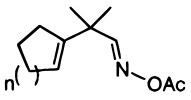
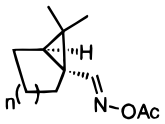


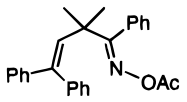
220a: n =1
220b: n =2
220c: n =3



221a: n =1
221b: n =2

206. The ADPM reaction can be extremely efficient as shown by the cyclization of oxime acetate **210b** that yields the corresponding cyclopropane **211b** with a quantum yield of 0.82.[156]

The studies carried out so far allow the establishment of some general rules on the scope of the ADPM rearrangement. Thus, aldoxime acetate **210a** reacts more efficiently than the corresponding methyl ketone derivative **210d** and the phenyl ketoxime acetate **222** does not undergo the rearrangement.[156] These results indicate that ketoxime acetates are less reactive in the ADPM mode than the corresponding aldoxime acetates. Aldoxime acetates with substituents at the γ-position that insure both, efficient energy transfer from the triplet sensitizer and stabilization of the 1,4-cyclopropyl biradical intermediates, undergo the ADPM rearrangement very efficiently. This is the situation for compounds **210a,b**, **210e**, **212**, **214**, **216**, and **218** where the alkene moiety is conjugated with phenyl or a vinyl groups. Disubstitution at that position by methyl groups, or other groups, as in compound **210c** also allows to observe the rearrangement although with lower efficiency. When the alkene moiety is incorporated to a medium-size ring, as in compounds **220a,b**, the rearrangement also takes place even in the absence of γ-substitution that would stabilize the biradical intermediates. In this instance the increase of the size of the ring affects the reaction adversely and oxime acetate **220c** is unreactive in the ADPM path.[160] It is interesting to note that the photochemical reactivity of the methyl ketones **72** related to the aldehydes **223**, used as precursors of the oxime acetates **220**, has been studied.[93] This work established that only the cyclobutenyl and cyclopentenyl ketones undergo the ODPM rearrangement on triplet-sensitized irradiation although as a secondary reaction path. The results obtained in the study of oxime acetates **220** show that the ADPM rearrangement is more general than the oxa-di-π-methane analog and avoids secondary reactions such as 1,3-acyl migration or intramolecular [2 + 2] cycloadditions.[93]



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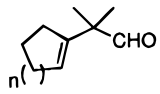
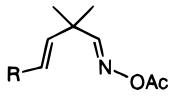
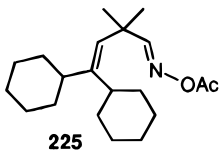


223
n = 1,2 or 3



224a-f
R = CO_2Et, CN, CH_2OAc, CH_2OMe, CO_2Bu^t, Cyclohexyl



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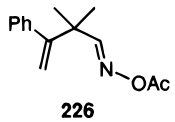

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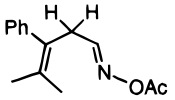

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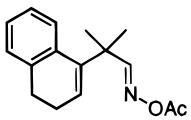
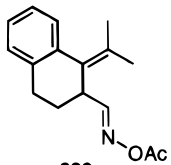


228

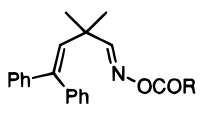


229

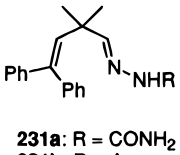
Oxime acetates without substituents at the γ-position that will insure sufficient stabilization of the 1,4-cyclopropyl biradical intermediates do not undergo the ADPM rearrangement. This is the case of oxime acetates **224** that give cis/trans isomerization[157b,158] and compound **225**,[157b] which is unreactive. Phenyl substitution at position 4 of the 1-aza-1,4-diene system promotes a different reaction. Thus, acetophenone-sensitized irradiation of oxime acetates **226** and **228** yields **227** and **229**, respectively, resulting from a 1,3-migration of the acetoxyimino group.[157a,161] These are the first examples of a 1,3-migration of C−N double bond in 1-aza-1,4-diene derivatives. Examples of the ADPM rearrangement of β,γ-unsaturated oxime esters, including yields and references are collected in Table 23.

B. The ADPM Rearrangement of Other C–N Double-Bond Derivatives

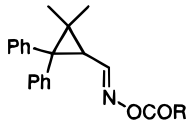
The ADPM reactivity of C−N double-bond-stable derivatives of β,γ-unsaturated aldehydes is not limited to oxime acetates. A study has shown that other oxime esters such as oxime benzoate **230a**[162] and oxime trifluoroacetate **230b**,[162b] and hydrazine derivatives such as semicarbazone **213a**,[162] acetyl hydrazone **231b**,[162b] benzoyl hydrazone **231c**,[162] and tosyl hydrazone **231d**,[163] also undergo the rearrangement. Acetophenone-sensitized irradiations of compounds **230a** and **231** brough about efficient conversion to the corresponding cyclopropyl derivatives **232a** and **233**, respectively, in yields ranging from 90% to 9%. The photocyclization of the trifluoroacetate derivative **230b** is very efficient and irradiation for a mere 10 min affords the cyanocyclopropane **234** (80%) resulting from thermal elimination of trifluoroacetic acid during the work-up procedure. This provides a new synthetic route to cyanocyclopropanes from derivatives of β,γ-unsaturated aldehydes since a direct path by the irradiation of β,γ-unsaturated nitriles fails.



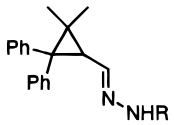
230a: R = Ph
230b: R = CF_3



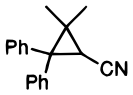
231a: R = $CONH_2$
231b: R = Ac
231c: R = COPh
231d: R = Tosyl



232a (90%)

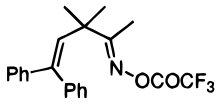


233 (71% to 9%)

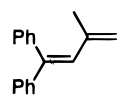


234 (80%)

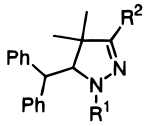
The results obtained in the irradiation of **230** and **231** clearly demonstrated that the ADPM rearrangement can be extended to different stable derivatives from β,γ-unsaturated aldehydes. However, these derivatives can also undergo alternative reactions apart from the ADPM rearrangement. Thus, ketoxime trifluoroacetate **235** does not undergo the ADPM rearrangement. In this instance acetophenone-sensitized irradiation of **235** brings about the formation of diene **236**.[162b]



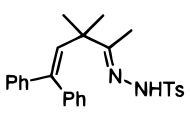
235



236 (40%)



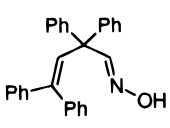
237a: R^1 = $CONH_2$, R^2 = H
237b: R^1 = Ac, R^2 = H
237c: R^1 = COPh, R^2 = H
237d: R^1 = Tosyl, R^2 = H
237e: R^1 = Tosyl, R^2 = Me



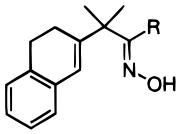
238

Competition between the ADPM rearrangement and alternative reaction paths has also been observed in the acetophenone-sensitized irradiation of hydrazine derivatives **231**. These compounds undergo, in addition to the ADPM rearrangement, a novel cyclization to afford dihydropyrazoles **237**. The keto derivative **238** undergoes exclusively the cyclization to the dihydropyrazole **237e**, in 75% yield. No ADPM product was obtained in this case. Again SET involvement from the alkene moiety to the acyl or tosyl groups may be responsible for this novel cyclization.[163] Examples of the ADPM rearrangement of β,γ-unsaturated imines and hydrazine derivatives, including yields and References are collected in Table 24.

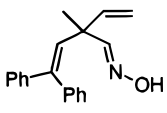
Literature precedents indicated that β,γ-unsaturated oximes were unreactive in the ADPM mode.[151,154] However, recent results have shown that these compounds can undergo the rearrangement with high chemical efficiency. This situation is observed in cases in which the biradical intermediates are highly stabilized as in compounds **239**, **240**, and **241** that afford the corresponding ADPM product **242**, **243** and **244** respectively, on acetophenone-sensitized irradiation.[164,165]



239



240a: R = H
240b: R = Me
240c: R = Ph



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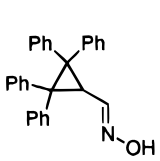
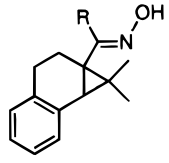
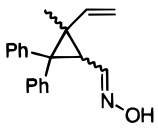


242 (74%)



243a: R = H (63%)
243b: R = Me (66%)
243c: R = Ph (20%)

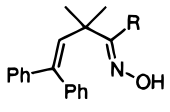


244 (30%)
ADPM

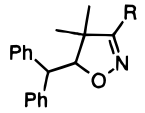
The ADPM rearrangement of the ketoxime derivatives **240b** and **240c** is very surprising since previous studies indicated that imines and oxime acetate derivatives from β,γ-unsaturated ketones were less reactive than those derived from the corresponding aldehydes.[156] Particularly, the efficient ADPM reactivity of **240c** is in clear contrast with the fact that phenyl ketoxime acetate **222** is photochemically inert.[156] The ADPM reactivity observed for ketoximes **240b** and **240c** might be due to the special characteristics of the triplet excited state of the dihydronaphthalene unit as demonstrated by Caldwell et al.[166]

However, there are other β,γ-unsaturated ketoximes such as **245** which do not undergo the ADPM rearrangement. In this instance an alternative reaction takes place, yielding the dihydroisoxazoles **246**, on acetophenone-sensitized irradiation.[167] A mechanism involving single electron transfer from the diphenylvinyl moiety to the ketoxime group has been proposed to account for this novel reaction. The above results have forced a reinvestigation of the photoreactivity of oxime **208**, previously reported as

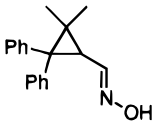
photochemically unreactive.[151] The reinvestigation showed that, contrary to the previous report, sensitized irradiation of **208** gives a mixture of the ADPM product **247** and the heterocycle **248** in comparable yields.[165]



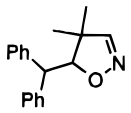
245a: R = Me
245b: R = Ph



246a: R = Me (15%)
246b: R = Ph (38%)



