Photocycloadditions: Control by Energy and Electron Transfer

Felix Müller and Jochen Mattay*

Organisch-Chemisches Institut der Universität Münster, Orléansring 23, DW-4400 Münster, Federal Republic of Germany

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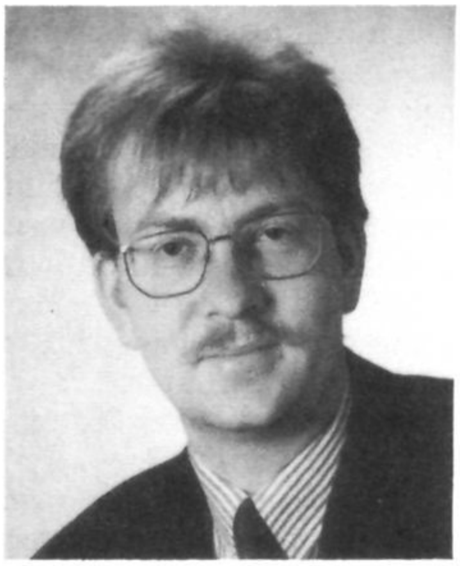
I. Introduction

The recent enormous development in the area of photoinduced electron transfer (PET) reactions[1,2] has opened up a new potentially important instrument for controlling synthetic processes which up until now could not be exploited entirely using classical energy-transfer techniques. Generally in these processes light induces the transfer of an electron from a donor (D) to an acceptor (A) molecule, thus creating a radical cation and a radical anion. One of these acts as the reactive synthon for an organic transformation (eq 1). The

$$A + D \xrightarrow{h\nu} A^{\bullet -} + D^{\bullet +} \qquad (1)$$

impact this process has on organic synthesis has already



Felix Müller was born in Münster, Federal Republic of Germany, in 1964. He studied chemistry at the Westfälische Wilhelms-Universität in Münster from 1983 to 1988, when he got the diploma degree. He then worked for McKinsey & Co., Inc., in Düsseldorf as a management consultant. In 1989 he did his compulsory service in the German Federal Army in a chemical laboratory unit as a developer for polarographic analytic procedures. In 1990 he joined the research group of Professor Mattay at University of Münster, where he is currently completing the requirements for his Ph.D. He had a student grant from the Studienstiftung des deutschen Volkes and has now a predoctoral grant from the same foundation.

Jochen Mattay was born in the southern part of Lower Saxony, Federal Republic of Germany, in 1946. After a training as Chemielaborant in the chemical industry, he studied chemistry at the Technische Hochschule (RWTH) Aachen, where he received a Dr. rer. nat. degree in 1978 (with H.-D. Scharf). After 15 months as a postdoctoral fellow in N. J. Turro's group at Columbia University (1979/1980), he joined the Institut für Organische Chemie of RWTH again and worked on his habilitation. In 1984 he became Privatdozent, and 1985 he was appointed professor at RWTH. In 1989 he moved to the University of Münster, where he still holds a professorship of organic chemistry. His research interests in a broader sense include synthetic and physical organic chemistry on both ground- and excited-state surfaces. Currently his group is involved in various aspects of electron-transfer chemistry, in asymmetric synthesis and catalysis, in applications of semiempirical methods to Diels–Alder reactions and radical additions, and in photoreactions of metal complexes aiming at synthetic applications.

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been discussed.[3,4] The regulative parameter leading to successful transformation is the free energy of formation of a solvent-separated ion pair.

This review will concern itself only with photocycloadditions controlled by PET or energy transfer. Within these limits we will discuss how the manifold photocycloadditions in organic synthesis can be influenced by these preparative techniques to lead to different targets. By "PET-controlled" we mean reactions proceeding via radical ion intermediates. All other sensitized and direct photoreactions are said to be "energy-controlled". By controlling reactions either in one direction or another, different product compositions result. When a reaction mode is changed, e.g., a substitution process is converted into a cycloaddition process or vice versa, or a process is made possible due to the changed reaction pathway, the resulting products are usually very different. On an intermediate level there is the change in the cycloaddition mode, that is, from a [2 + 2] cycloaddition to a [4 + 2] cycloaddition (the reverse is true when thermal means are not used). Of less obvious significance, but of great importance to the preparative chemist, there is a change in both the regio- and stereoselectivity.

We have decided to organize this review from the point of view of types of cycloaddition, ranging from [2 + 2] via [3 + 2] and [4 + 2] to the larger ones. This order should make it easier for the reader to locate reaction types without necessarily reading the entire review. After a short theoretical section, we will start with a comprehensive discussion of the [3 + 2] cycloaddition of azirines as an example of PET's influence in reactivity and of arene cycloadditions as an example of PET's influence in cycloadditions. The following sections will cover other cycloadditions.

II. Theoretical Aspects

The complete theory of photochemistry cannot possibly be covered in this review. There are several comprehensive reviews in the literature.[1-9] Nevertheless, we intend to outline briefly the energy- and electron-transfer processes as manifested in the well-known Weller equation[10] and the influence and consequences of medium effects.

Photochemical irradiation of molecules leads to excited species in both the singlet and triplet states.[6-8] Since not every molecule can be excited directly, the use of sensitizers has been common since the early days of photochemistry. A sensitizer, by transferring its energy to the substrate, enables it to react. The most commonly used process is triplet-triplet energy transfer. Among the most commonly used sensitizers are ketones and dyes such as rose bengal.[6-8]

In polar solvents, such as acetonitrile, sensitization can lead to the transfer of an electron since a charged species can be stabilized in the polar solvent. The question of which process is preferred in a given reaction can be answered easily by using the Weller equation. The Weller equation is introduced here in a simplified version

$$\Delta G = E_{1/2}^{\mathrm{ox}}(\mathrm{D}) - E_{1/2}^{\mathrm{red}}(\mathrm{A}) - \Delta E_{\mathrm{excit}} + \Delta E_{\mathrm{coul}} \tag{2}$$

where $E_{1/2}^{\mathrm{ox}}(\mathrm{D})$ and $E_{1/2}^{\mathrm{red}}(\mathrm{A})$ are the half-wave potentials of the donor and acceptor, respectively, as measured in acetonitrile. $\Delta E_{\mathrm{excit}}$ is the excitation energy of the donor or acceptor, depending on which of the two is to be excited, and ΔE_{coul} is the Coulomb interaction energy of the radical ions at defined distance and in a given solvent. ΔE_{coul} can be obtained from the Born equation,[10b] which together with the relevant parameters is accessible from the literature or by measurement. To some extent the decisive component of the Weller equation is the Coulomb term ΔE_{coul}. In many cases it decides whether ΔG becomes positive or negative. In the first case, the electron-transfer process of a donor-acceptor system is thermodynamically forbidden (endergonic process, $\Delta G > 0$). If ΔG is negative, the process is thermodynamically allowed and exergonic. Depending on the polarity of the solvent, several intermediates can be involved. The excited acceptor-donor pair may form an exciplex (EXC) and radical ions which are classified by their distance from each other as contact ion pairs (CIP), solvent-separated ion pairs (SSIP), and free-radical ions (FRI). The dominance of any of these species is controlled by the polarity of the solvent as shown in

$$\mathrm{A} + \mathrm{D} \xrightarrow{h\nu}$$

$$\underset{\text{EXC}}{(\mathrm{A}^{\delta-}\mathrm{D}^{\delta+})_{\mathrm{s}}} \longleftrightarrow \underset{\text{CIP}}{(\mathrm{A}^{\bullet-}\mathrm{D}^{\bullet+})_{\mathrm{s}}} \longleftrightarrow \underset{\text{SSIP}}{(\mathrm{A}_{\mathrm{s}}^{\bullet-}\mathrm{D}_{\mathrm{s}}^{\bullet+})} \longleftrightarrow \underset{\text{FRI}}{\mathrm{A}_{\mathrm{s}}^{\bullet-} + \mathrm{D}_{\mathrm{s}}^{\bullet+}}$$

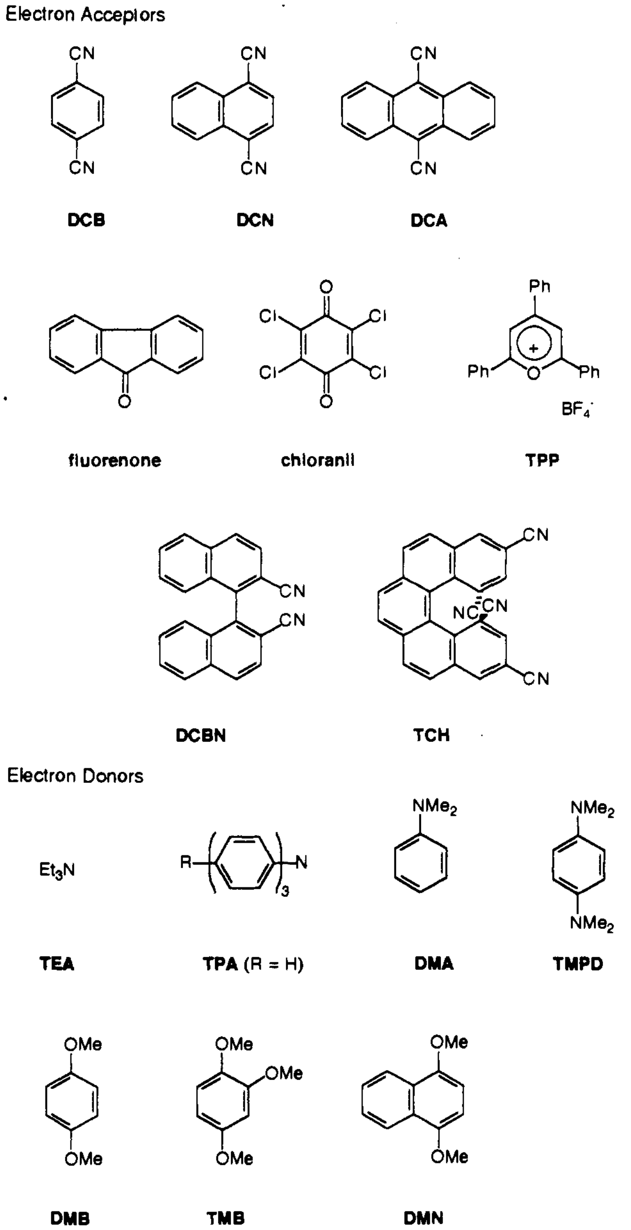
$$\xrightarrow{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad} \varepsilon \tag{3}$$

The charge-transfer process is strongly favored in solvents such as acetonitrile. It is possible to get an almost completely diffusion-controlled reaction.[10b] Nevertheless, not all reaction mixtures prepared according to this recipe will result in good quantum and product yields. This is due to the fact that the reverse electron-transfer reaction is also allowed, leading to reformation of starting materials.[10c] This is especially true if ΔG is strongly negative. This is the Marcus-inverted region of electron transfer.[11] The reverse reaction is excluded only in very fast reactions or where the "special salt effect" operates.[3,12]

The reaction path can be influenced by appropriate choice of an electron-transfer sensitizer since these differ in their half-wave potentials. Scheme 1 depicts the most important electron-transfer sensitizers. In this paper their abbreviations are used.

From the above two processes employed in cycloadditions, i.e., the energy transfer and the electron transfer, the reaction paths diverge to give different product-forming mechanisms. Energy transfer is basic to pericyclic reaction patterns.[6-8] The basic photochemical reaction of olefins, namely the [2 + 2] cycloaddition, is either a concerted process or goes on a triplet diradical mechanism, which depends on substrate and sensitizer. The [2 + 2] cycloaddition in particular is one of the most intensively investigated reactions since its detection at the beginning of the century.[13] Several photoinduced 1,3-dipolar cycloadditions proceed in the same way.[14] Many of these extremely common reactions have now been modified by changing reaction conditions so that electron transfer becomes predominant. Consequently, there is often a dramatic change in reactivity. This change is often accompanied by a loss in stereoselectivity, since the radical ions formed do not react according to pericyclic patterns.

Scheme 1. Some Typical Electron Acceptors and Donors[a]



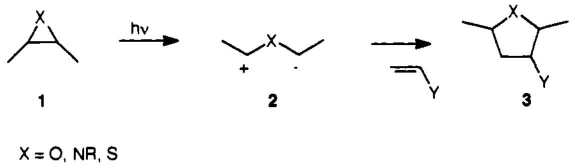
[a] For half-wave potentials and excitation energies see refs 2 (Part C, p 1), 57b, and our own references.

Besides classic energy-transfer chemistry, there exists today a great number of well-known photochemical cycloaddition reactions proceeding by electron transfer. In this review we hope to compare the different types of photocycloadditions in the light of either PET control or energy transfer and to discuss the influence of modern electron-transfer techniques on subsequent product formation. We draw the reader's attention to several new reviews on cycloadditions, some of which cover areas beyond the scope of this review.[15-23]

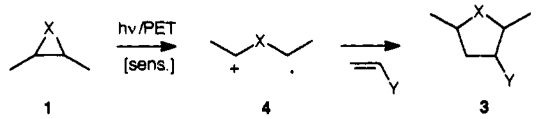
III. Reactivity Control and the Mode of Photocycloaddition Pathway Choice

We shall now discuss in more detail two reactions that exemplify the available electron-transfer options. A comparison of the recently developed [3 + 2] cycloaddition of azirines with the longer established 1,3-dipolar cycloaddition gives a good example of how the reactivity can be influenced. In the second part of this section we will discuss both energy- and electron-transfer control of possible cycloaddition modes for arene cycloadditions.