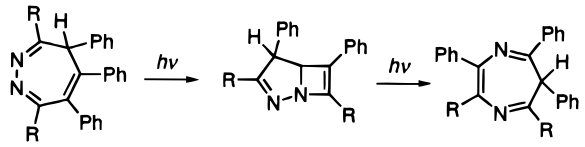
247



248

From the foregoing it is clear that β,γ-unsaturated oximes, which were previously considered photochemically inert, can undergo synthetically useful photochemical reactions. Examples of the ADPM rearrangement of β,γ-unsaturated oximes, including yields and references are collected in Table 25. The ADPM rearrangement has also been observed in some heterocyclic systems. Thus, 4*H*-1,2-diazepines **249** rearrange to 6*H*-1,4-diazepines **250** via a 1,2-diazabicyclo[3.2.0]hepta-2,6-diene **251** in a process that can be considered as an example of an ADPM reaction (Scheme 40).[168] In another study dihydrobenzocarbazoles **252** undergo a photochemical rearrangement to indenoquinolines **253**. An ADPM mechanism, as shown in Scheme 41, is proposed to account for this result.[169] The ADPM rearrangement has been extended to bridged cyclic compounds as the dihydroquinoxalinobarrelene (**254**) that yields the ADPM product **255** (20%), both on direct and sensitized irradiations (Scheme 42).[170]

Scheme 40

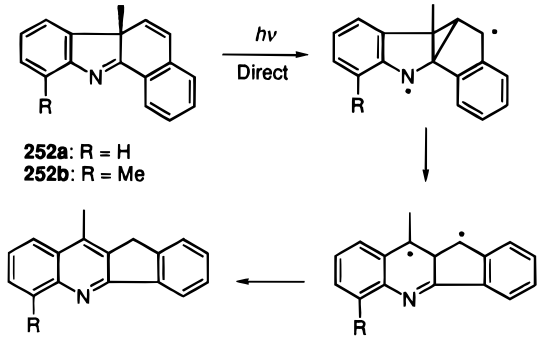


249: R = Me or Ph

251

250

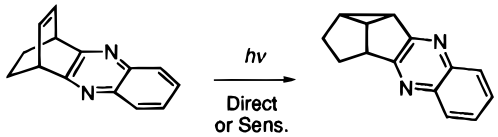
Scheme 41



252a: R = H
252b: R = Me

253a: R = H (21%)
253b: R = Me (42%)

Scheme 42

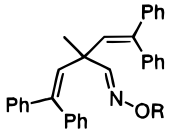


254

255 (20%)

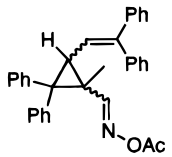
C. Competition between the DPM and ADPM Processes

As has been mentioned above, the first example of competition between the DPM and ADPM rearrangements was described by Nitta et al.[149a] in the direct irradiation of oximes **202** (Scheme 35). The results obtained showed that, while oxime **202a** undergoes both reactions, oxime **202b** yields the ADPM product exclusively. In another study aimed at detecting intramolecular competition between the all-carbon di-π-methane (DPM) rearrangement and the ADPM process, acetophenone-sensitized irradiation of oxime acetate **256a** affords the cyclopropane **257a**, resulting from the DPM process, in 84% yield.[164] Similar DPM rearrangement was observed for the corresponding oxime trifluoroacetate **256b** that gives the nitrile **258**, in 90% yield. This nitrile is formed from the photoproduct **257b** by thermal elimination of trifluoroacetic acid during work up. These are examples of triplet DPM reactivity in acyclic substrates where the central carbon has only one electron-withdrawing group. There is only one case of such reactivity in the aryl di-π-methane process.[171] However, oxime trifluoroacetate **259** undergoes the ADPM rearrangement exclusively affording cyclopropane **260**, in 30% yield, again resulting from thermal elimination of trifluoroacetic acid. The selectivity observed for compounds **256** and **259** is interpreted as being dependent on the relative stabilities of the corresponding 1,4-bridged biradical intermediates.[164] Similar results have been obtained in a study of the photochemical reactivity of the related β,γ-unsaturated aldehydes **198** and **200** (see section III.H).[146]

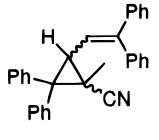


256

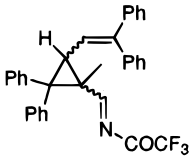
256a: R = Ac
256b: R = $COCF_3$



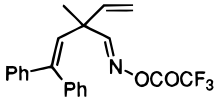
257a (84%)
DPM



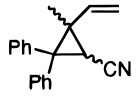
258 (90%)
DPM



257b

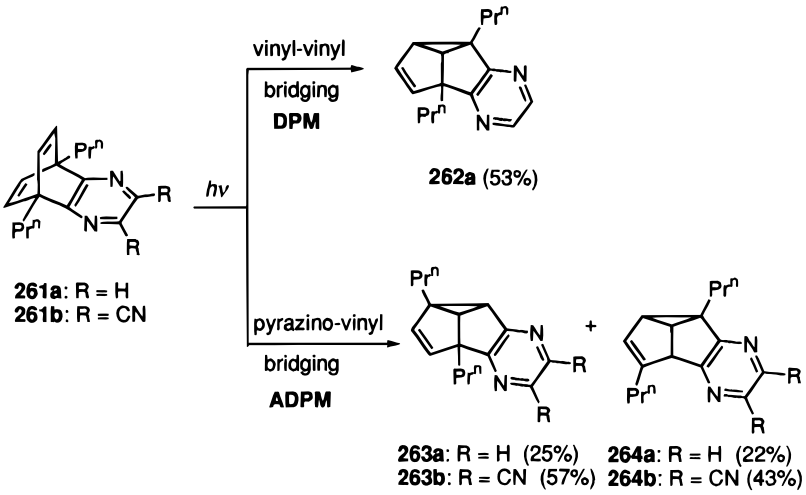


259



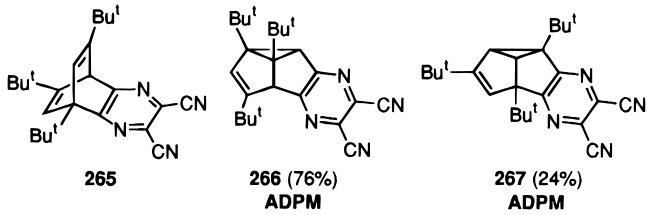
260 (30%)
ADPM

Scheme 43



The competition between the di-π-methane and the aza-di-π-methane rearrangements has also been studied in the photochemistry of the pyrazine derivatives of barrelene **261a,b**.[172] Direct or acetophenone-sensitized irradiation of these brings about the formation of pyrazinosemibullvalenes in a typical di-π-methane process (Scheme 43). Thus, compound **261a** gives **262a** (53%), by a DPM path, and two other products **263a** (25%) and **264a** (22%), resulting from an ADPM rearrangement. However, compound **261b** yields semibullvalenes **263b** (57%) and **264b** (43%) coming from an ADPM rearrangement exclusively.

Similar regioselectivity was observed for pyrazinobarrelene **265** that affords **266** (76%) and **267**

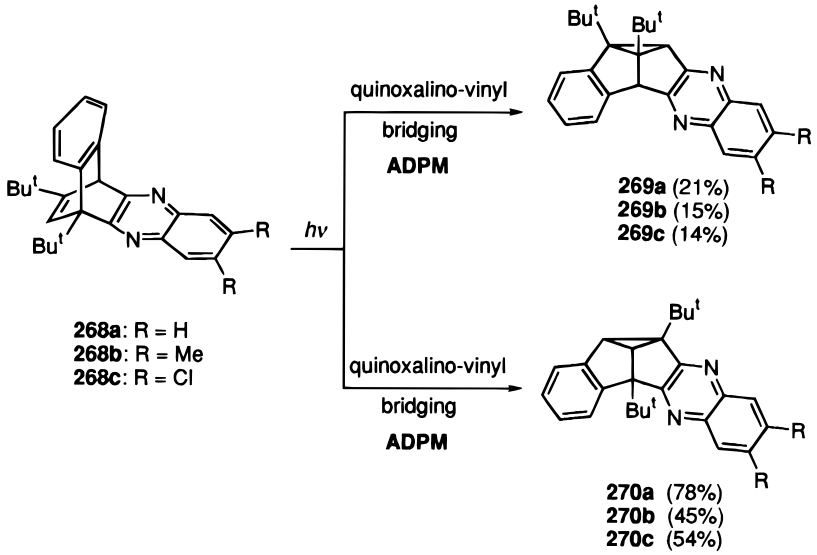


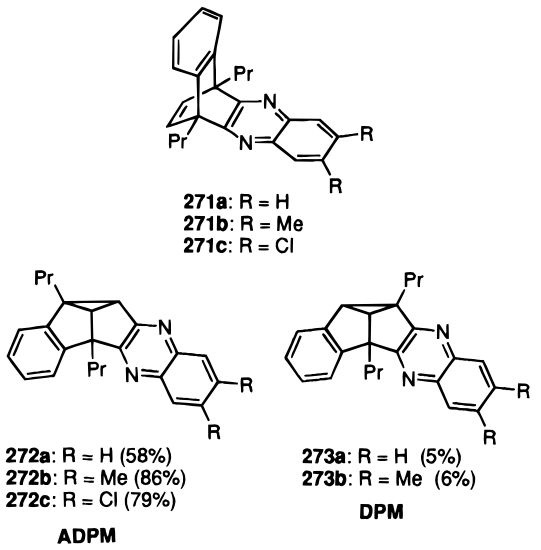
(24%) again as a result of an ADPM process. Benzoquinoxalinobarrelenes **265**−**267** also show a preference for the ADPM rearrangement. Thus, direct and sensitized irradiations of compounds **268** give benzoquinoxalinosemibullvalenes **269** and **270**, resulting from a quinoxalino−vinyl bridging exclusively (Scheme 44).[173]

However, benzoquinoxalinobarrelenes **271a** and **271b** give the corresponding ADPM compounds **272a** and **272b** as the major products in addition with a small percentage of the DPM products **273a** and **273b**.[173] The incorporation of a chlorine atom as in **271c** enhances the quinoxalino−vinyl bridging and again the ADPM product **272c** is obtained exclusively. These results show that the ADPM reaction can compete favorably with the di-π-methane rearrangement in this system. Examples of competition between the DPM and the ADPM rearrangements, including yields and references are collected in Table 26.

From all the foregoing is clear that the ADPM rearrangement of different C−N double-bond derivatives from β,γ-unsaturated aldehydes is very general and has considerable synthetic potential. The reaction takes place in cases in which the triplet energy is efficiently transferred from the sensitizer to the alkene part of the molecule generating a T_1 (π,π^*)

Scheme 44





excited state. The stabilization of the biradical intermediates by the adequate substitution at the γ-position of the β,γ-unsaturated system is also important in promoting the reaction. When these conditions are not fulfilled other alternative reactions such as *E*/*Z* isomerization or cyclizations to different heterocycles can take place. The novel photochemical synthesis of heterocyclic systems by irradiation of 1-aza-1,4-diene derivatives may also have synthetic utility.