Scheme 2



Scheme 3



A. [3 + 2] Azirine Cycloadditions

The growing demand in the 1950s for an efficient synthesis of five-membered rings meant that the search to discover a convenient analogue of the Diels–Alder reaction was under way. In 1960 Huisgen formulated the concept of 1,3-dipolar cycloadditions.[24] Although there are many thermal approaches to generating 1,3-dipoles, the photochemical methods are limited. Generally, three-membered heterocycles such as **1** are opened to form the 1,3-dipole **2** (Scheme 2).

The ensuing reaction with a dipolarophile thus leads to a five-membered heterocycle **3**.[25] This process was investigated extensively using oxiranes and aziridines as well as azirines and has proved to be a useful preparative technique widely employed in organic synthesis. The reaction's main advantage is its high diastereoselectivity because the reaction is believed to be concerted,[26] although one disadvantage is its limited reactivity. Because of the impossibility of generating a 1,3-dipole from such a cyclopropane unit, this reaction proved to be useless in the synthesis of five-membered rings. In fact, the ring opening of these three-membered systems via PET leads not to dipoles but, via a one-electron oxidation, to radical cations which can be trapped by olefins under formation of carbocycles (Scheme 3).

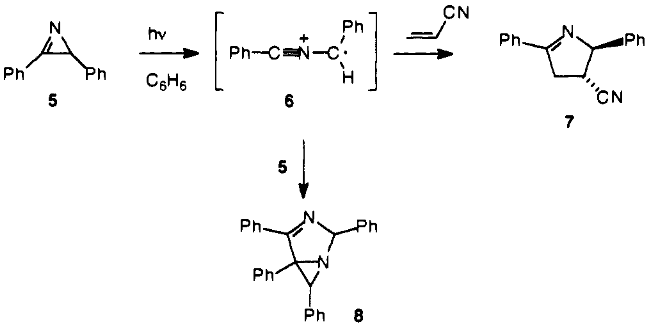
The oxidative ring opening is achieved by adding an electron-deficient sensitizer, e.g., an aromatic compound with electron-withdrawing groups. Among these, 1,4-dicyanonaphthalene (DCN) and 9,10-dicyanoanthracene (DCA) are the most common. The irradiation wavelength is chosen according to the sensitizer used, λ = 350 nm for DCN or λ = 450 nm for DCA. The sensitizers accept an electron from the substrate, thus opening the ring and forming a radical cation. The radical cation then reacts with a double bond. Due to the fact that this process is not concerted, there is no diastereoselectivity in the addition step. On the other hand, the high reactivity of the radical cation makes it a useful synthon.

In 1960, while completing his concept of 1,3-dipolar cycloadditions and as a first test of his theory, Huisgen published the first synthesis of the nitrile ylide system.[27] However, it was not until 12 years later that Padwa and Schmid showed that azirines can undergo photochemically induced electrocyclic ring opening.

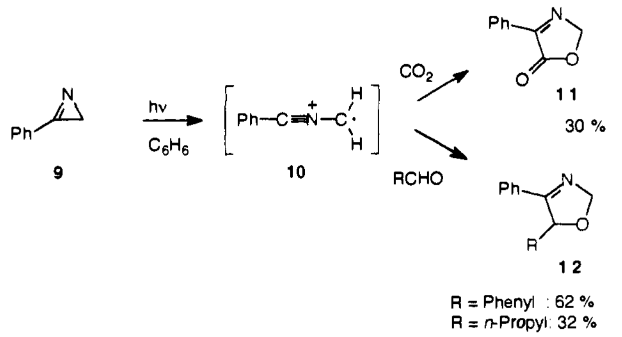
Table 1. Relative Reactivity of Olefins toward the Nitrile Ylide 6

dipolarophile	rel rate	dipolarophile	rel rate
methyl crotonate	1	dimethyl acetylenedicarboxylate	540
diphenylazirine	3	maleonitrile	2300
acrylonitrile	180	fumaronitrile	189000

Scheme 4



Scheme 5



Padwa showed that ylides react with olefins,[28,29] and by using Pyrex equipment, he succeeded in irradiating the n→π* transition only of the aryl-substituted azirine 5 (λ = 280 nm). The reaction proved to be highly diastereoselective, with the pyrrolidine 7 formed quantitatively in a diastereomeric excess of 80% (Scheme 4).

Reactivity studies[30] showed that only olefins with acceptor substituents react with the nitrile ylide. Otherwise, the ylide 6 was able to attack the C=N double bond of the unopened azirine 5, leading to a 1,3-diazabicyclo[3.1.0]hex-3-ene 8. Some reactivities are given in Table 1.

Trapping experiments gave no indication of an intermediate other than the nitrile ylide being involved,[31] and it is assumed that the addition to the nitrile ylide is simultaneous and not sequential.

Schmid investigated the nature of the nitrile ylide for the first time using low-temperature UV spectroscopy.[32] The 2,3-diphenylazirine ylide 6 has a strong band at λ = 350 nm. Investigations[33,34] show that ylides open according to first-order kinetics. Acrylonitrile acts as a scavenger with rate constants of about 10^6 dm^3 mol^{-1} s^{-1}.

The reactions of azirines with carbonyl compounds under photochemical irradiation have also been investigated.[35] 3-Oxazolines 12 were isolated in good yields, and on reacting with carbon dioxide only 4-phenyl-3-oxazolin-5-one (11) was formed (Scheme 5).

When imines were used as dipolarophiles, no cycloadduct was detected.[36] Due to the necessary short-wavelength irradiation, aliphatic azirines led to photofragmentation rather than to cycloaddition.[37]

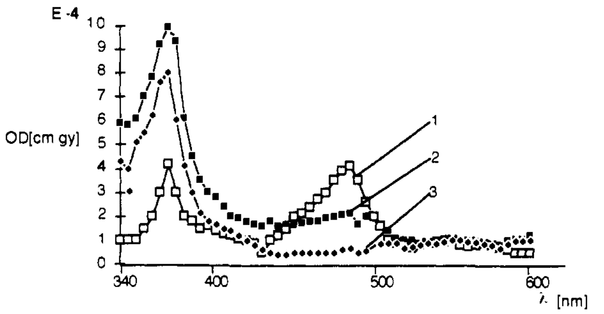


Figure 1. Electron pulse radiolysis spectrum of 5 (4 mM) in n-butyl chloride. Conditions: Van-de-Graaf generator, 3 MeV; pulse, 100 ns. Time windows: 1, 2.5–2.8 μs; 2, 3.5–4.0 μs; 3, 9.0–10.0 μs.

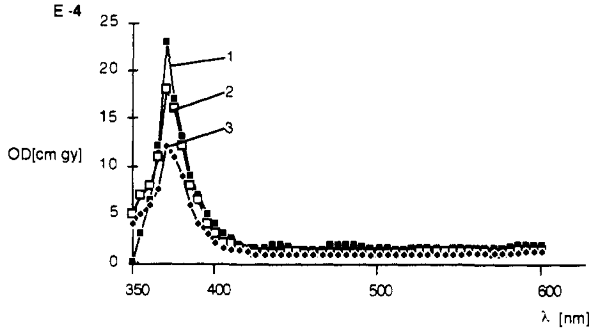


Figure 2. Electron pulse radiolysis spectrum of 5 (20 mM) and benzylidenepropylimine (2 mM) in n-butyl chloride. Conditions: Van-de-Graaf generator, 3 MeV; pulse, 100 ns. Time windows: 1, 2.9–3.1 μs; 2, 9.0–10.0 μs; 3, 90–100 μs.

These limitations led to the conclusion that a PET-sensitized ring opening of azirines might provide a useful synthon in the preparation of heterocycles in spite of a loss in diastereoselectivity. Irradiation of 2,3-diphenylazirine (5) with DCN as sensitizer in acetonitrile with an excess of acrylonitrile showed that both diastereomers of 7 were formed in a 1:1 yield.[38] Trapping with 2,2,2-trifluoroethanol showed the sequential addition of the olefin to a 2-azaallenyl radical cation intermediate 13 (Scheme 6).

Compound 16 is not detectable if there is no PET catalyst. The lifetime and kinetics of 13 have been determined by electron pulse radiolysis[39] (see Figure 1). The UV absorbance of the 2-azaallenyl radical cation of 5 is λ = 485 nm, whereas the ylide absorbs at λ = 350 nm. The lifetime of this radical cation is about 1.4 μs. The structure of the radical cation was calculated as being linear shaped.[40] The radical is scavenged by benzylidenepropylimine with a rate constant of 7.8 × 10^9 dm^3 mol^{-1} s^{-1} in n-butyl chloride, which is much faster than the ylide 6 (Figure 2). The PET-induced cycloaddition of azirines 17 with imines leads to N-substituted imidazoles 19a–e in reasonable yields. Under PET conditions the intermediate, a dihydroimidazole, could not be detected as it was oxidized directly to the imidazole. Due to the imines being less reactive, the 2-azaallenyl radical cations also react to give 1,3-diazabicyclo[3.1.0]hex-3-ene compounds in a side reaction (Scheme 7; Table 2). Since irradiation (λ = 350 nm) is only performed to excite the DCN and not the azirine, it is also possible to use aliphatic azirines as starting compounds.

Scheme 6

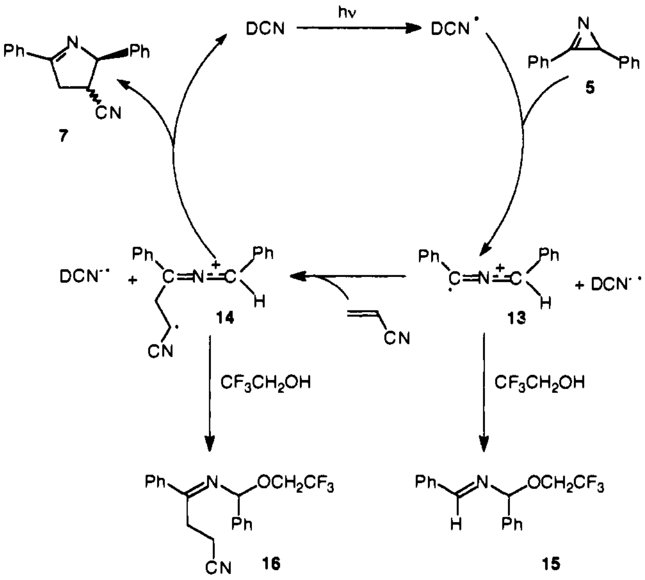


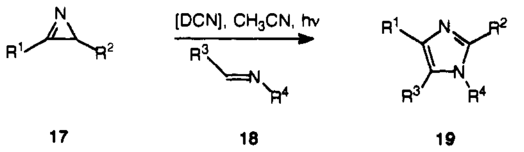
Table 2. Yields of Imidazoles Synthesized by PET-Induced [3 + 2] Cycloaddition of Azirines with Imines

compd	R^1	R^2	R^3	R^4	yield, %
19a	phenyl	phenyl	phenyl	*n*-propyl	87
19b	phenyl	phenyl	*p*-anisyl	*n*-propyl	82
19c	phenyl	H	*n*-propyl	*n*-propyl	35
19d	*n*-butyl	H	*n*-propyl	*n*-propyl	40
19e	phenyl	CH_2OH	*n*-propyl	*n*-propyl	32

Table 3. Yield Dependence of Ring Size for Imidazolophanes and Pyrrolophanes

bridge size *n* (methylene units)	yield of imidazolophane, %	yield of pyrrolophane, %
4	0	0
5	2	9
6	27	56
10	9	20

Scheme 7



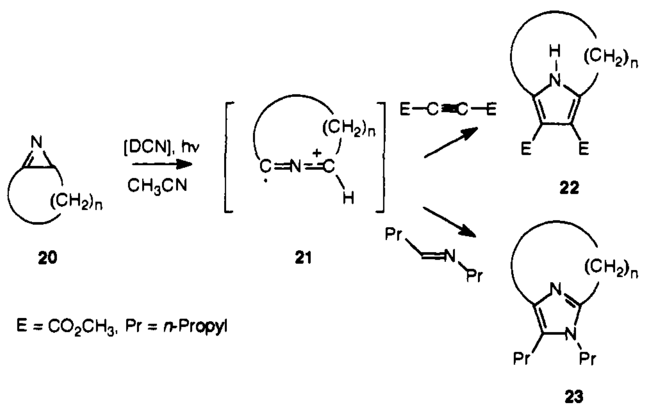
Under analogous conditions, bicyclic azirines **20** are synthons in the synthesis of heterophanes.[41] Imidazolophanes **23** can also be prepared but in smaller yields. Pyrrolophanes **22** give substantially better yields (Scheme 8).

Very small bridges are not available using this procedure. The minimum size available is five methylene units. The yields are best for medium sized rings (Table 3).

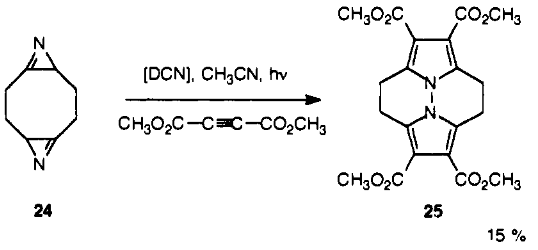
The PET-sensitized reaction of a tricyclic azirine **24** does not lead to a similar [2,2]pyrrolophane but instead to the 8a,8b-diazacyclopent[*f*,*g*]acenaphthene derivative **25** through closure of an N–N bridge (Scheme 9).

A tetracisazirine derived from 1,4,7,10-cyclododecatetrone can be transformed by four sequential [3 + 2] cycloadditions with dimethyl acetylenedicarboxylate under PET conditions to a porphyrinogen, which is oxidized in situ to a porphyrin octamethyl ester.[42]

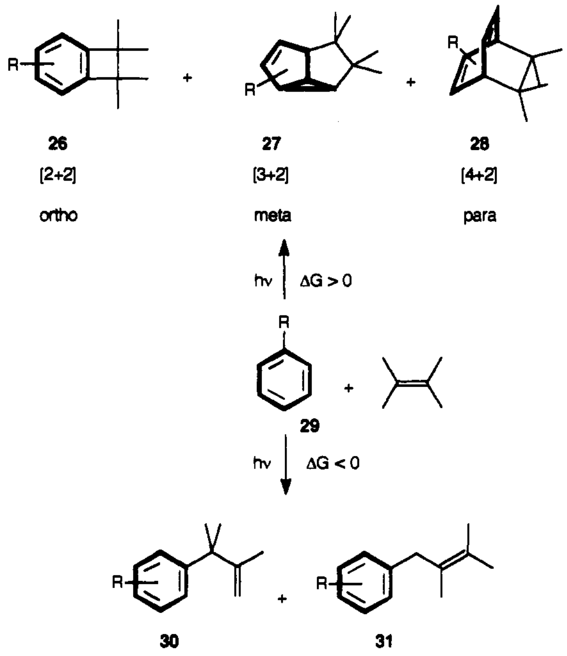
Scheme 8



Scheme 9



Scheme 10

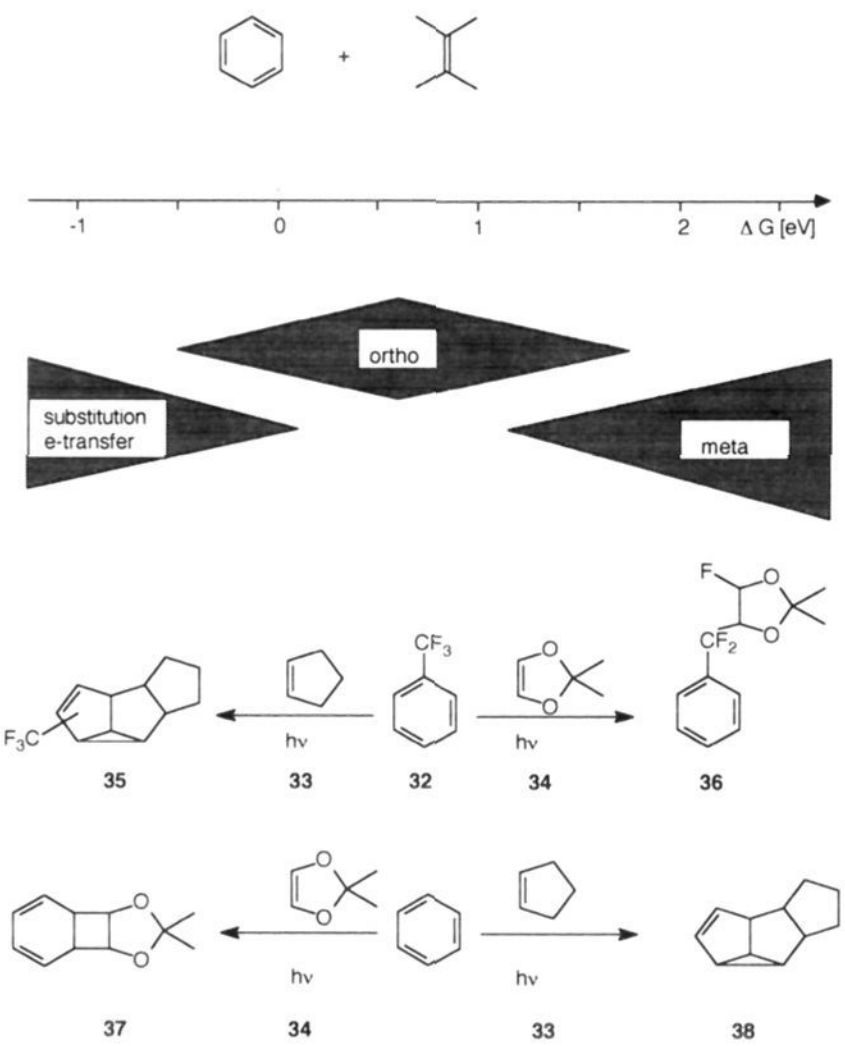


In summary, these examples show that the reactivity of azirine synthons in [3 + 2] cycloadditions can be controlled either by energy transfer or electron transfer. Although the scope of these cycloadditions is restricted to aryl-substituted azirines in the former case, PET provides a new route to various types of heterocycles including new heterophanes.

B. Arene Photocycloadditions

The photocycloaddition of arene compounds to olefins varies somewhat from the other reactions reviewed in this paper (Scheme 10): Arenes **29** can be added to alkenes in a [2 + 2] cycloaddition (ortho) to give **26**, in a [3 + 2] cycloaddition (meta) to give **27**, and

Scheme 11



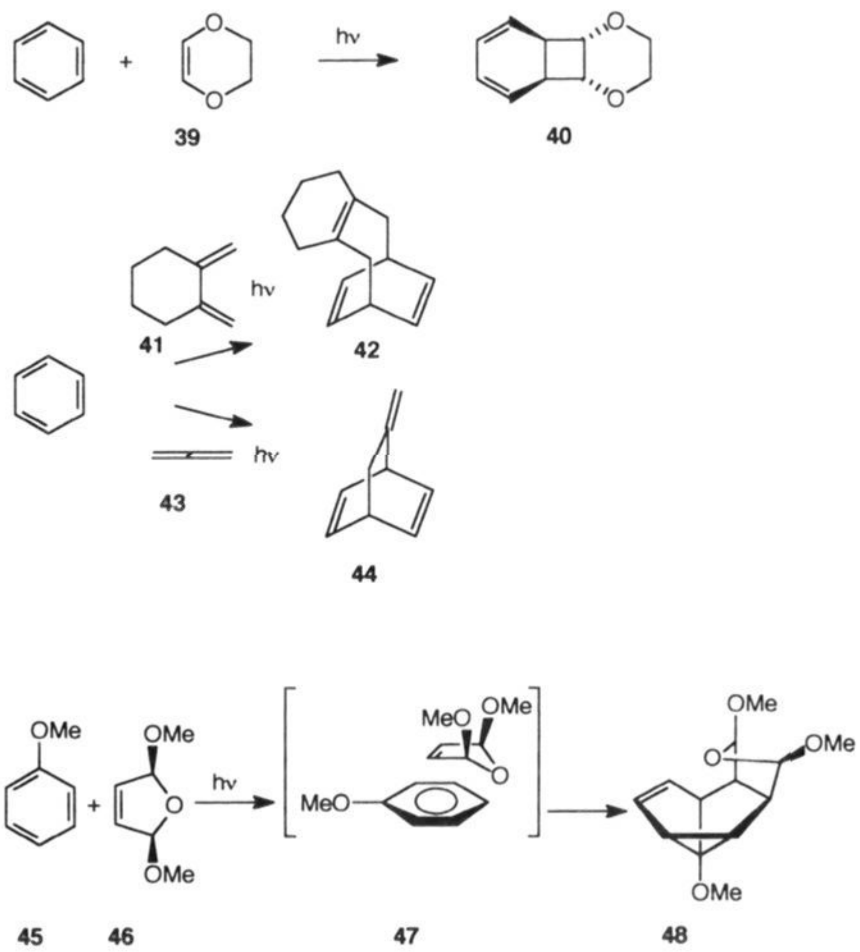
sometimes even in a [4 + 2] cycloaddition (para) to give **28**. In addition to these cycloadditions, the substitution reaction leading to **30/31** also occurs. Several reviews covering arene photocycloadditions have appeared in the literature.[3,4,19,43–45]

If the ΔG calculated from eq 2 is negative and electron-transfer conditions prevail, the substitution path is preferred.[46] For electron-rich olefins, if the value of ΔG becomes positive up to ca. 1–1.5 eV, then the ortho addition process becomes possible.[47] For example, the reaction of benzene with dioxene **39** leads only to the ortho adduct **40**.[48] A positive free enthalpy greater than about 1.5 eV nevertheless strongly indicates the formation of the meta adduct. This empirical correlation between the ΔG values of electron transfer calculated according to the Weller equation and the choice of reaction modes is shown schematically in Scheme 11. Two examples will serve to clarify how changing the olefin can affect the applicability toward the reaction mode (cycloaddition, **35**, vs substitution, **36**) and the mode of cycloaddition (ortho cycloaddition, **37**, vs meta cycloaddition, **38**). Further examples are discussed in the literature.[43,46,47]

Because of its empirical character, the ΔG correlation should only be applied to reactions within a substrate series. It is independent, whether or not a particular exciplex is actually involved in the photoreaction between the arene and the olefin. Despite this lack of a molecular basis, the ΔG correlation is important in classifying known reactions and in predicting new ones. It is surprising that even with benzonitrile such a correlation can be developed including the [2 + 2] cycloaddition to the cyano group.[47,49]

There are only a few cases where the para adduct is formed. Where the conjugated olefins **41** or the allenes **43** are the cycloaddition substrates, irradiation gives **42** and **44** as the major products (Scheme 12).[50a]

Scheme 12



Gilbert[50b] and Cornelisse[51] have studied the photocycloaddition of conjugated dienes to benzene rings. Apart from the interesting mechanistic aspects, the meta addition is by far the most important arene photocycloaddition due to the fact that it is the only route by which such products can be formed.[3a,43–45]

The diastereoselectivity of meta photocycloadditions has recently been studied.[52] There is strong evidence that stereoselectivity is controlled during the reaction of the olefin with the excited arene (eventually via an exciplex **47**) in such a way that the electron-donating groups in a system such as **45/46** are directed as far away from each other as possible.[52] The nature of the products supports the view that a molecular recognition step is involved in the excited state. The electron-rich methoxy group in anisole is incorporated into position 1 of the meta adduct. The new anellated ring in **48** is preferentially formed in the endo position.

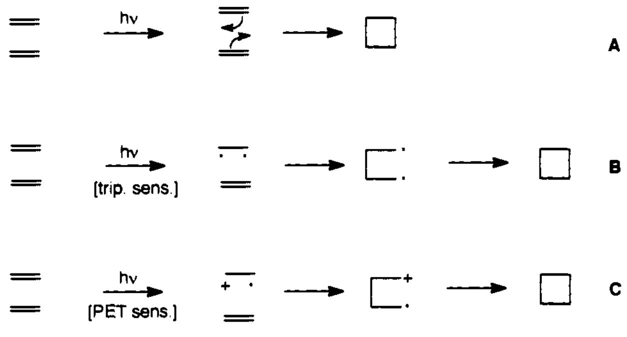
Many complex natural products can only be synthesized by meta photocycloaddition. Cedrene[53a] and more recently Laurene[53b] have been prepared. The substitution process has been recently investigated using both DCN and phenyl ethers.[54]

Arene photocycloadditions are representative of cycloadditions to all common ring sizes, from three- to six-membered rings. Together with electron transfer controlled substitution reactions they represent another example of how the free enthalpy controls the reaction pathway.

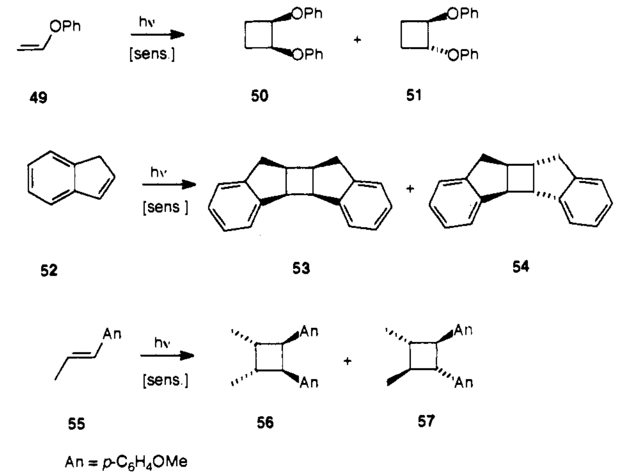
IV. [2 + 2] Cycloadditions

The [2 + 2] cycloaddition is often the first choice in the synthesis of four-membered rings. Thermal [2 + 2] cycloadditions are limited in both scope and usefulness.[55] Most olefins, acetylenes, and carbonyl compounds are susceptible only when photochemical irradiation is involved. Whereas the concerted process via the first excited singlet state of one starting

Scheme 13



Scheme 14



compound (path A, Scheme 13) is only of theoretical interest, the more common method involves triplet states and proceeds at least in two steps via a biradical species (path B).[56]

The introduction of photoinduced electron transfer made the use of [2 + 2] cycloadditions more attractive. Both reactivity and regioselectivity were greatly improved. The process is similar to that outlined in section III. A sensitizer such as DCN or DCA capable of PET oxidations is irradiated and accepts an electron from the olefin. The radical cation generated adds to the olefin, and through a back electron transfer or a chain mechanism such as electron transfer from the cyclobutane radical cation to another olefin molecule, the cyclobutane is formed (Scheme 13, path C).[57]

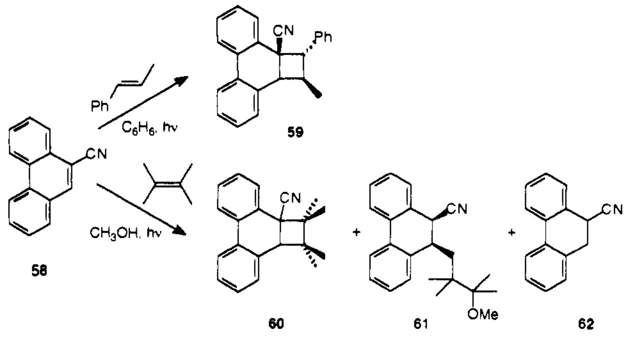
In this section we will first discuss the reactions of olefins including aryl olefins, followed by enone cycloadditions, and finally the reactions of carbonyl compounds in the Paternò–Büchi reaction.