V. Experimental Conditions

A. Practical Aspects of Using Sensitizers

Our discussion here applies to much of organic photochemistry, since the di-π-methane rearrangement is perfectly typical from the experimental standpoint. The first question is whether one should use a sensitizer or not, and this has been discussed above in connection with the "free rotor" effect. Thus, for acyclic "divinyl methane"-type reactants, direct irradiation is the method of choice while for bicyclics and other reactants with constrained π-systems, sensitization often is needed for optimum yields. In using a sensitizer there are several considerations. (1) One must pick a sensitizer of sufficient triplet energy to excite the reactant ground state. (2) The sensitizer must absorb light at a wavelength where reactant does not absorb too strongly, and the sensitizer's concentration must be high enough, such that, at that wavelength essentially all of the light is absorbed by the sensitizer and not by the starting material. Thus, one wants energy delivered via the sensitizer to the reactant and not directly to the reactant. (3) The sensitizer should be reasonably separable from the reactant and products. (4) One must adjust the concentration of reactant to be low enough that the singlet excited state of the sensitizer, formed by light absorption, has time to convert itself to the needed triplet before collision of the initially formed singlet with reactant. Otherwise one will merely deliver singlet excitation to the reactant. (5) The concentration of reactant cannot be so low that the triplet sensitizer molecule will decay to useless ground state before collision with reactant and triplet energy transfer. (6) There are other, practical matters such as having a sensitizer which, itself, is unreactive and stable. It should be soluble in solvents being used. However, such items are subject to common sense and need not be considered further here.

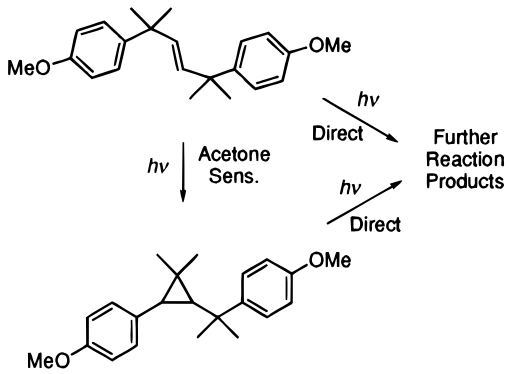
Turning now to specifics, we note that acetophenone is a particularly useful sensitizer. It is removable under high vacuum at room temperature, it absorbs light in the 300−350 nm region where many reactants are relatively transparent, and it has a reasonably high triplet energy of 74 kcal/mol. Acetone has a still higher triplet energy in the neighborhood of 80 kcal/mol but absorbs only weakly and at shorter wavelengths. Benzophenone absorbs in the 300−360 nm region and has a 69 kcal/mol triplet energy, but separation from photoproduct requires chromatography or careful recrystallization.

B. The Role of Reactant Concentration

With regard to concentrations to be used, it is helpful to recognize that most ketone triplets have lifetimes at room temperature in solution of about 10 μs which corresponds to a rate of disappearance by decay of about 10^5 s^{-1}.[174] The bimolecular rate of diffusion in most ordinary solvents will be close to 5×10^9 L mol^{-1} s^{-1}. Thus, at a reactant concentration of 10^{-3} M, the pseudounimolecular rate of collision of triplet with the reactant will be 5×10^6 s^{-1} which is 1 order of magnitude faster than the decay and loss of the sensitizer triplet. This means that nine of 10 triplet sensitizer molecules will collide successfully with the ground-state reactant. Another point to be considered is whether we need to concern ourselves with any singlet energy transfer with these concentration conditions. Since, many ketone singlet excited states are converted to their triplets at rates above 10^{10} s^{-1}, and we have just decided that the collision of an excited state with reactant will occur at a pseudounimolecular rate of about 5×10^6 s^{-1} at the selected concentration, we note that excited singlet collisions are too slow to give difficulty. However, if one were to use a hydrocarbon sensitizer one needs to be more cautious and redo the calculation, since hydrocarbon singlets do not convert to their triplets at comparably rapid rates.

In brief, using a reactant concentration in the range of 5×10^{-3} to 10^{-3} M, we can be fairly assured that triplet sensitization will occur efficiently without danger of a singlet energy transfer. A final practical point to be considered in deciding whether or not to use a sensitizer is the relative reactivity of the triplet excited states of reactant and product. If one has a situation in which the starting material reacts fairly efficiently on sensitization (i.e. as the triplet), but the initial photoproduct is unreactive, then there may well be a real advantage to employing a sensitizer for the photoreaction. Particularly if the primary photoproduct reacts efficiently as the excited singlet (i.e. on direct irradiation), the use of a sensitizer may become a necessity. One such example is given in Scheme 45.[49] In this case the triplet photoproduct is unreactive toward further reaction and is obtained nicely under sensitized conditions. However, although this initial photoproduct is formed on direct irradiation, it reacts rapidly onward as a singlet and

Scheme 45



a triplet and only very low yields of photoproduct can be obtained without use of a sensitizer.

C. Choice of Solvents for Irradiation

Clearly, solvents used for photochemical syntheses need to be optically transparent in the spectral region used. Additionally they should not react with starting materials, products, or excited states involved. Finally, they need to dissolve reasonable quantities of the reactants and products. *tert*-Butyl alcohol is an ideal solvent in satisfying essentially all of these criteria in most instances. In particular, *tert*-butyl alcohol does not have hydrogen atoms which are readily abstractable by (e.g.) n-π* excited states of ketones. Benzene is another solvent which does not have easily abstractable hydrogen atoms, and for reactants being irradiated at 300 nm and higher, there is no light absorption problem. Acetonitrile is another solvent which has been useful. For water-soluble compounds with unreactive starting materials and products, irradiation in aqueous solution can work well as long as there are no photochemical intermediates sensitive to water. Solvents such as ether, pentane and hexane not only have abstractable hydrogen atoms but also are flammable and run the risk of ignition by electrical equipment employed. Nevertheless, they have seen use.

D. Wavelength of Irradiation

Most of the di-π-methane reactants of interest have chromophores absorbing at wavelengths above 300 nm. This simplifies the photolysis procedure, since Pyrex transmits ultraviolet wavelengths above this point and cuts off most light below this region. Such a filter is termed a "short cut-off" type. There is no need to concern oneself about cutting off light of wavelengths longer than absorbed by the reactant or sensitizer since this light will be transmitted harmlessly. Hence, although "long cut-off filters" are available, they are most often not needed.

The main objective, however, is to maximize the amount of light absorbed (a) by the reactant, but not by the product in direct irradiations, and (b) by the sensitizer and neither the reactant nor the product in sensitized photolyses. This means that one should have ultraviolet spectra of all components and compute the absorbances of each compound at the concentration employed. There will be instances where one wishes to have a short cut-off filter at wavelengths longer than 300 nm to accomplish this objective. Cupric sulfate in 5% sulfuric acid cuts off nicely at wavelengths in the 300−320 nm region, depending on concentration. Sodium metavanadate cuts off in the 320−360 nm region, again depending on its concentration. A variety of inorganic short cut-off filters is known.[175] However, the disadvantage is that one then needs to circulate such filter solutions, instead of cooling water, through the irradiation apparatus and in the process one needs to cool the circulating filter solution. Most often Pyrex is adequate and filter solutions are unnecessary.

E. The Apparatus

While there is considerable flexibility in the apparatus employed, probably one of the most simple and commonly used choices for photochemical uses is the "Hanovia Immersion Well" type.[176] The well is used with cylindrical flasks of varying sizes. Usually the well is fabricated of quartz. However, Pyrex can be used for work above 300 nm. If quartz is used, then it is convenient to have Pyrex tubing available to surround the lamp and filter light below 300 nm for those runs where this is desired. Other tubing, filtering light below different cut-off points, can be used where available.

The flask used for the solution being irradiated should have a nitrogen inlet and outlet with provision for magnetic stirring at the bottom. The nitrogen inlet can be a 10/30 joint with ~1 mm polyethylene tubing leading to the flask bottom. This provides purging of oxygen prior to and during irradiation.

Alternatively, one can use apparatus more suitable to quantitative work as well as permitting more choices of filter solutions to provide relatively narrow ranges of wavelengths. One such choice is the "Wisconsin Black Box" [175] which consists of a six inch parabolic reflector machined from a cylindrical aluminum solid cylinder. A mercury or mercury−xenon lamp is then mounted at the focus of the parabola to give a six inch diameter beam.

Another type of apparatus which has been commonly used is the "Rayonet Reactor" which consists of a number of low-pressure mercury lamps mounted in an array surrounding the reaction vessel and with a reflector surrounding these. While the apparatus is commercially available,[177] it also can be constructed using readily available and inexpensive germicidal lamps. Such ordinary low-pressure lamps emit almost a single mercury line at 254 nm which often is not suitable for general purposes, since products as well as reactants and sensitizers tend to absorb at this wavelength. However, lamps coated with phosphors emitting at longer wavelengths (e.g. 300 nm, 360 nm) are available. These afford rather wide ranges of ultraviolet light which are sometimes too broad, sometimes 80−100 nm in wavelength spread, for a given purpose.

VI. Conclusions

This review has dealt with representative examples of the various types of di-π-methane rearrangements from a synthetic viewpoint. For inclusion examples needed to have product isolation and a report of actual yields. We limited the survey to the all-carbon

di-π-methane, the oxa-di-π-methane, and the aza-di-π-methane versions of the reaction. Other interesting variations such as the di-π-borane, di-π-ethane, and di-π-propane were reserved for future reviews when a larger number of examples have been reported. Our overall intent has been to provide representative examples from the literature.

One of the roles of the di-π-methane rearrangement is to provide routes to compounds not as readily constructed by other means. We hope that this review will help the more conventional organic synthetic chemists to include these photochemical alternatives in their arsenal of synthetic approaches.

Although this article has had a synthetic objective, one cannot help but note the mechanistic facets of the reaction, namely involving state multiplicity, regioselectivity, stereochemistry, and the relationship between structure and reactivity.