A. [2 + 2] Olefin Cycloadditions

1. [2 + 2] Cycloadditions Involving Phenyl Vinyl Ether, Indene, and Anethole

The reactions we are about to discuss have one feature in common: they are all [2 + 2] cycloadditions which can occur through either energy or electron transfer, differing only in their diastereoselectivity. The reaction of phenyl vinyl ether was studied by Shigemitsu.[58] Using acetophenone as a triplet sensitizer, 7% of the cis adduct **50** and 6% of the trans adduct **51** are formed (Scheme 14).[59] Using DCA as a PET catalyst changed the yield to 30% **50** and 25% **51**.[59] This dimerization was shown to proceed via radical cation intermediates, probably via a chain mechanism.[60]

Scheme 15



The indene case is a good example of a PET-controlled reaction with high diastereoselectivity.[61,62] The anti head-to-head adduct **54** is formed in a diastereomeric excess of 96%. When dicyanobenzene (DCB) is used as a catalyst, there is no head-to-tail dimer formation.[63] On the other hand, under energy-transfer conditions the ratio of **54** decreases to 84% with benzophenone as sensitizer and to 70% by direct irradiation via S_1 and T_1.[63]

The reactions of anethole **55** were investigated by Nozaki[64] in the energy-transfer case and by Lewis[65] in the PET case. Good selectivities are observed in either direction. The direct irradiation leads exclusively to the cis isomer **56** in 35% yield, as well as recovered anetholes (cis/trans isomers). The irradiation with 9-cyanoanthracene (CA) as the PET sensitizer yields **57** in 33% yield with a diastereomeric excess of 95%.

2. Reactions of 9-Cyanophenanthrene

In this reaction electron transfer leads to different product formation than the energy-transfer pathway. Direct irradiation of 9-cyanophenanthrene (**58**) in benzene produces an exciplex with β-methylstyrene with a very high diastereoselectivity (diastereomeric excess >98%), leading to the cyclobutane adduct **59**.[66] The PET reaction with 2,3-dimethyl-2-butene, in methanol, however, leads to the formation of the substitution product **61** (20–30%) and the dihydrophenanthrene **62** (50%) as well as the cycloadduct **60** in only 10% yield (Scheme 15). **58** is supposed to react here as an electron acceptor with 2,3-dimethyl-2-butene, thus giving **61** and the reduced dihydrophenanthrene **62**.[67]

B. Enone [2 + 2] Photocycloadditions

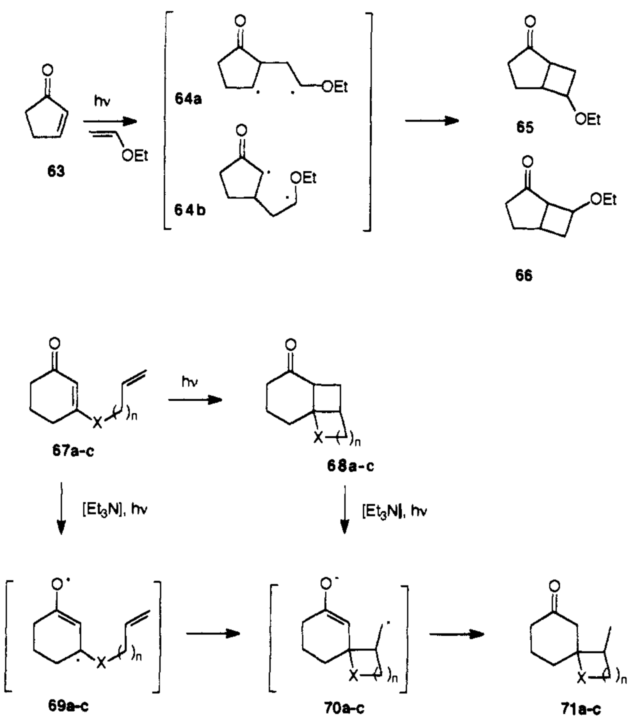
The chemistry of enone [2 + 2] photocycloadditions has been thoroughly reviewed.[17,68] Only the latest developments in energy- and electron-transfer-induced [2 + 2] cycloadditions of enone systems will be presented here.

The direct irradiation reaction of enone **63** has been shown to proceed via a 1,4-diradical intermediate, according to path B discussed in the introduction of this section. The intermediates **64a**/**64b** (1:1) were trapped using hydrogen selenide.[69] Weedon showed that although the head-to-tail isomer **65** is preferentially formed, if the alkene is electron rich, both diradicals are formed in roughly the same yield (Scheme 16).[70] These results imply that, at least for the reaction of **63** with ethyl vinyl ether, the regiochemistry of enone cycloaddition is not governed by the orientation of the

Table 4. Yields of Cycloadducts at Direct Irradiation and of Spirocyclic Products under PET Conditions

compd	X	*n*	irradiation conditions	[2 + 2] adduct 68, %	spiro adduct 71, %
67a	O	2	direct	82	
67a	O	2	PET		50
67b	O	3	direct	70	
67b	O	3	PET		53
67c	CH_2	2	direct	95	
67c	CH_2	2	PET		40

Scheme 16



reactant in the exciplex precursor as has long been assumed ("Corey's hypothesis"). It appears that it is the relative efficiency of cyclobutane formation and the subsequent cleavage to the precursors which determine the regioisomer ratio (Table 4).

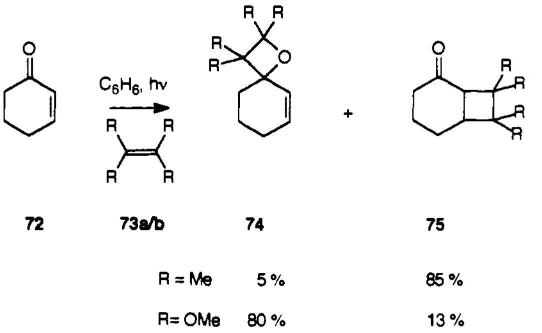
When enones undergo the PET reaction instead of the oxidative process discussed in section IV.A, a reductive process involving an amine as both the electron donor and reduction agent occurs. The irradiation of cyclohexenone with triethylamine produces a radical anion which recombines with the amine radical cation to form a β-(ethylamino) ketone.[71]

This method has been used for intramolecular enone–olefin systems.[72,73] Whereas under energy-transfer conditions only the cyclobutanes **68a–c** are formed, irradiation in acetonitrile with the donor triethylamine leads to spirocyclic products **71a–c** either directly or via **68** and **70**.

The intermolecular [2 + 2] cycloaddition under PET conditions produces some interesting as well as useful new features. When cyclopentene was added to a cyclohexenone derivative in acetonitrile/triethylamine, a new route to the biologically important hirsutene backbone was found. The cyclobutane rearranges to the three-anellated cyclopentane system.[73]

Recently, Maruyama showed that under certain conditions a PET-promoted [2 + 2] cycloaddition between 1,4-naphthochinones and electron-rich alkenes is also possible.[74]

Scheme 17



Margaretha and co-workers irradiated cyclohexenone **72** with either 2,3-dimethyl-2-butene **73a** (R = Me) or tetramethoxyethylene **74b** (R = OMe) and isolated a cyclobutane adduct **75** with a selectivity of 19:1 and an oxetane **74** with a selectivity of 6.1:1, respectively (Scheme 17).[75] The authors assume that the mechanism involves the formation of an exciplex from the triplet sensitized enone and, preferably, an olefin such as **73a**, leading to **75**. On the other hand, the enone can accept an electron from the electron-rich olefin **73b** (ΔG strongly negative), which under PET conditions leads preferentially to oxetane formation.

C. [2 + 2] Cycloadditions with Carbonyl Compounds

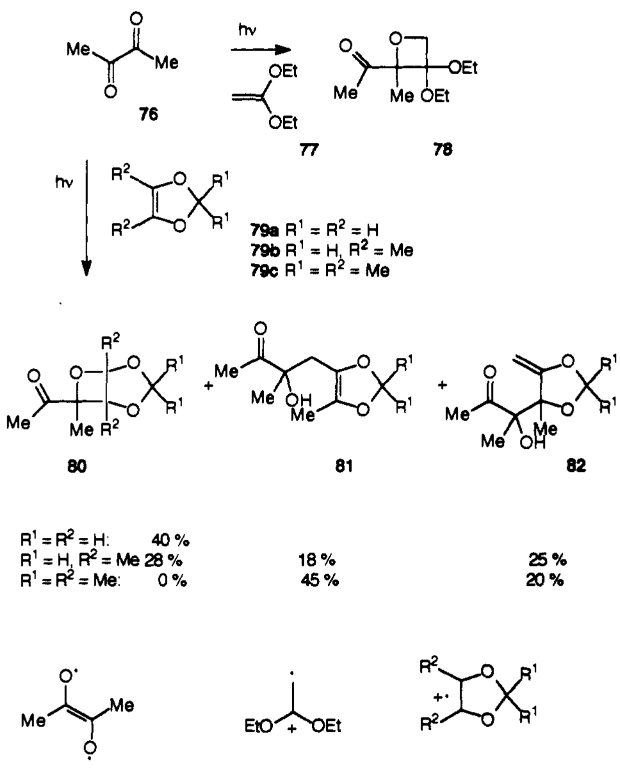
1. Paternò–Büchi Reaction

The reaction of cyclohexenone **72** and either **73a** or **74b** described above lies somewhere between a [2 + 2] cycloaddition with olefins and the Paternò–Büchi reaction. We will now show how PET reactions have extended the synthetic potential of both the Paternò–Büchi reaction and related reactions with imines and nitriles.

The Paternò–Büchi reaction has been well reviewed and its mechanism thoroughly studied.[76] Scharf has recently proposed the "isoinversion principle" for predicting the stereoselectivity of this and other stereoselective reactions with chiral substituted carbonyl compounds and alkenes, respectively.[77] Other stereoselective Paternò–Büchi reactions involve the use of ketene *S,S*-dithioacetals as the olefin components[78] and trimethyl silyl enol ether functionalization at the olefin side.[79] Turro used adamantone derivatives as the rigid carbonyl components.[80] Griesbeck has recently proposed electron transfer as a selectivity condition in the Paternò–Büchi reaction.[81]

Perhaps the best established example of the influence of electron transfer in Paternò–Büchi reactions is the case of 2,3-butanedione (**76**).[82] Two factors should be taken into consideration. First, with 1,1-diethoxyethene (**77**) only one regioisomer, **78**, is formed. This is explained by "polarity reversal of the reactivity through photoinduced electron transfer".[83] With 1,3-dioxoles **79**, more reduction products **81**/**82** are formed depending on the ΔG of electron transfer. For example, with **79a** ($E^{\mathrm{Ox}}_{1/2}$ = 0.76 V vs $Ag/AgNO_3$) only cycloadducts are formed (oxetane **80** in addition to a 1,4-dioxene adduct) whereas with **79c** (0.42 V) only reduction to **81** and **82** is observed (Scheme 18). Due to its intermediate oxidation potential **79b** (0.48 V) gives mixtures of all products **80–82**.[82]

Scheme 18



The reactive intermediates involved have been detected by ESR spectroscopy. The 1,3-dioxole donates an electron to the butanedione. Both the dioxole radical cations 85 and the butanedione radical anion 83 have been detected. The electron transfer is then followed by substitution and proton transfer from a methylene group of the dioxole. Finally, the diketone is reduced to an α-keto alcohol. The high regioselectivity observed in the reaction of 76 and 77 can be explained by coupling of the intermediate radical ions 83 and 84 via the corresponding atomic centers with the highest spin densities (the oxygen of 83 and CH_2 of 84).[82,83]

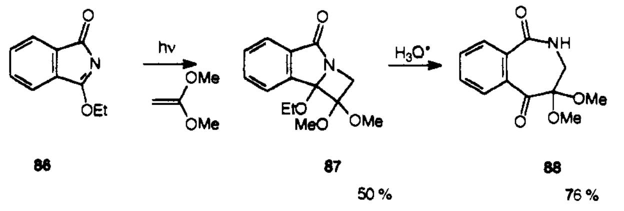
Similar observations have been made for benzophenone, whereas the Paternò–Büchi reaction of benzyl and dioxoles yields only oxetanes.[84]

2. [2 + 2] Cycloadditions with Nitriles, Imides, and Imines

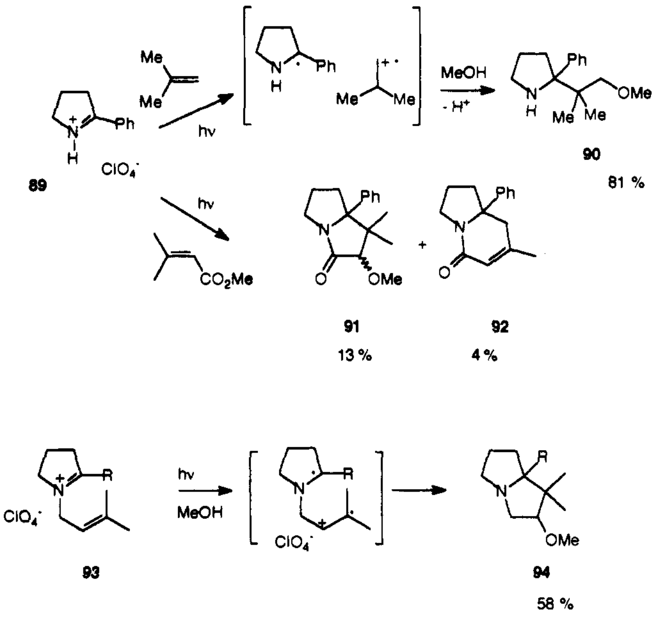
Photocycloadditions to various C–N functional groups have also been investigated for both the energy- and the electron-transfer paths.

A good example of a PET reaction is the well-studied imine/iminium salt reaction. Mariano has reviewed this topic.[85] Although triplet reactions of compounds such as 86 and 1,1-dimethoxyethene lead via [2 + 2] cycloadducts like 87 to azepinediones 88, the reaction is not widely used (Scheme 19).[86] On the other hand, the PET approach leads to a multitude of reactions, including several useful cycloadditions. The irradiation of the iminium salt 89 in the presence of an isobutene leads to an electron transfer from the olefin to the iminium group with an iminium radical and an olefin radical cation resulting. The anti-Markovnikov addition of methanol and recombination lead to 90 in high yield. With β,β-dimethyl-acrylate, poor yields of two cycloaddition products, 91 and 92, are formed (Scheme 20).[87]

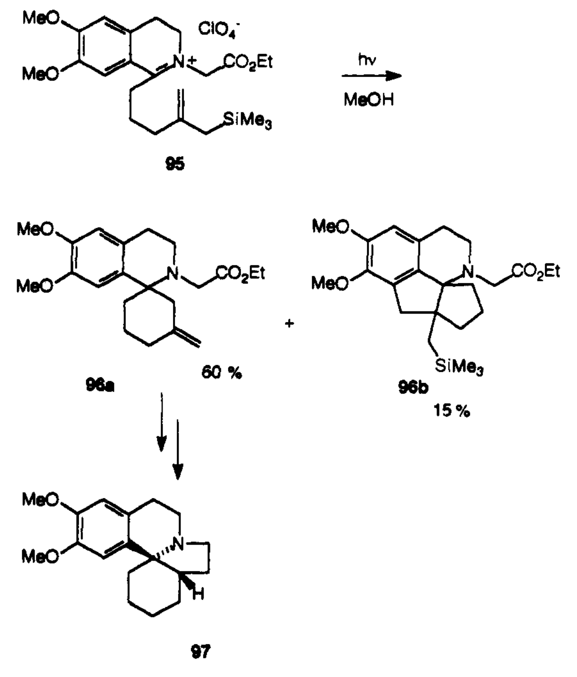
Scheme 19



Scheme 20



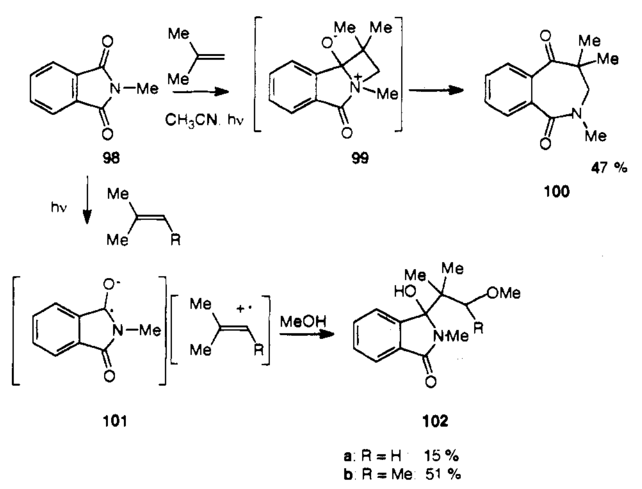
Scheme 21



The intramolecular cyclization of 93, leading to 94, proceeds in much better yield.[88] A nine-step synthesis of the erythrinane alkaloid 97 from 95 using PET cyclization gives an overall yield of 7.8%.[89] This reaction shows a remarkable solvent dependence. In acetonitrile 96b is formed in 24% yield in addition to 23% of 96a (Scheme 21).[89b]

N-Methylphthalimide 98 is another good starting material for comparative photocycloadditions and

Scheme 22



related reactions. The selectivity of these reactions can be rationalized using the Weller equation.[90a,91]

If the reaction proceeds under energy-transfer conditions ($\Delta G > 0$), an azepinedione **100** is formed, possibly via an exciplex and a [2 + 2] cycloaddition intermediate.[90] On the other hand, a negative free enthalpy leads to electron transfer on irradiation and to reduction products **102** similar to those formed in the butanedione reaction. For example, alkenes such as 1-pentene yield only azepinediones due to their high oxidation potentials. Isobutene is an intermediate case because of a slightly positive ΔG (cf. Scheme 22). The introduction of another methyl group (2-methyl-2-butene) shifts ΔG into the exergonic region. Consequently, electron-rich alkenes of this type form photoreduction products of the type **102** exclusively.[91a] In this case, the involvement of radical ion pairs has been shown.[91b] Reactions of this type have been recently extended to other imides[91c,d] as well as to [3 + 2] cycloadditions with cyclopropanes.[91e]

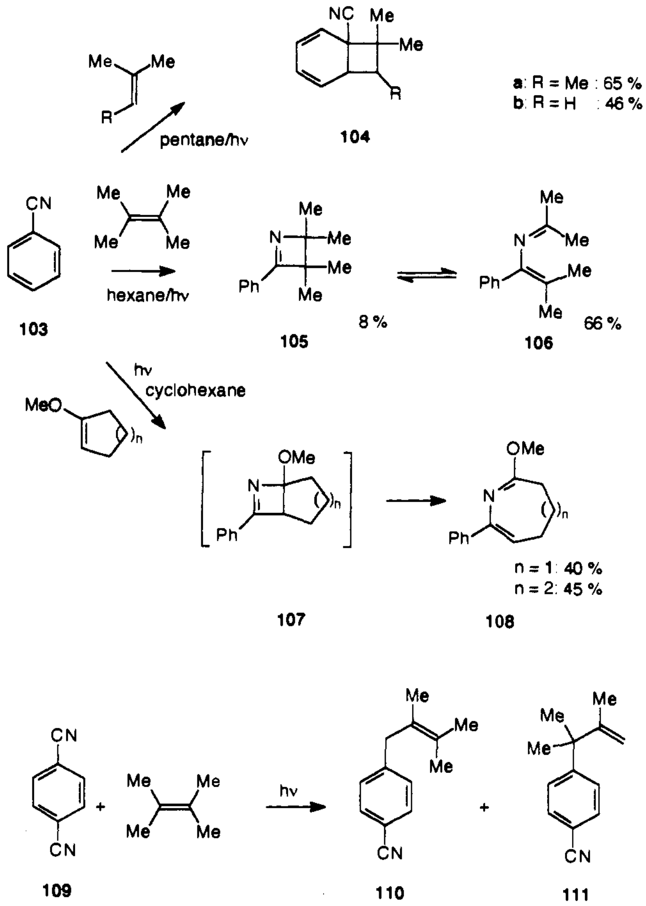
Finally we will discuss the nitrile group using benzonitrile as the substrate but without going into its potential as a partner in meta photocycloadditions. Here we will focus on three types of reactions where the selectivities also strongly depend on the free enthalpy of electron transfer. Cycloaddition to either the arene ring or the nitrile group leads to the bicyclo[4.2.0]-octadienes **104** and azetines **105** or the 2-azabutadienes **106**/**108** (Scheme 23). Substitution in the aromatic moiety yields products of the type **110**/**111**.[49]

The latter process is only observed if $\Delta G < 0$ and requires strong electron acceptors such as dicyanobenzene **109**. Besides the typical substitution products **110** and **111**, olefin dimerization products are also formed.[92a] In the endergonic region, however, azetines and ortho cycloadducts are produced.[49,92b] Here again ΔG controls the cycloaddition mode with 2,3-dimethyl-2-butene and cyclic enol ethers azetines **105** and 2-azabutadienes **106**/**108** only are formed due to ΔG = 0.1–0.3 eV, whereas isobutene and 2-methyl-2-butene mainly yield bicyclo[4.2.0]octadienes **104** ($\Delta G > 0.8$ eV).[47,49] It remains to be seen whether or not this ΔG selectivity also applies in the case of other nitriles.

D. Cycloreversions

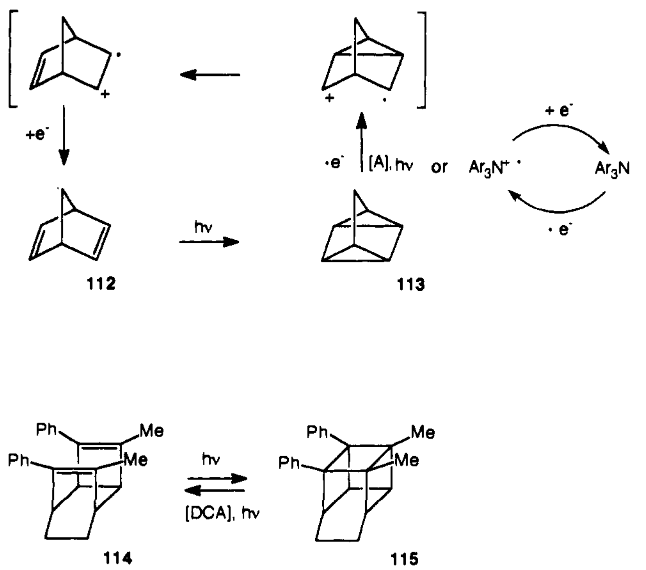
The [2 + 2] cycloreversion of cyclobutane, cyclobutene, and related systems is of interest not only because it is a theoretically interesting and useful reaction but also because it is the biological process involved when UV-radiation damaged DNA is reconstructed and for storage model systems of solar energy.[93] Basically, cycloreversion is the opposite of cycloaddition. In such cases, the energy-transfer-induced [2 + 2] cycloaddition is reversed through an electron transfer. It goes without saying that this is by no means a kind of *perpetuum mobile*. The norbornadiene **112**–quadricyclane **113** system, however, has been investigated in depth from a theoretical point of view[94] as well as from the point of view of a potential energy storage system (Scheme 24).[95]

Scheme 23

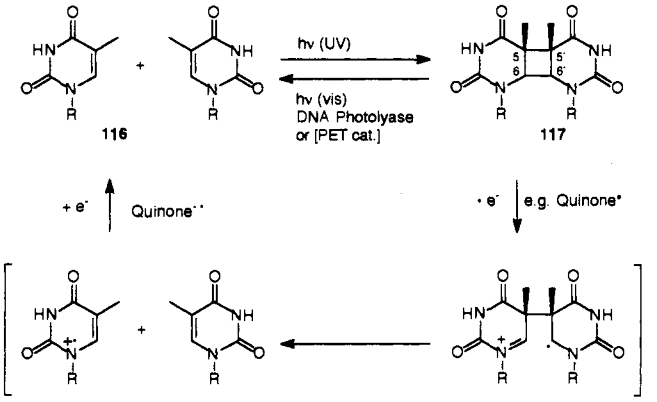


The intramolecular energy controlled cycloaddition reaction proceeds via excited singlet and triplet states.[94c] Until Roth's fundamental CIDNP studies,[94] the interconversion of **112** and **113** via their radical cations remained controversial. He provided strong evidence that two discrete radical cations with lifetimes greater than several nanoseconds are derived from **112** and **113**. In contrast, the triplet energy surface shows only one minimum, which explains its different reactivity. Norbornadiene **112** is readily converted via the triplet state to quadricyclane **113**, whereas the radical cations show conversion in the opposite direction only. These results prompted Jones and co-workers to search for efficient electron-acceptor catalysts for the **113** → **112** conversion.[96] They found an interesting solvent dependence indicating the involvement of different types of solvated ion pairs (contact ion pairs as well as solvent-separated ion pairs). The highest quantum yield obtained was for 1,2,4,5-tetracyanobenzene (Φ = 0.18). Recently, Gassman et al. developed an electrochemical "switch"

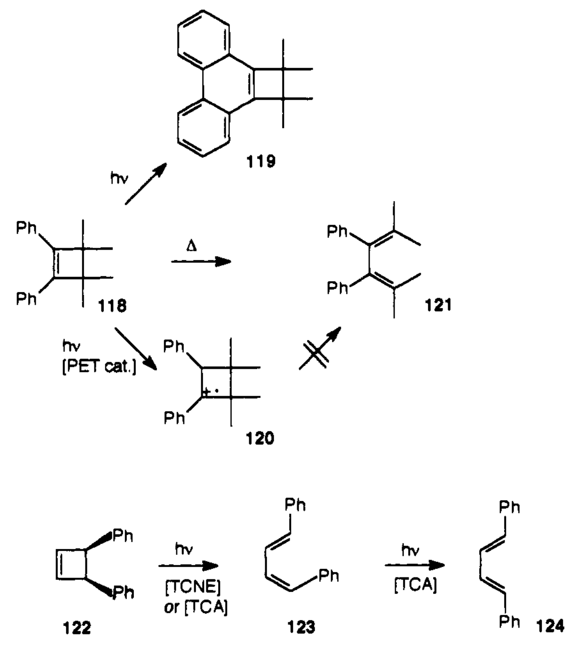
Scheme 24



Scheme 25



Scheme 26



TCA = 2,6,9,10-tetracyanoanthracene

for the controlled release of the thermal energy of 113 by using a triarylamine–triarylaminium radical cation pair.[97]

The ring-opening cycloreversion reactions of arylated cage molecules have been reported by Hasegawa, Yamashita, and co-workers.[98] The cage compound 115 previously prepared from the diene 114 by direct irradiation at λ = 300 nm can also be opened by photosensitization using various cyanoarenes. The isomerization, when carried out in nonpolar solvents, is one of few examples of an adiabatic exciplex mechanism. It behaves, in fact, similarly to the hexamethyl Dewar benzene system. On the other hand, in a polar solvent such as acetonitrile, 115 isomerizes to 114 via an electron-transfer mechanism. Since the conversion rates for both cycloaddition and cycloreversion are near 100%, the system appears to be a promising potential solar energy store.