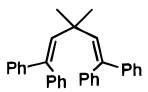
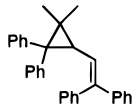
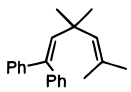
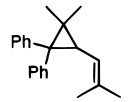
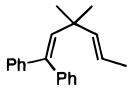
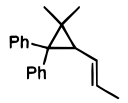
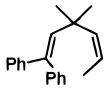
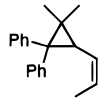
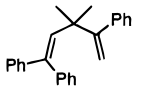
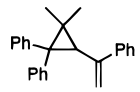
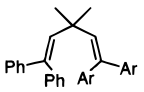
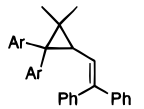
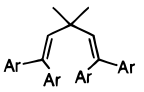
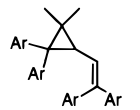
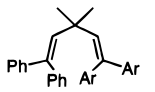
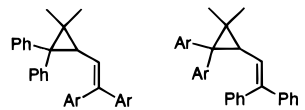
VII. Acknowledgments

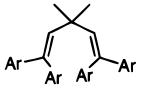
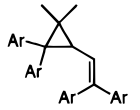
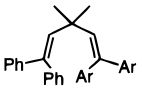
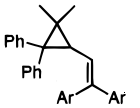
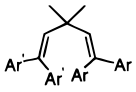
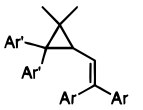
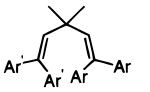
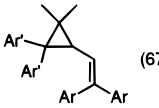
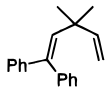
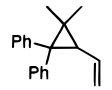
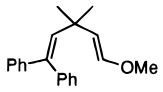
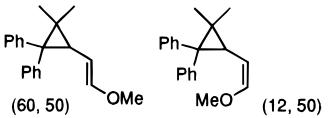
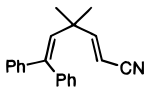
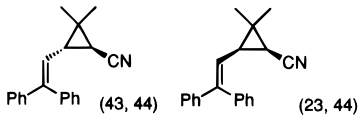
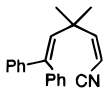
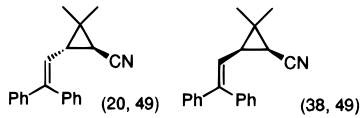
H.E.Z. acknowledges with appreciation the support of the National Science Foundation. D.A. expresses his appreciation for support by the Direcion General de Investigacion Cientifica y Tecnica (Grant No. PB94-0238) and the European Union (Contract No. CHRX-CT93-0152).

VIII. Tabular Survey

The examples given in the tables are selected with the aim of being representative. In particular, examples were chosen where sufficient detail is available, including actual yields and precise conditions. However, it needs to be recognized that the literature is immense and the goal here is selectivity. Many examples in natural product synthetic work involve complex structures without providing operational information available in less-involved systems, and these are not included. The categories chosen are representative of the most studied types of systems. In these tables, for each example, both the yield and the extent of conversion are given in parentheses, in this order. In the few cases selected where actual absolute yields were not given, the product ratio is designated.

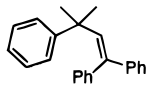
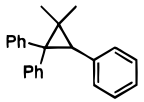
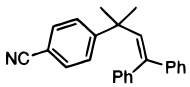
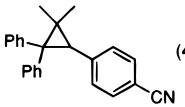
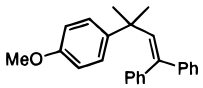
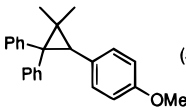
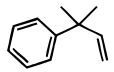
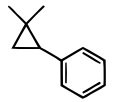
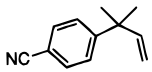
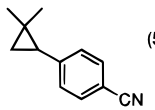
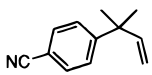
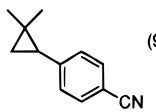
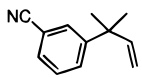
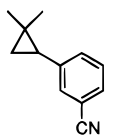
Table 1. Di-π-methane Rerrangements of Acyclic Systems

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Direct	 (97, 29)	3
	Direct	 (42)	9c
	Direct	 (98, 17)	9a
	Direct	 (90, 90)	9a
	Direct	 (73, 13)	41
 Ar = *p*-CN-C_6H_4	Direct	 (66) Ar = *p*-CN-C_6H_4	13
 Ar = *p*-CN-C_6H_4	Direct	 (89, 35) Ar = *p*-CN-C_6H_4	13
 Ar = *p*-MeO-C_6H_4	Direct	 (73, 15) Ar = *p*-MeO-C_6H_4 (19, 15)	14

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
 Ar = *p*-MeO-C_6H_4	Direct	 (58, 53) Ar = *p*-MeO-C_6H_4	14
 Ar = *p*-Me_2N-C_6H_4	Direct	 (45) Ar = *p*-Me_2N-C_6H_4	14
 Ar = *p*-MeO-C_6H_4 Ar' = *p*-Cl-C_6H_4	Direct	 (80, 43) Ar = *p*-MeO-C_6H_4 Ar' = *p*-Cl-C_6H_4	42
 Ar = *p*-MeO-C_6H_5 Ar' = *p*-CN-C_6H_4	Direct	 (67, 47) Ar = *p*-MeO-C_6H_5 Ar' = *p*-CN-C_6H_4	42
	Direct or Acetophenone Sens.	 (83, 23)	12
	Direct	 (60, 50) (12, 50)	12
	Direct	 (43, 44) (23, 44)	12
	Direct	 (20, 49) (38, 49)	12

	Direct or Acetophenone Sens.	(100, 85)	43		Direct	(95)	19	
	Direct	(39)	43		Benzophenone Sens.	(72, 79)	8	
	Direct or Acetophenone Sens.	(98, 56)	19		Acetophenone Sens.	(90)	43	
	Acetophenone Sens.	(95)	19		Acetophenone Sens.	(65, 66)	8	

Table 2. Di-π-methane Rearrangements of Aryl−Vinyl Systems

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Direct	 (47, 73)	5
	Direct	 (41, 48)	5
	Direct	 (54, 67)	5
	Direct	 (80)	44, 45
	Direct	 (57, 49)	45
	Acetone Sens.	 (96, 56)	45
	Acetone Sens.	 (97, 50)	45

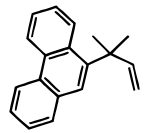
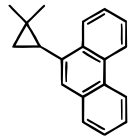
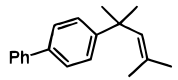
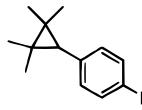
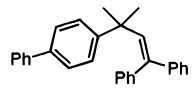
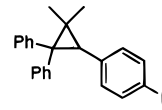
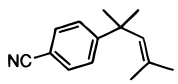
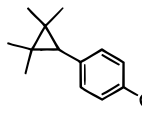
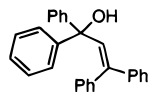
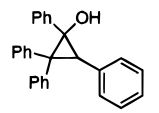
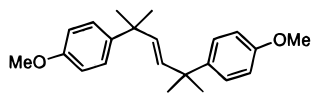
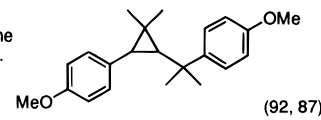
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Xanthone Sens.	 (58, 32)	46
	Acetophenone Sens.	 (72)	47
	Acetophenone Sens.	 (62, 47)	47
	Acetone Sens.	 (93)	47
	Direct	 (48, 75)	48
	Acetone Sens.	 (92, 87)	49

Table 3. Di-π-methane Rearrangements of Monocyclic Systems

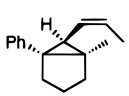
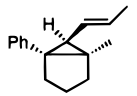
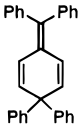
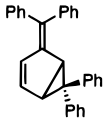
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.	Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Direct	 (79)  (6)	36,37,38		Direct or Benzophenone Sens.	 (38)  (24)	39
	Direct	 (80)	20				

Table 4. Di-π-methane Rearrangements of Fused Alicyclic Systems

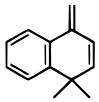
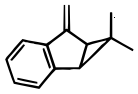
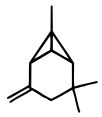
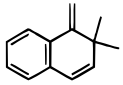
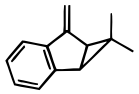
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.	Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Direct	 (96, 67)	40		Acetone Sens.	 (50)	50
	Direct	 (94, 38)	40				

Table 5. Di-π-methane Rearrangements of Bicyclo[2.2.2]octatrienes

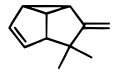
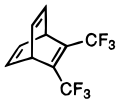
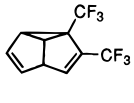
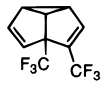
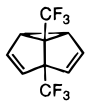
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.	Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Acetone Sens.	 (50, 59)	2, 7, 21		Acetone Sens.	 (33)	51
	Acetone Sens.	 2 :  1 :  1	22				

Table 6. Di-π-methane Rearrangements of Benzobarrelenes

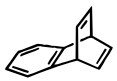
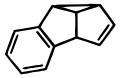
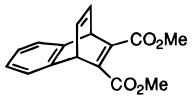
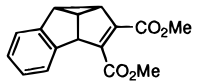
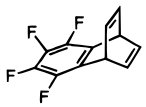
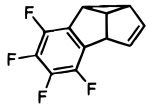
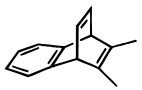
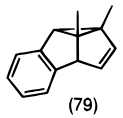
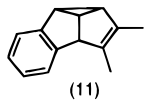
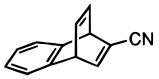
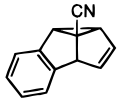
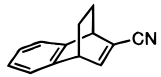
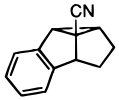
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.	Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Acetone Sens.	 (63, 47)	11		Acetone Sens.	 (30)	24
	Acetone Sens.	 (66)	23		Acetophenone Sens.	 (79)  (11)	25
	Acetophenone Sens.	 (56, 90)	17		Acetone Sens.	 (72, 55)	26

Table 7. Di-π-methane Rearrangements of Dibenzobarrelenes

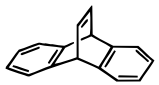
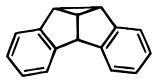
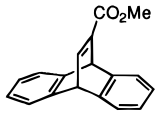
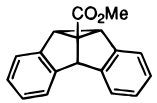
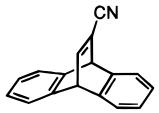
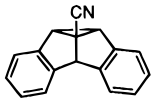
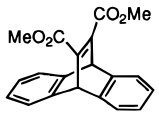
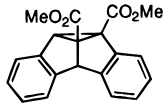
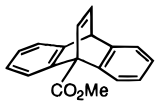
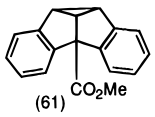
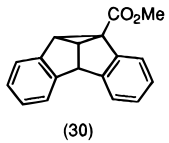
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.	Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Acetone Sens.	 (85)	27,28		Acetone Sens.	 (96)	27
	Acetone Sens.	 (80)	27		Acetone Sens.	 (75)	27
	Acetone Sens.	 (61)  (30)	27				