UV damage in DNA is mainly due to the [2 + 2] cycloaddition of pyrimidine 116, which can be reversed in biological systems by DNA photolyase and in model systems by electron-transfer catalysis.[99] An elegant experiment using uracil photodimers linked with a β-idoethyl radical unit clearly showed that the fragmentation of $117^{\bullet+}$ (Scheme 25) proceeds stepwise through sequential cleavage of the 6,6′ and 5,5′ bonds;[99b,c] CIDNP studies showed this to be the case.[94b] In nonenzymatic systems, both the electron-abstraction and electron-transfer mechanisms involving photodimer–radical anions can operate.[99e]

Whereas the cycloreversion of cyclobutanes leads to the separated olefin components, the cycloreversion of cyclobutenes should lead to butadienes. Although this reaction has been thoroughly investigated not only from a theoretical point of view[94b,100] and in frozen media[101] but also using mass spectroscopy,[102] it had not been examined as a potential synthetic process in solution. Schuster found that this process is in fact possible using thermochemical means.[103] Photochemical irradiation under energy-transfer conditions afforded the phenanthrene derivative 119 (Scheme 26). Nevertheless, conversion or the cyclobutene radical cation 120 to a butadiene radical cation was not possible.

Miyashi and co-workers were the first to open a cyclobutene radical cation in solution.[104] The irradiation of cis-cyclobutene 122 with tetracyanoethylene led, via a stereospecific conrotatory electrocycloreversion, to *cis,trans*-butadiene 123. The selectivity was controlled by a charge-transfer complex. Using TCA as a catalyst afforded the same butadiene in an electron-transfer process and, on prolonged irradiation, *trans,trans*-butadiene 124. In this case, no CT absorbance was observed, and the lack of stereoselectivity makes a PET process likely. Kochi has used this process for generating dienes in PET-promoted [4 + 2] cycloadditions (see section VI.C).[105]

V. [3 + 2] Cycloadditions with Three-Membered Rings

We will expand our discussion in section III to cover other [3 + 2] cycloadditions performed under energy or electron transfer.

A. [3 + 2] Cycloadditions with Oxiranes

Although the preparation of carbonyl ylides from oxiranes is possible under thermal conditions,[106] the

Scheme 27

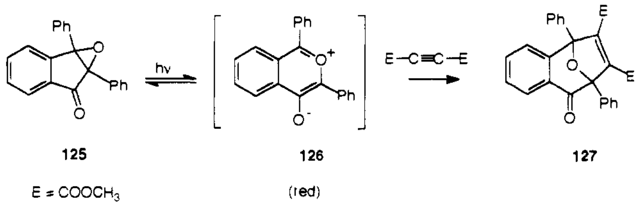
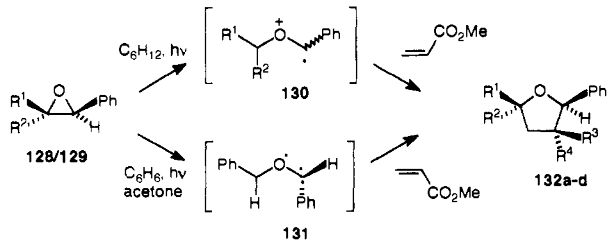


Table 5. Adduct Yields with and without Acetone as Sensitizer

stilbene oxide	solvent	total adduct yield, %	rel adduct ratios, % 132a	132b	132c	132d
128	cyclohexane	20	17	5	36	24
129	cyclohexane	18	61	26	6	7
128	benzene/acetone	99	23	10	40	27
129	benzene/acetone	99	23	10	40	27

Scheme 28



128 : $R^1 = Ph$, $R^2 = H$ **129** : $R^1 = H$, $R^2 = Ph$
132a: $R^1 = H$, $R^2 = Ph$, $R^3 = CO_2Me$, $R^4 = H$
132b: $R^1 = H$, $R^2 = Ph$, $R^3 = H$, $R^4 = CO_2Me$
132c: $R^1 = Ph$, $R^2 = H$, $R^3 = CO_2Me$, $R^4 = H$
132d: $R^1 = Ph$, $R^2 = H$, $R^3 = H$, $R^4 = CO_2Me$

synthetic potential is limited due to the substitution pattern. Irradiation of an indenone-2,3-oxide **125** leads to the formation of the carbonyl ylide **126** through a reversible photochromism.[107] The carbonyl ylide can be trapped using dimethyl acetylenedicarboxylate to yield **127** (Scheme 27). Cyclopentadienone oxides behave similarly.[107b]

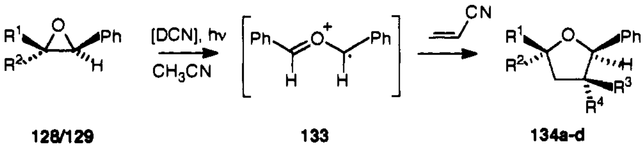
Direct irradiation and the triplet sensitized reaction of *cis*- and *trans*-stilbene oxide **128/129** have been investigated.[108a] The direct irradiation (λ = 254 nm) of **128/129** leads to the tetrahydrofuran adducts in poor yield due to competitive reactions such as the formation of deoxybenzoin (Scheme 28). What is remarkable is the retention of the stilbenoxide stereochemistry. This is a result of an allowed photochemical disrotatory opening of the stilbene oxide, leading to a planar carbonyl ylide **130** whose geometry is preserved through resonance delocalization.

The sensitized reaction occurring in a solvent–acetone mixture leads to a stilbene oxide in its triplet excited state. If this forms an orthogonal biradical **131**, then steric information cannot be transferred to the substrate. In this case the yield of cycloadducts is quantitative with no formation of side products (Table 5). In an independent study, Griffin and co-workers generated acyclic carbonyl ylides from a series of dicyanooxiranes which were trapped with simple alkenes such as *cis*- and *trans*-2-butene.[108b] Both the thermal and the photochemical ring-opening processes occur with retention of alkene configuration. Unsymmetric alkenes give high regioselectivities.

Table 6. Adduct Yields with and without DCN as Sensitizer

stilbene oxide	sensitizer	total adduct yield, %	rel adduct ratios, % 134a	134b	134c	134d
128	none	23	48	44	4	4
129	none	25	7	3	50	40
128	DCN	100	47	40	6	7
129	DCN	100	38	32	16	16

Scheme 29



128 : $R^1 = Ph$, $R^2 = H$ **129** $R^1 = H$, $R^2 = Ph$
134a: $R^1 = Ph$, $R^2 = H$, $R^3 = CN$, $R^4 = H$
134b: $R^1 = Ph$, $R^2 = H$, $R^3 = H$, $R^4 = CN$
134c: $R^1 = H$, $R^2 = Ph$, $R^3 = CN$, $R^4 = H$
134d: $R^1 = H$, $R^2 = Ph$, $R^3 = H$, $R^4 = CN$

Arnold and Albini have elucidated the behavior of stilbene oxides under photoinduced electron-transfer conditions.[109] Similarly, irradiation at $\lambda > 300$ nm of **128** and **129** with acrylonitrile in acetonitrile, using DCN as sensitizer, leads to the analogous tetrahydrofuran compounds in quantitative yields (Scheme 29; Table 6). Whereas there is no change in stereoselectivity in the reaction of **128** (*Z* isomer) under direct irradiation and sensitization conditions, this is not the case for the *E* isomer **129**. One explanation is the preferred formation of the *E,E* isomer **133** from **128** and **129**, which controls the stereochemistry of product formation. The cyano group orientation is nonselective, and the diastereoselectivity differs from that of the acetone-sensitized reaction.

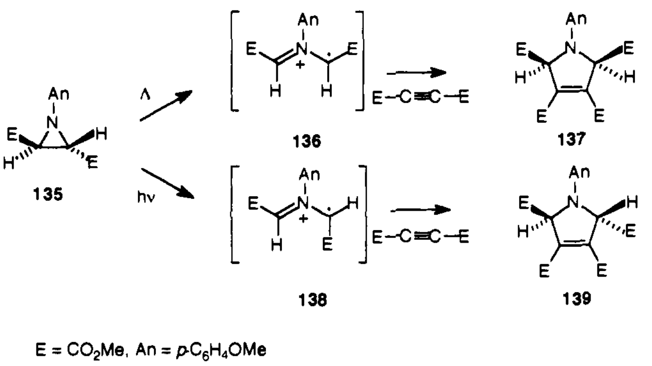
Whiting has used the PET-controlled [3 + 2] cycloaddition of oxiranes to olefins to build lignans using different dipolarophiles.[110] The reaction takes place only with acceptor-substituted olefins. Since regioselectivity is limited, the substitution pattern of the oxirane must be symmetrical. He prepared highly polarized oxiranes, which had acceptor substituents on one phenyl and a donor group on the other; however, they showed no regioselectivity. This greatly limits the preparative scope of the reaction.[111]

Schaap et al. prepared ozonides by trapping carbonyl ylide radical cations with oxygen.[112] X-ray analysis confirmed the structure of the 2,3-epoxybornane ozonide, which was isolated in 65% yield.[113]

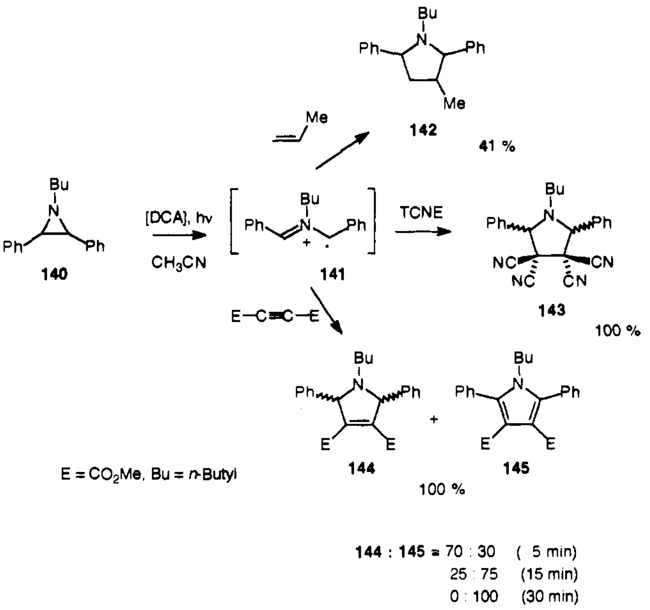
B. [3 + 2] Cycloadditions with Aziridines

The 1,3-dipolar cycloaddition of aziridine is in complete agreement with the theory of electrocyclic processes.[114] The thermal opening of *trans*-aziridine **135** proceeds conrotatory, leading to cis conformation of the product **137**, whereas the photochemical opening of **135** leads, via a disrotatory intermediate, to the trans product **139** (Scheme 30). Stereoselectivity is high (diastereomeric excess >98%). A sufficiently reactive dipolarophile, such as dimethyl acetylenedicarboxylate or tetracyanoethylene, can intercept the azomethine ylide dipole **136/138** before cis–trans isomerization is

Scheme 30



Scheme 31



crucial. Less reactive compounds lead to reduced selectivity.

The PET-sensitized photolysis of aziridines, using the same dipolarophiles, however, affords analogous cycloadducts without any diastereoselectivity. This is due to the isomerization step of the azomethine radical cation proceeding much more quickly.[115] The DCA-catalyzed ring opening of aziridine 140 leads to an azomethine radical cation 141, which readily adds to these same dipolarophiles to yield 143–146 (Scheme 31). The greater reactivity of the radical species leads to cycloadducts with less reactive compounds, such as propene, in 41% yield to give 142. Aziridines and oxiranes are similar in that 1,3-dipolar cycloadditions are diastereoselectively advantageous, whereas [3 + 2] cycloadditions of radical cations are reactively favored.