Table 8. Di-π-methane Rearrangements of Condensed Benzobarrelenes

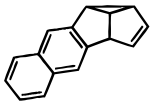
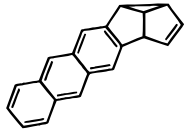
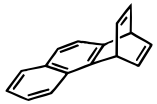
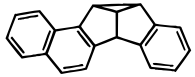
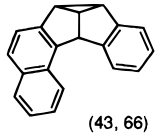
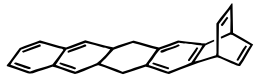
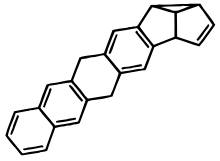
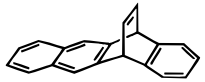
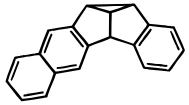
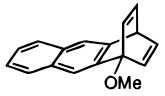
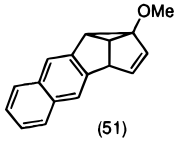
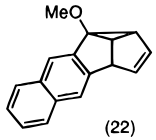
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.	Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Direct or Benzophenone Sens.	 (45)	29		Direct or Acetophenone Sens.	 (89)	15
	Benzophenone Sens.	 (43, 66)  (43, 66)	29		Direct	 (64)	30
	Direct	 (81, 57)	16	 OMe	Direct	 OMe (51)  MeO (22)	31

Table 9. Di-π-methane Rearrangements of Bicyclo[2.2.1] derivatives

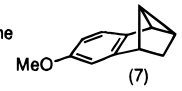
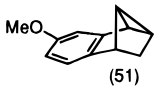
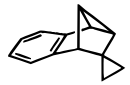
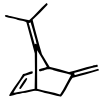
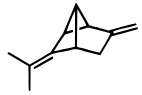
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.	Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Acetophenone Sens.	 (95)	32,33		Acetophenone Sens.	 1 : 9 (83 total)	35
 MeO	Acetophenone Sens.	 MeO (7)  MeO (51)	18		Acetone Sens.	 (75)	52
 NC	Acetophenone Sens.	 NC (90)	18		Acetone Sens.	 (75)	53
 O_2N	Direct or Benzophenone Sens.	 O_2N (85)	34		Acetone Sens.	 (56)	53
 CN	Acetophenone Sens.	 CN (65)	35				

Table 10. Oxa-di-π-methane Rearrangements of Acyclic β,γ-Unsaturated Ketones

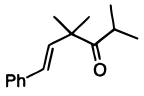
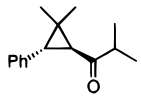
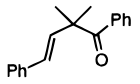
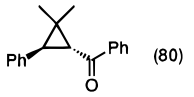
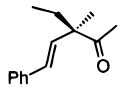
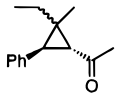
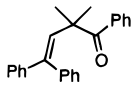
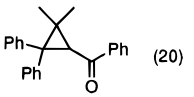
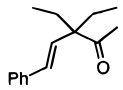
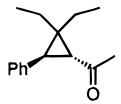
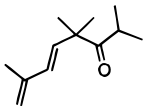
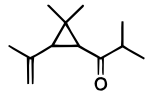
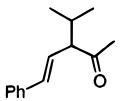
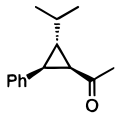
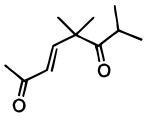
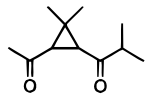
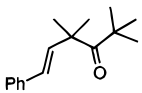
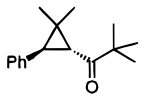
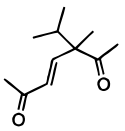
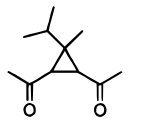
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.	Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Acetophenone Sens.	 (93)	85		*p*-Benzoylbiphenyl Sens.	 (80)	86
	Chrysene Sens.	 (31)	59		Benzophenone Sens.	 (20)	86
	*p*-Benzoylbiphenyl Sens.	 (90)	86		Benzophenone Sens.	 (20)	87
	*p*-Benzoylbiphenyl Sens.	 (70)	86		Direct	 (20)	87
	*p*-Benzoylbiphenyl Sens.	 (80)	86		Direct	 (25)	87

Table 11. Oxa-di-π-methane Rearrangements of Cycloalkenyl Ketones

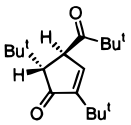
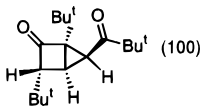
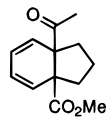
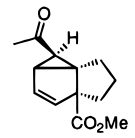
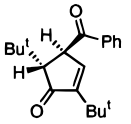
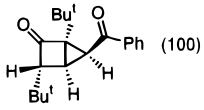
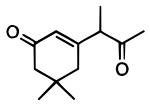
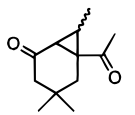
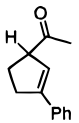
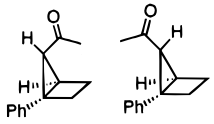
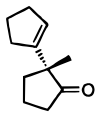
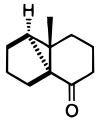
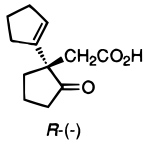
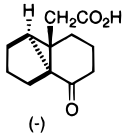
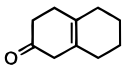
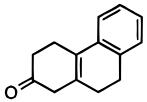
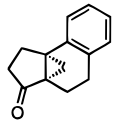
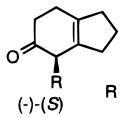
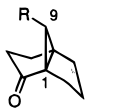
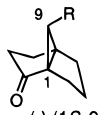
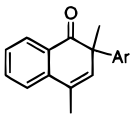
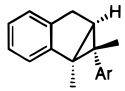
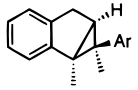
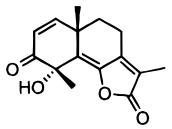
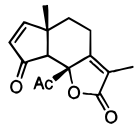
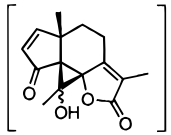
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.	Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Direct	 (100)	71		Direct	 (32)	94
	Direct	 (100)	71		Direct	 (75)	87
	Different Sens. (61-74 kcal/mol)	 3 : 1 (65)	66				

Table 12. Oxa-di-π-methane Rearrangements of Cyclic Ketones

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Acetone Sens.	 (49)	70
 *R*-(-)	Acetone Sens.	 (-) (73)	69,70
	Direct	 (>50)	78,95
	Acetophenone Sens.	 (56)	101
 (-)-(*S*) R = $CH(OMe)_2$	Acetone Sens.	 (-)-(1*S*, 9*S*) 2 :  (-)-(1*S*, 9*R*) 1 (20)	58
 Ar = *p*-$MeOC_6H_4$	Direct	 (43)  (12)	98
	Acetophenone Sens.	 (45) *via* 	100

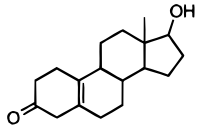
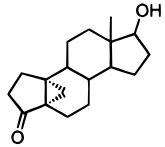
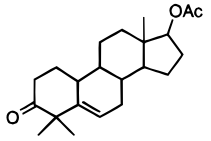
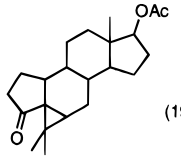
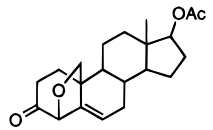
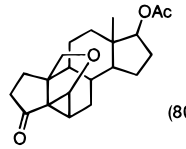
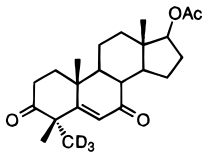
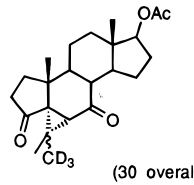
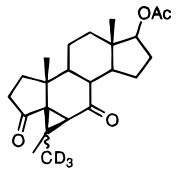
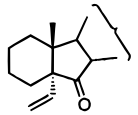
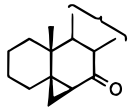
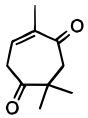
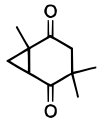
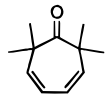
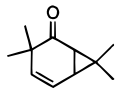
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Direct	 (55)	95
	Acetone Sens.	 (19)	99
	Acetone Sens.	 (80)	99
	Direct	 (30 overall) 	56
	Acetone Sens.	 (52)	102
	Direct	 (34)	87
	Benzophenone Sens.	 (82)	97

Table 13. Oxa-di-π-methane Rearrangements of Spiro Ketones

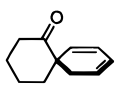
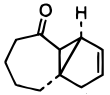
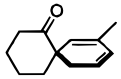
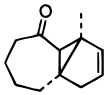
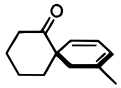
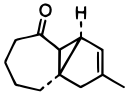
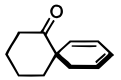
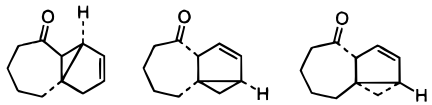
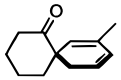
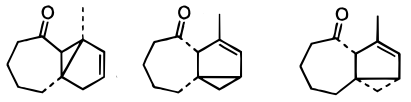
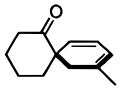
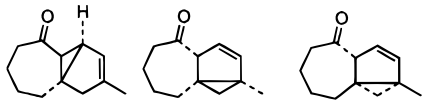
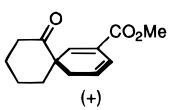
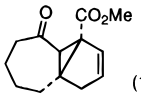
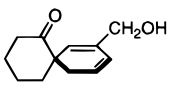
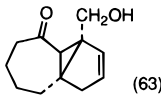
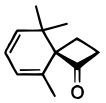
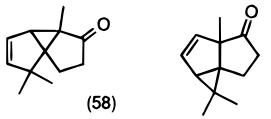
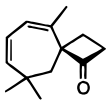
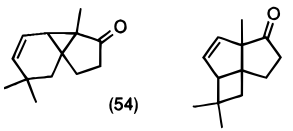
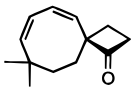
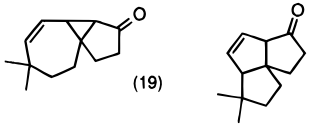
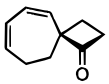
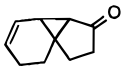
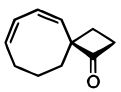
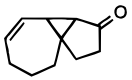
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Direct	 (19)	103
	Direct	 (45)	103
	Direct	 (65)	103
	Acetone Sens.	 (25) (15) (5)	103
	Acetone Sens.	 (58) (15) (4)	103
	Acetone Sens.	 (19) (34) (6)	103
 (+)	Direct or Acetone Sens.	 (+)-*t* (100)	104
	Direct	 (63)	104
	Michler's ketone Sens.	 (58) (24)	105
	Michler's ketone Sens.	 (54) (25)	105
	Michler's ketone Sens.	 (19) (21)	105
	Michler's ketone Sens.	 (28)	105
	Michler's ketone Sens.	 (64)	105

Table 14. Oxa-di-π-methane Rearrangements of Bicyclo[3.2.0]heptenones

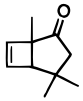
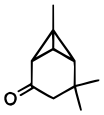
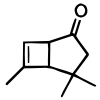
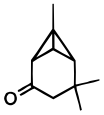
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.	Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Acetone Sens.	 (70)	50,106		Acetone Sens.	 (59)	50
	Acetone Sens.	 (64)	50				

Table 15. Oxa-di-π-methane Rearrangements of Bicyclo[2.2.1]heptenones

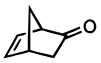
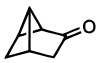
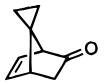
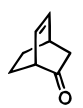
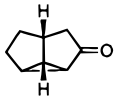
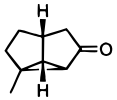
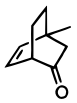
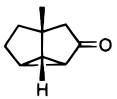
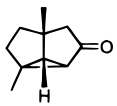
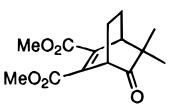
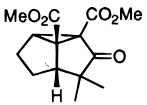
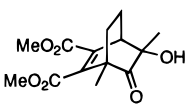
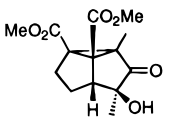
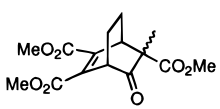
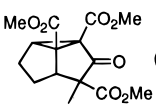
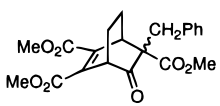
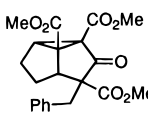
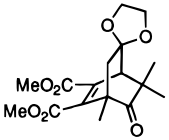
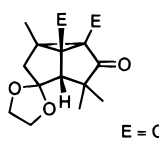
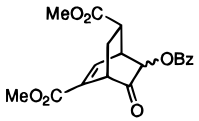
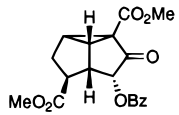
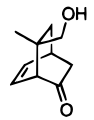
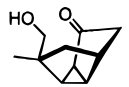
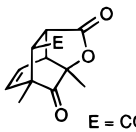
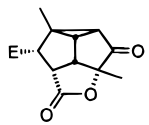
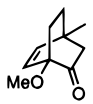
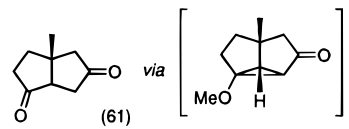
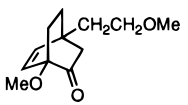
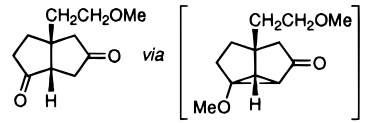
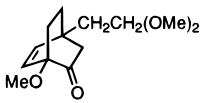
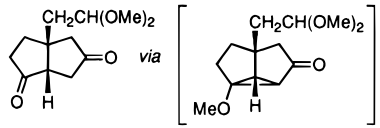
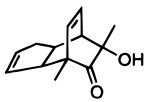
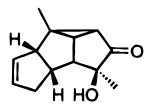
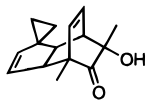
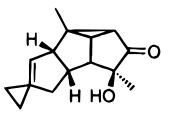
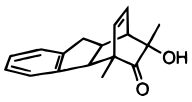
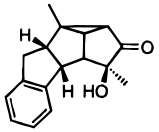
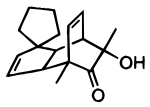
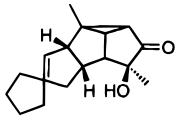
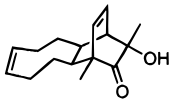
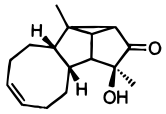
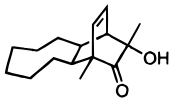
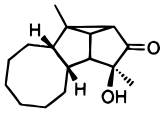
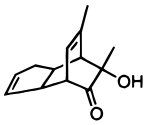
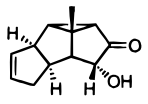
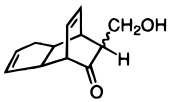
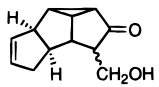
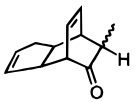
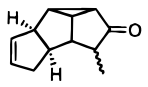
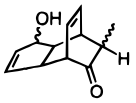
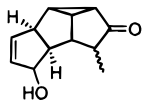
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.	Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Acetone Sens.	 (75)	53,62		Acetone Sens.	 (70)	53,62

Table 16. Oxa-di-π-methane Rearrangements of Bicyclo[2.2.2]octenones

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
 1*S*, 4*R* (-) 1*R*, 4*S* (+)	Acetone Sens.	 (84-85) 1*R*, 5*S* (+) 1*S*, 5*R* (-)	68,107,108
	Acetophenone Sens.	 (85-90)	107
	Acetophenone Sens.	 (85-90)	107
	Acetophenone Sens.	 (72)	108
	Acetophenone Sens.	 (76)	110a
	Acetophenone Sens.	 (37)	132
	Acetophenone Sens.	 (51)	117
	Acetophenone Sens.	 (60-65)	117
	Acetophenone Sens.	 (94) $E = CO_2Me$	110b

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Acetone Sens.	 (60)	122
	Acetone Sens.	 (91)	113
 $E = CO_2Me$	Acetone Sens.	 (49) $E = CO_2Me$	110a
	Acetophenone Sens.	 *via* (61)	108
	Acetone Sens.	 *via* (≥ 75)	115
	Acetone Sens.	 *via* (84)	108,115
	Acetone Sens.	 (55)	118a,c
	Acetone Sens.	 (60)	118a,c

	Acetone Sens.		(50)	118a,c
	Acetone Sens.		(50)	118b,c
	Acetone Sens.		(51)	118b,c
	Acetone Sens.		(50)	118b,c
	Acetone Sens.		(40)	118c
	Acetone Sens.		(55)	118c
	Benzophenone Sens.		(38)	118c
	Acetone Sens.		(45)	118c

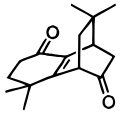
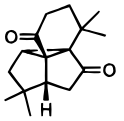
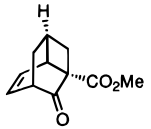
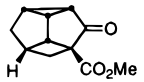
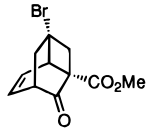
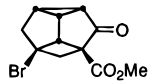
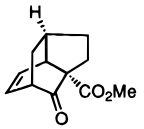
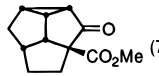
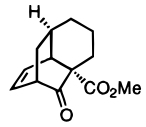
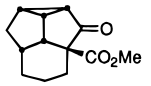
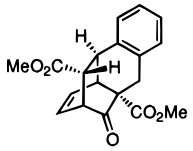
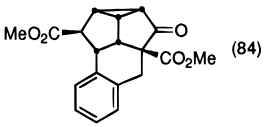
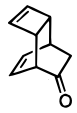
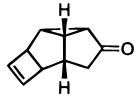
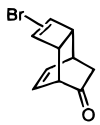
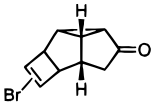
	Direct		(78)	119
	Acetophenone Sens.		(66)	120
	Acetophenone Sens.		(86)	120
	Acetone Sens.		(75)	120
	Acetophenone Sens.		(89)	120
	Acetophenone Sens.		(84)	120
	Acetone Sens.		(66)	121
	Acetone Sens.		(44)	121

Table 16 (Continued)

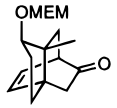
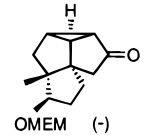
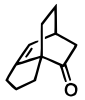
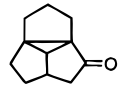
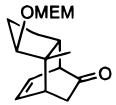
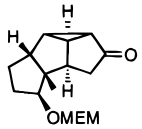
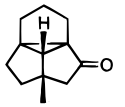
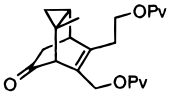
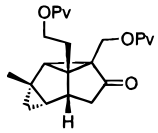
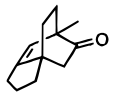
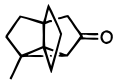
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.	Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
 (+) MEM = $CH_2OCH_2CH_2OCH_3$	Acetone Sens.	 (70)	109		Acetone Sens.	 (85)	111a
 MEM = $CH_2OCH_2CH_2OCH_3$	Acetone Sens.	 (72)	109a		Acetone Sens.	 (65)	111a,c
 Pv = Pivaloyl	Acetone Sens.	 (91)	112		Acetone Sens.	 (50)	111