Only oxygen is capable of intercepting the radical cation before isomerization.[116] The DCA-sensitized reaction of either a *cis*- or a *trans*-2,3-diphenylaziridine with oxygen leads stereoselectively to the cis-configurated cycloadduct in 80% yield.

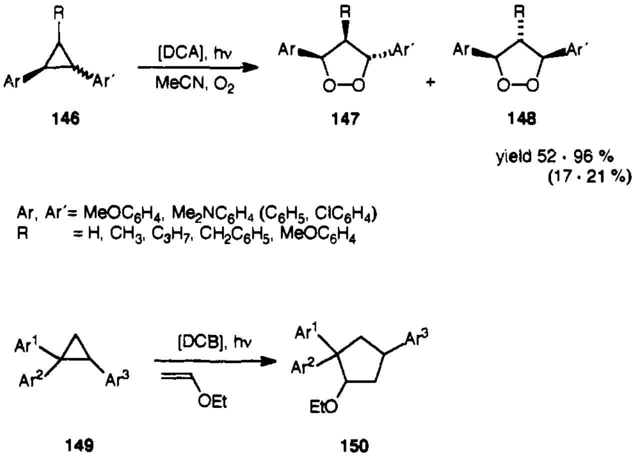
C. [3 + 2] Cycloadditions with Cyclopropanes

[3 + 2] cycloadditions of cyclopropanes are different.[117] Most work was done on the intramolecular conversion of vinylcyclopropanes by thermal[118] or photochemical,[119] or nowadays PET sensitized,[120] ring expansion. Since these reactions are rearrangements rather than true cycloadditions, they will not be discussed here.

Table 7. Effect of Cyclopropane Substituents on the Yield of Cycloadducts

compd	Ar^1	Ar^2	Ar^3	yield of **150**, %
149a	*p*-anisyl	*p*-anisyl	phenyl	50
149b	*p*-anisyl	phenyl	phenyl	36
149c	phenyl	phenyl	phenyl	2
149d	phenyl	phenyl	*p*-nitrilophenyl	0

Scheme 32



It is not possible for a 1,3-dipole to be formed from a cyclopropane, and the only route for ring opening with energy transfer under photochemical conditions is in rigidly strained systems such as for the tricyclo[3.2.1.$0^{2,4}$]oct-6-ene system.[121] According to Prinzbach, this isomerization can also be rationalized in terms of an intramolecular [3 + 2] cycloaddition of a cyclopropane to a π bond.

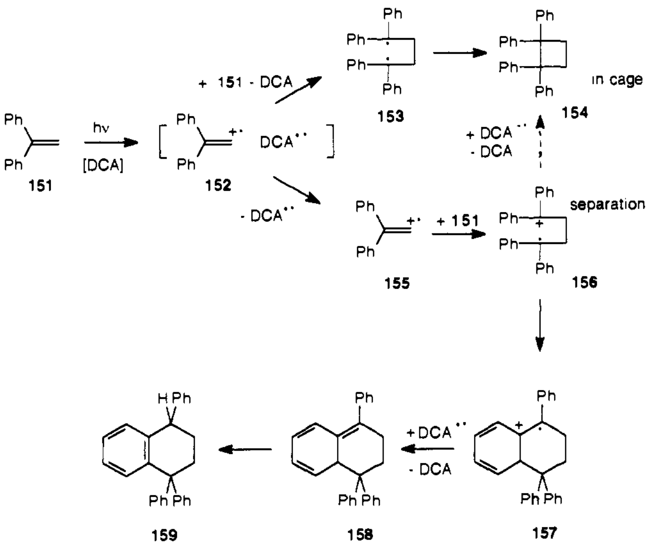
The first intermolecular cycloaddition reaction with cyclopropanes 146 was the PET-sensitized oxygenation, leading to 1,2-dioxolanes 147 and 148 (Scheme 32).[122] As the intermediate radical cation is extremely electron poor, it has to be stabilized with electron-donating substituents.

Under these conditions the dioxolanes are formed in good yields with high stereoselectivity (Ar = Ar' = p-$MeOC_6H_4$, R = CH_3; 147/148 = 9).[122c] Note that for R = H the ratio of the stereoisomers is reverted (ca. 3:7).[122b] From these results one may ascribe a similar influence of substituents at the 3-position of 1,2-diarylcyclopropanes as was observed for oxiranes and aziridines (see above).

Kamata and co-workers found an interesting variation of the PET oxidative ring opening of cyclopropanes.[123] In the presence of strong acids the cyclopropane is opened to the corresponding carbenium ion, which, upon irradiation, oxidizes another cyclopropane to its radical cation. The latter can also be scavenged by oxygen to form 1,2-dioxolanes. Strained cyclopropanes[124a] and bicyclo[1.1.0]butanes[124b] can also react under PET conditions, yielding 3,4-epoxyketones presumably via cyclic peroxides.

Tomioka was the first to carry out an intermolecular [3 + 2] cycloaddition with an olefin. Cyclopentane 150 was formed from 149 and ethyl vinyl ether in 50% yield as well as variable amounts of an acyclic addition product and triarylpropenes.[125]

Scheme 33



Contrary to previous reactions, in this case the olefin partner is an electron-rich vinyl ether which cannot be used as a dipolarophile in other reactions. With acceptor-substituted olefins there was no product formation observed; moreover, the substitution pattern of cyclopropane 149 was crucial, as Table 7 shows. The reaction has a high regioselectivity but a low diastereoselectivity, as can be predicted from the radical cation intermediate. It should be mentioned that aryl-substituted cyclopropanes also form cyclopentanes with tetracyanoethylene under thermal conditions.[117]

D. Other [3 + 2] Photocycloadditions

The potential of azirine photocycloadditions has already been discussed (section III). Thiiranes are not known to undergo 1,3-dipolar reactions under energy-transfer conditions; they tend to desulfurize during irradiation. Nevertheless, it has been reported that under PET conditions with tetracyanoethylene both as a catalyst and as a reaction partner there were in fact tetrahydrothiophene compounds isolated.[126]

As for other three-membered rings, the substitution pattern of the thiranes is crucial; i.e., high yields require donor substitution (e.g., anisyl groups).

In conclusion, we emphasize that the possibility of controlling reactivity and selectivity of intermediates by selecting a PET or an energy-transfer path is the main characteristic of [3 + 2] photocycloadditions.

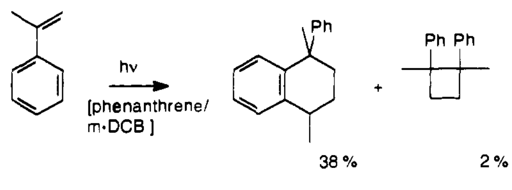
VI. [4 + 2] and Higher-Order Cycloadditions

Among the features of photoinduced electron transfer is the possibility of performing [4 + 2] cycloadditions under ambient conditions. However, not all are concerted and have the high diastereoselectivity which is possible under thermal conditions in a classic Diels–Alder reaction.[4,22] After discussing the most important examples, those of 1,1-diphenylethene and 1,3-cyclohexadiene, as well as several recent new reactions, we will conclude this section with cycloadditions leading to eight-membered rings.

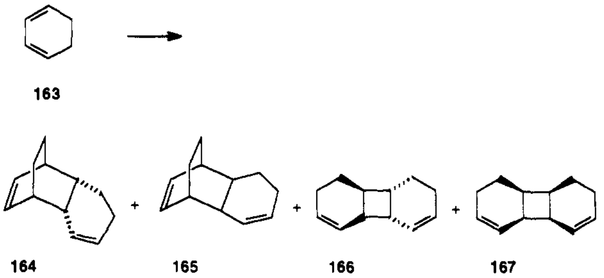
A. Dimerization of 1,1-Diphenylethene

Among the classic examples of the different reactivities of radical ion pairs and free-radical ions is the dimerization reaction of 1,1-diphenylethene (151). In 1973 Arnold showed that 151 leads to the formation of a tetrahydronaphthalene 159 under PET conditions (Scheme 33).[127] Further investigations by Farid[129] found the cyclobutane derivative 154, which up until then had escaped detection due to its thermal lability and its sensitizer dependence.[128]

Scheme 34



Scheme 35



When 151 is irradiated with DCA as the electron-transfer sensitizer, a geminate radical ion pair is formed. If this pair stays in contact, it will further react with 151 to form a dimeric radical cation in a cage, transfer the electron back from the DCA radical anion, and then go on to form the cyclobutane 154 from the diradicalic intermediate 153. If the concentration of diphenylethene is sufficiently small, the radical ions may separate and the alkene radical cation 155 react with another 151 to form a radical cation adduct 156. When not in a solvent cage, this has a prolonged lifetime and undergoes both 1,6 and 1,4 cyclization in a ratio of 6:1. Through back electron transfer the 1,6-adduct 157 forms a triene 158 which was trapped earlier with acrylonitrile.[128] The dependence of product formation on the concentration of olefin and on the sensitizer (neutral or cationic)[129] and quenching experiments favor this mechanism.[59]

Whereas anethole, as mentioned in section IV.A.1., only yields cyclobutane adducts, α-methylstyrene (160) on irradiation under PET conditions predominantly reacts to give the 1-phenyltetrahydronaphthalene derivative 161 (Scheme 34).[130] There are reports of other mixed cycloaddition reactions of this kind.[131]

B. [4 + 2] Cycloadditions with Cyclohexadiene

If a Diels–Alder reaction is not successful under thermal conditions, then the use of Lewis acid catalysis as well as high pressures and photoinduced electron-transfer methods has proven useful. For example, the dimerization of cyclohexadiene (163) has been investigated under a wide variety of conditions.[3,4,59,132-139] The thermal reaction produces low yields of the favored endo adduct 164.[140a] Direct irradiation leads preferably to the [2 + 2] cycloaddition products 166/167 and the exo-[4 + 2] adduct 165 (Scheme 35).[140c] The use of energy-transfer sensitizers such as phenanthrene or

Table 8. Reaction Conditions and Product Ratios in the Dimerization of 163

no.	reaction conditions[a] + sensitizer	yield	164	165	166	167	ref
1	Δ	32	4	1			137
2	hν, direct (neat)			1.4	1.9	1	140c
3	hν, phenanthrene	76		1	3.3	1.1	134
4	hν, benzophenone	71		1	4	1	134
5	hν, *p*-chloranil (0.1 M)	42	30	2	(1)		133
6	hν, DCN, CH_3CN	41	33	4	3	1	134
7	hν, DCA, CH_3CN	33	10	1	traces		134
8	hν, DCBN,[b] CH_3CN	80	35	4	2	1	134
9	hν, DCN, C_6H_6 (0.11 M)	75	1	6	(main products)		136
10	hν, DCN, C_6H_6 (2.1 M)	50	4	3	(min products)		136

[a] In general, 0.2 M of 163 if not otherwise stated. [b] DCBN, 1,1′-binaphthalene-2,2′-dicarbonitrile.

benzophenone leads to improved yields and greater diastereoselectivity, giving the anti-cycloadduct 166 as main product.[134] Irradiation under PET conditions, however, leads to the endo adduct 164 with improved yield and selectivity.[133,134]

Because thermal radical cation generators such as aminium hexachloroantimonates lead to the endo adduct 164 also,[132,135] the selectivity of the reaction can be explained by the radical cation intermediate formed from 163.[141] Schuster found that preferential formation of the endo adduct 164 even in benzene as solvent occurs because DCN is acting as an acceptor in the triplex reactive intermediate: [DCN...CHD...CHD] (see entry 10 of Table 8).[133,136,137]

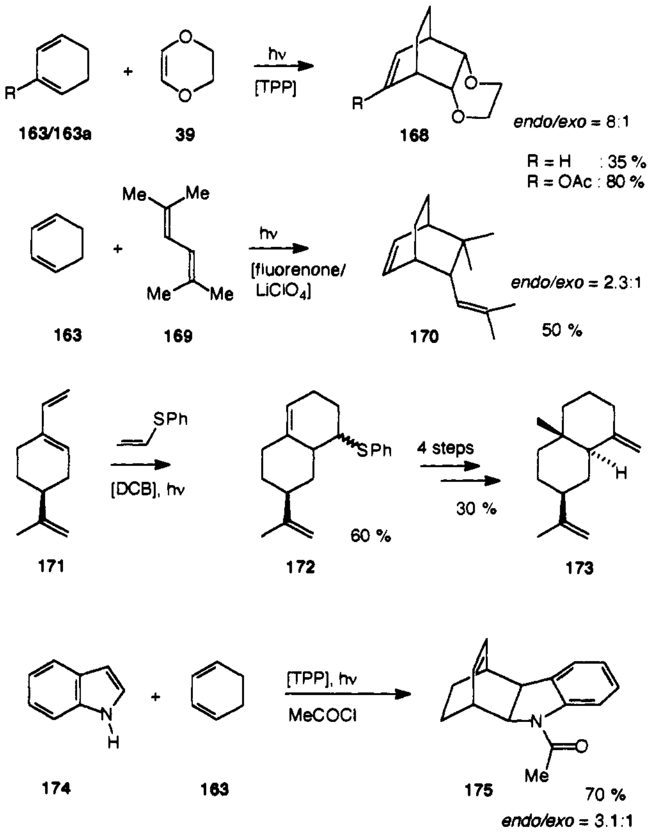
Molecules disposed toward intramolecular cycloaddition give better yields, although still worse than those under thermal conditions.[142] The mechanism of the radical cation Diels–Alder reaction is well documented with respect to both photochemical conditions[3b] and thermal conditions.[22]