Table 17. Oxa-di-π-methane Rearrangements of Bicyclo[2.2.2]octendiones

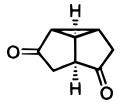
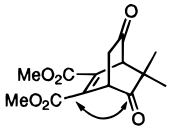
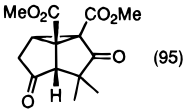
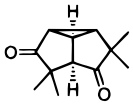
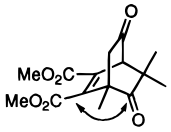
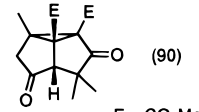
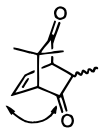
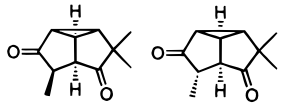
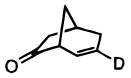
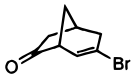
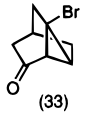
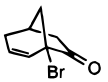
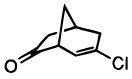
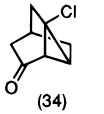
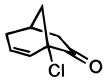
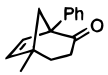
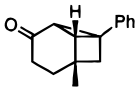
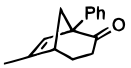
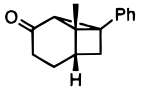
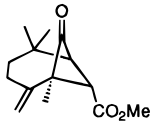
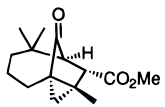
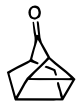
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.	Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Acetone Sens.	 (75)	123b		Acetophenone Sens.	 (95)	110b
	Acetone Sens.	 (60-65)	123b		Acetophenone Sens.	 (90) E = CO_2Me	110b
	Direct and Acetone Sens.	 10 : 1 (70-74)	123				

Table 18. Oxa-di-π-methane Rearrangement of Other Bridged Cyclic Enones

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Acetone Sens.	 (71)	124
	Acetone Sens.	 (33)  (26)	124
	Acetone Sens.	 (34)  (13)	124
	Acetone Sens.	 (60)	125
	Acetone Sens.	 (48)	125
	Acetone Sens.	 (32) 1*R**, 3*S**, 4*S**, 5*S**	128
	Acetone Sens.	 (25)	129

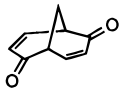
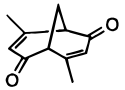
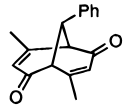
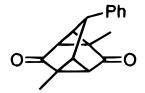
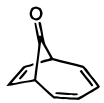
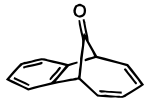
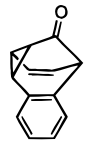
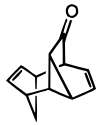
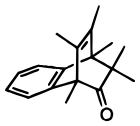
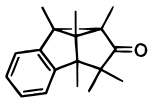
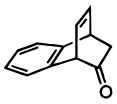
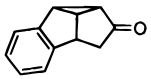
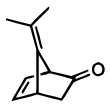
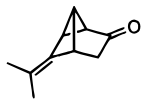
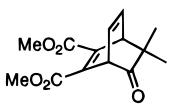
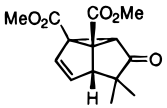
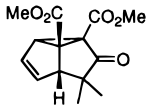
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Direct	 (58)	126
	Direct	 (20)	126
	Direct	 (24)	126
	Benzophenone Sens.	 (78)	127
	Benzophenone Sens.	 (83)	127
	Direct or Sens.	 (60)	63

Table 19. Competition between the DPM and the ODPM Processes

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Acetone Sens.	 (26) **ODPM**	130
	Acetone Sens.	 (21-27) **ODPM**	55, 67,68
	Acetone Sens.	 (62) **ODPM**	53
	Acetophenone Sens.	 (>49)  (>2) **ODPM** **DPM**	135

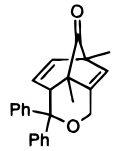
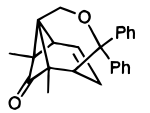
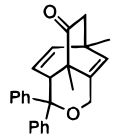
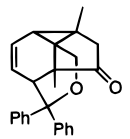
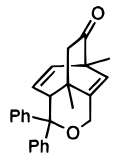
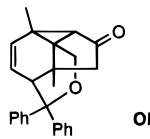
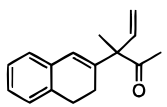
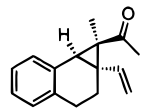
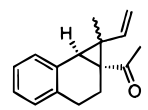
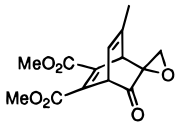
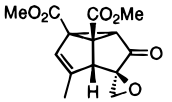
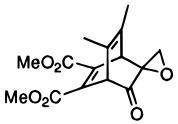
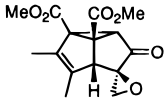
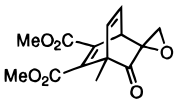
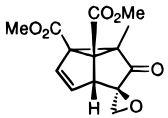
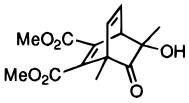
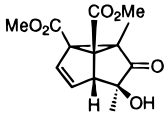
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Benzophenone Sens.	 (70) **DPM**	134
	Benzophenone Sens.	 (80) **DPM**	134
	Benzophenone Sens.	 (69) **ODPM**	134
	4-benzoylbiphenyl Sens.	 (52) **DPM**  (34) **ODPM**	136

Table 20. Competition between the DPM and the ODPM Processes: The Di-π-methane Rearrangement of Bicyclo[2.2.2]octadienones

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Acetophenone Sens.	 (42)	132
	Acetophenone Sens.	 (73)	132
	Acetophenone Sens.	 (46)	132
	Acetophenone Sens.	 (57)	132

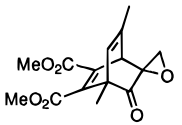
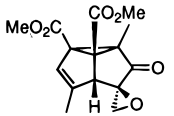
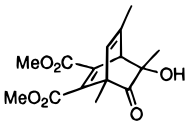
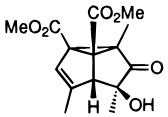
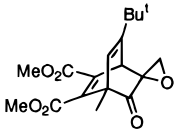
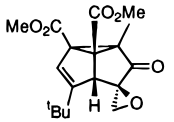
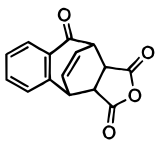
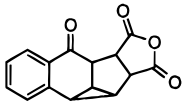
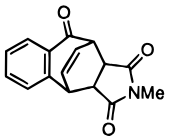
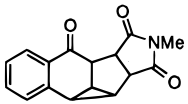
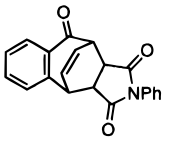
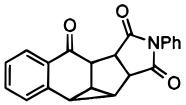
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Acetophenone Sens.	 (53)	132
	Acetophenone Sens.	 (40)	132
	Acetophenone Sens.	 (61)	132

Table 21. Competition between the DPM and the ODPM Processes: The Di-π-methane Rearrangement of Ethenobenzocycloheptenones

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Direct or Acetone Sens.	 (52-93)	133
	Direct or Acetone Sens.	 (61-84)	133
	Direct or Acetone Sens.	 (50-68)	133

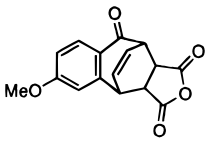
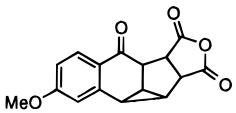
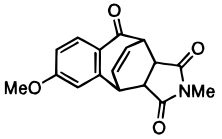
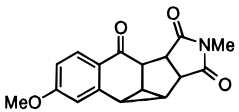
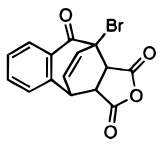
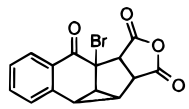
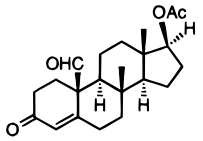
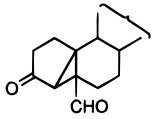
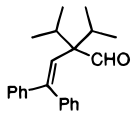
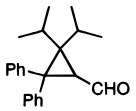
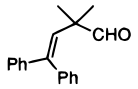
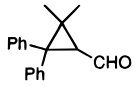
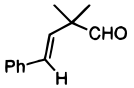
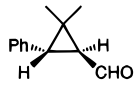
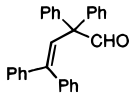
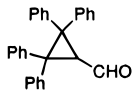
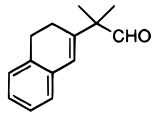
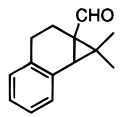
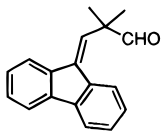
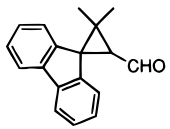
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Direct or Acetone Sens.	 (90-93)	133
	Direct	 (63)	133
	Direct	 (72)	133

Table 22. Oxa-di-π-methane Rearrangement of β,γ-Unsaturated Aldehydes

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Direct or Acetophenone Sens.	 (30)	144
	Acetophenone Sens.	 (100)	145
	*m*-Methoxyacetophenone Sens.	 (57)	146
	Acetophenone Sens.	 (90)	146
	Acetophenone Sens.	 (82)	146b
	Acetophenone Sens.	 (83)	146b
	Acetophenone Sens.	 (96)	146b

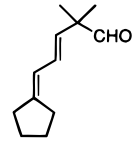
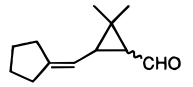
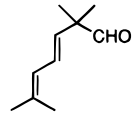
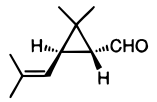
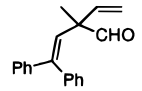
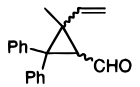
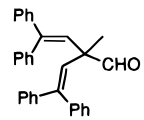
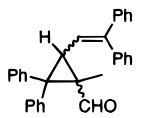
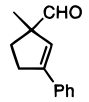
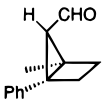
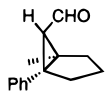
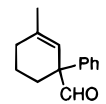
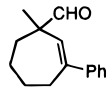
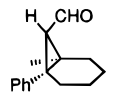
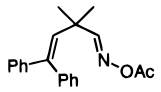
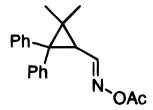
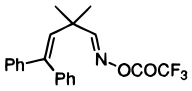
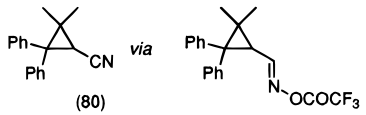
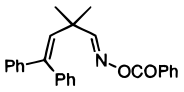
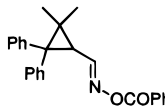
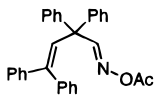
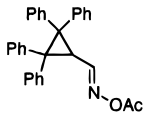
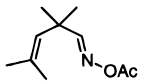
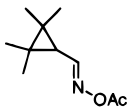
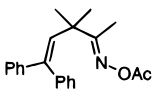
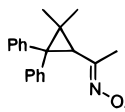
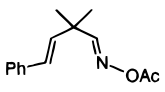
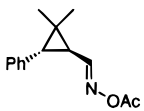
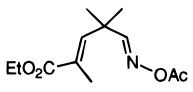
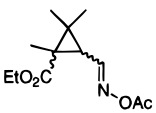
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	*m*-Methoxyacetophenone Sens.	 (47)	146b
	*m*-Methoxyacetophenone Sens.	 (52)	146b
	Acetophenone Sens.	 (19) **ODPM**	146b
	Acetophenone Sens.	 (48) **DPM**	146b
	Acetophenone Sens.	 (90)	146
	Acetophenone Sens.	 (25)  (25)	146
	Acetophenone Sens.	 (25)	146b

Table 23. Aza-di-π-methane Rearrangements of β,γ-Unsaturated Oxime Esters

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Acetophenone Sens.	 (86)	155,156
	Acetophenone Sens.	 (80)	162b
	Acetophenone Sens.	 (90)	162
	Acetophenone Sens.	 (90)	156
	Acetone Sens.	 (12)	156
	Acetophenone Sens.	 (18)	156
	Acetophenone Sens.	 (71)	157
	Acetone Sens.	 (28)	158

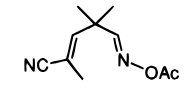
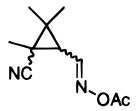
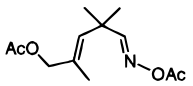
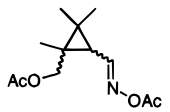
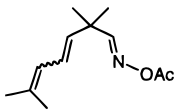
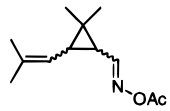
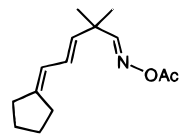
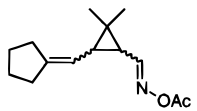
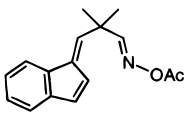
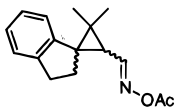
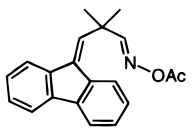
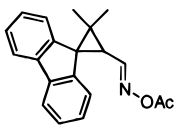
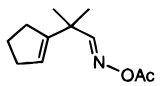
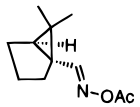
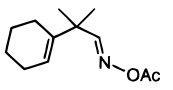
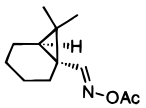
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Acetone Sens.	 (54)	158b
	Acetone Sens.	 (21)	158b
	Acetophenone Sens.	 (45)	159a
	Acetophenone Sens.	 (67)	159a
	Acetophenone Sens.	 (59)	159a
	Acetophenone Sens.	 (60)	159a
	Acetone Sens.	 (76)	160
	Acetone Sens.	 (24)	160

Table 24. Aza-di-π-methane Rearrangements of β,γ-Unsaturated Imines and Hydrazone Derivatives

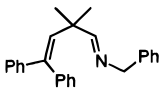
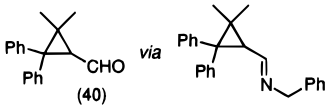
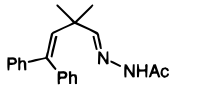
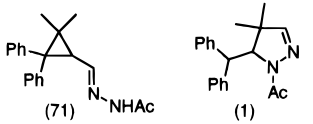
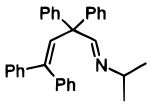
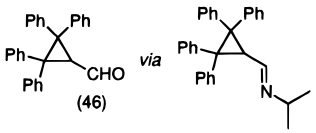
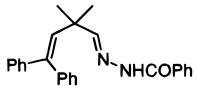
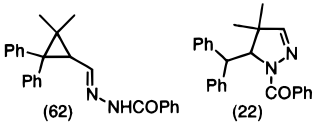
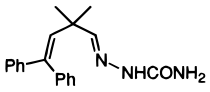
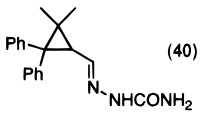
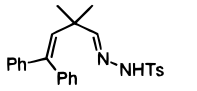
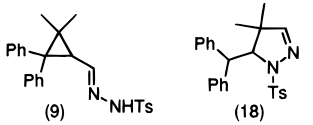
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.	Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Acetophenone Sens.	 (40) via	150		Acetophenone Sens.	 (71) (1)	162,163
	Acetophenone Sens.	 (46) via	151		Acetophenone Sens.	 (62) (22)	162,163
	Acetophenone Sens.	 (40)	162		Acetophenone Sens.	 (9) (18)	162,163

Table 25. Aza-di-π-methane Rearrangements of β,γ-Unsaturated Oximes

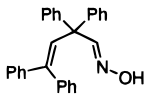
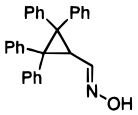
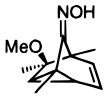
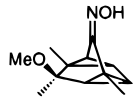
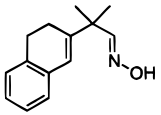
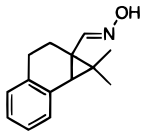
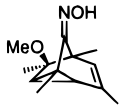
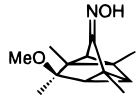
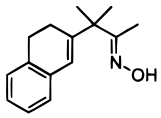
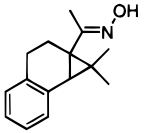
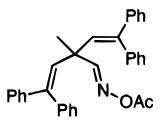
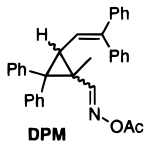
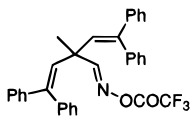
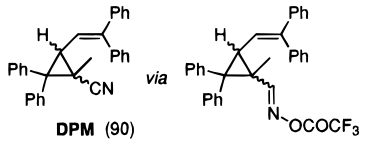
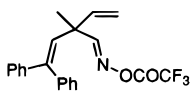
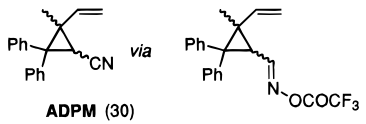
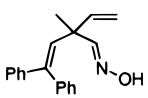
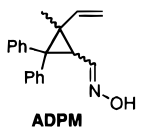
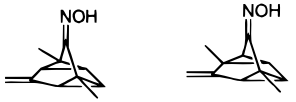
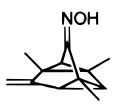
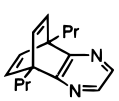
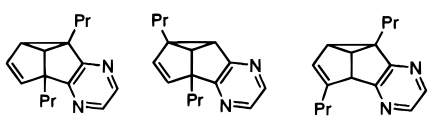
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.	Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Acetophenone Sens.	 (74)	164		Direct	 (20)	149b
	Acetophenone Sens.	 (63)	164		Direct	 (57)	149b
	Acetophenone Sens.	 (66)	164				

Table 26. Competition between the Di-π-methane and Aza-di-π-methane Processes

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Direct or Acetophenone Sens.	 **DPM** (84)	164
	Direct or Acetophenone Sens.	 **DPM** (90) *via*	164
	Direct or Acetophenone Sens.	 **ADPM** (30) *via*	164
	Direct or Acetophenone Sens.	 **ADPM** (30)	164
	Direct	 **DPM** (24) **ADPM** (55)	149a
	Direct	 **ADPM** (54)	149a
	Direct or Sens.	 **DPM** (53) **ADPM** (25) **ADPM** (22)	172

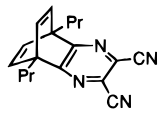
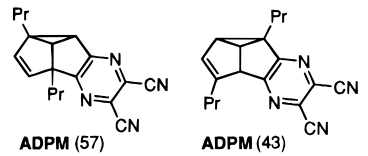
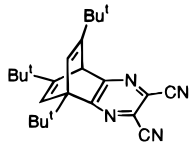
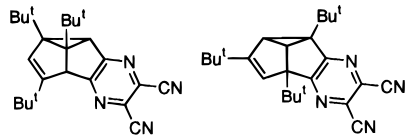
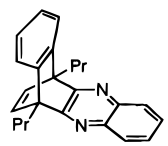
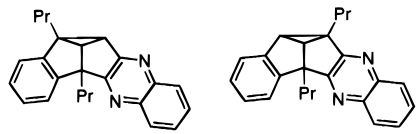
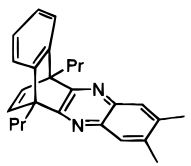
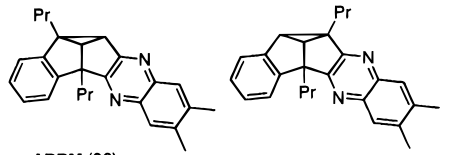
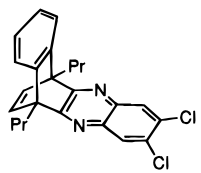
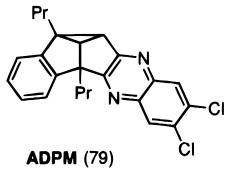
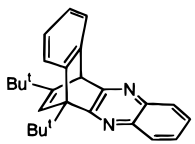
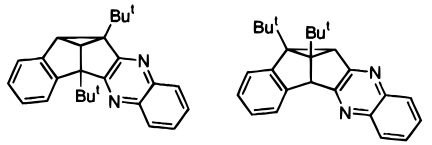
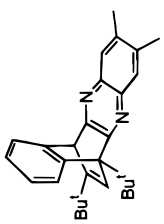
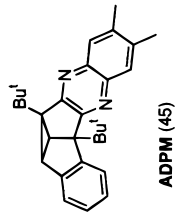
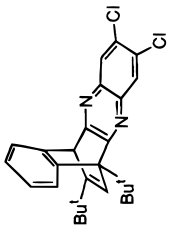
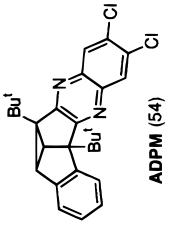
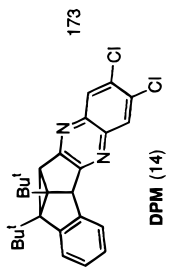
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Direct or Sens.	 **ADPM** (57) **ADPM** (43)	172
	Direct or Sens.	 **ADPM** (76) **ADPM** (24)	172
	Direct or Sens.	 **ADPM** (58) **DPM** (5)	173
	Direct or Sens.	 **ADPM** (86) **DPM** (6)	173
	Direct or Sens.	 **ADPM** (79)	173
	Direct or Sens.	 **ADPM** (78) **ADPM** (21)	173

Table 26 (Continued)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Direct or Sens.	 **DPM** (15) **ADPM** (45)	173
	Direct or Sens.	 **ADPM** (54)  **DPM** (14)	173

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