Other cyclohexadiene derivatives have been dimerized and reacted with other dienophiles in cycloadditions under PET conditions. Products such as 168 and 170 have been isolated with varying diastereoselectivities.[3,4,132,133]

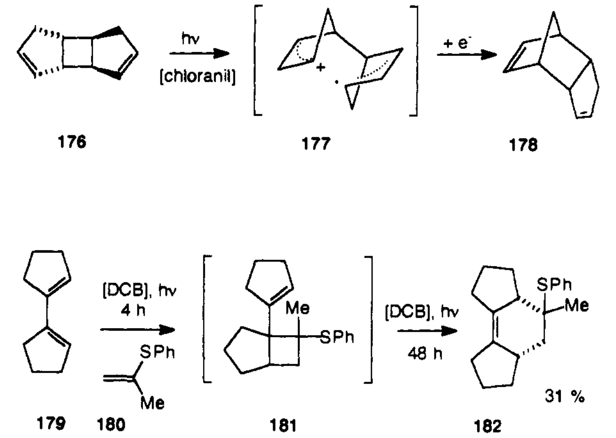
Although it is well established that different types of radical ion pairs are involved,[3,4,137] the mechanism is still not fully understood.[143] However, only recently the reaction has been used for stereoselective synthesis. The short and elegant synthesis of (−)-β-selinene 173 from the Wittig adduct 171 of the commercially available (−)-perillaldehyde is one example (Scheme 36).[144] Using the indole dienophile 174 and the scavenger acetyl chloride under PET conditions, it was possible to produce [4 + 2] cycloaddition products with cyclohexadiene 163.[145]

Without acetyl chloride, the yields are very low due to the highly oxidizable [4 + 2] adduct of 163 and indole 174 itself. Cyclohexadiene dimers were not detected, implying that the indole gives a radical cation only. The electron-transfer catalyst 2,4,6-triphenylpyrylium tetrafluoroborate (pyrylium salt) was used, and the endo product 175 gave a 70% yield with a diastereomeric excess of 54%.

Scheme 36



Scheme 37

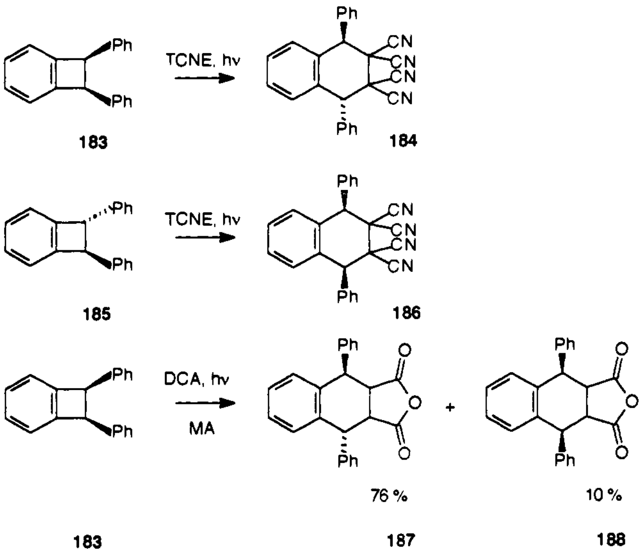


Occasionally, the cyclobutanation competes with the Diels–Alder reaction. By using an electron-transfer catalyst, this reaction can be circumvented in some cases by utilizing the radical cation vinylcyclobutane rearrangement giving the [4 + 2] cycloadduct: 167 gives 165 and 166 gives 164.[22,146] The irradiation of the photodimer of cyclopentadiene 176 with 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil) as sensitizer leads to the formation of the endo-Diels–Alder adduct 178 (Scheme 37).[147] Bauld has shown that the cyclobutane adduct 181 on prolonged irradiation with an electron-transfer catalyst reacts via a vinylcyclobutane rearrangement to give 182.[148]

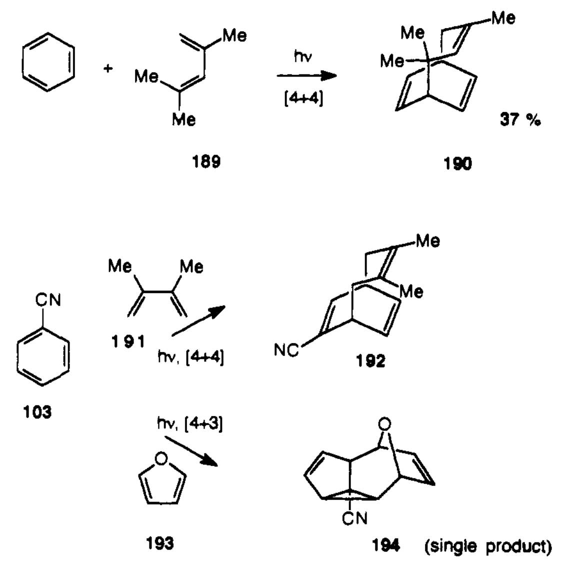
C. [4 + 2] Benzocyclobutene Cycloadditions

The cycloreversion of cyclobutenes has been used for fast [4 + 2] cycloadditions (see section IV.D).[105] When the charge-transfer absorption band is irradiated at λ = 380 nm, either *cis*- or *trans*-1,2-diphenylcyclobutene 183/185 reacts with tetracyanoethylene (TCNE) with conrotatory ring opening of the cyclobutene (Scheme 38). The cycloaddition takes place quantitatively to form one diastereomer 184/186, as a result of a fast collapse of the contact ion pair.[105]

Scheme 38



Scheme 39



When DCA is used as the electron-transfer catalyst, besides **187**, significant amounts of **188** as a result of the cycloaddition between **183** and maleic anhydride were found.[105] In the electron-transfer process it is presumed that isomerization takes place when the radical cation of **183** is transformed into a longer-lived solvent-separated radical ion pair. Chloranil sensitization of **183** in the presence of TCNE behaved similarly but with diminished stereoselectivity.

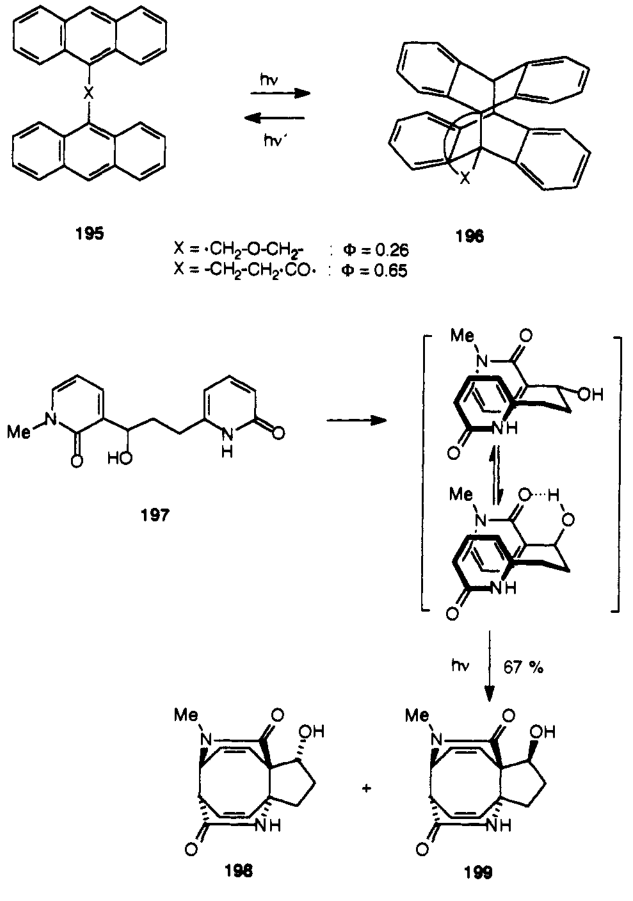
D. Higher-Order Cycloadditions

To the best of our knowledge, cycloadditions to medium sized rings via photoinduced electron transfer have not been reported. Nevertheless, there are also larger rings that can be formed via energy-transfer processes. We will focus on only three types which have been developed recently.

Not only dienes but aromatic compounds can act as 4π adducts in [4 + 2] as well as [4 + 4] cycloadditions. The latter has its roots in the early work of Kraft and Koltzenburg[149] and was developed by Yang and coworkers,[150] who synthesized a whole series of paracycloadducts from cisoid 1,3-dienes.[151] Although 2,4-dimethylpenta-1,3-diene (**189**) gives the [4 + 4] adduct **190** in moderate yields, the fixed cisoid 1,2-bis(methylene)cyclohexane gives mixtures of the meta-1,4-[4 + 3] and para-1,4-[4 + 4] adducts depending on reactant concentration (cf. section III.B).[50a] With anthracenes, more efficient [4 + 4] cycloadditions are possible.[152] Recently, Gilbert and co-workers found striking effects on the introduction of electron-acceptor groups into the benzene ring.[153] For example, benzonitrile (**103**) adds to 2,3-dimethylbutadiene to give a single [4 + 4] cycloadduct **192** (Scheme 39).[153,154] With furan, however, a meta adduct resulting from a [4 + 3] cycloaddition is formed exclusively. It is concluded that secondary orbital interactions between the arene substituent and furan are controlling both the mode and the stereoselectivity.[151,153] More examples are found in literature reviews.[19,155]

The dimerization of aromatic compounds leads also to polycyclic structures with cyclooctadiene subunits (e.g., **195** → **196**) (Scheme 40).[157] This type of [4 + 4] cyclodimerization has been the subject of continuous interest for both synthetic and mechanistic reasons (cf. H. D. Becker, this issue).[63b,157-159]

Scheme 40

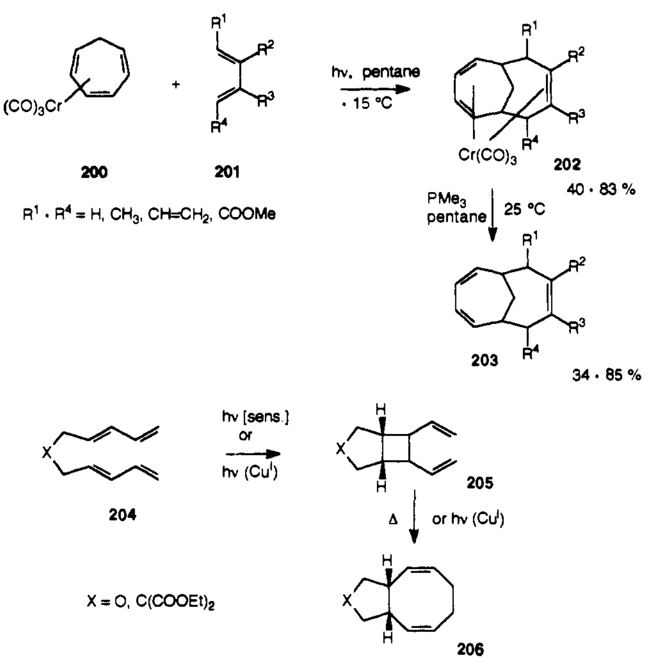


EtOH : **198** : **199** = 11 : 1
MeCl$_2$: **198** : **199** = 3 : 4

An interesting example has recently been reported by Sieburth and Chen.[160] In an intramolecular [4 + 4] photocycloaddition two stereoisomers **198** and **199** are formed from a tethered 2-pyridone **197**. The stereochemistry is influenced by the intramolecular H bond and is subject therefore to solvent control.

Although thermal [6 + 4] cycloadditions have been known for some time,[161] it was not until Kreiter's

Scheme 41



fundamental studies on the chromium[162] and molybdenum[163] tricarbonyl complexes of cycloheptatrienes and heptafulvenes that the photochemical equivalent was established. These complexes are added to dienes to form bicyclo[4.4.1]undeca-2,4,8-trienes **203**.[163] Recently, Rigby and co-workers studied the stereoselectivity of this transition-metal-mediated [6 + 4] cycloaddition[164a] and extended it to a [6 + 2] cycloaddition.[164b]

The strategy of these higher-order cycloadditions, i.e., the use of metals as templates, is similar to the [2 + 2] cycloadditions of alkenes using copper(I) catalysts.[165] When this method is applied to bisdienes of the type **204**, an indirect route to cyclooctadienes is opened up (Scheme 41).[156,166]

VII. Conclusion

This review has endeavored to cover the growing synthetic potential of photocycloaddition reactions since the development of electron-transfer reactions. The rapid evolution of new techniques has enabled the organic chemist to overcome many of the inherent limitations of classic photocycloadditions. In many cases not only are certain reactions made possible but a far greater selectivity is available. Whereas classic energy-transfer-controlled photocycloadditions were confined to [2 + 2] and some [3 + 2] reactions, it is now possible to carry out [4 + 2] reactions with the aid of electron-transfer control. Highly selective higher-order cycloadditions are particularly suited to the use of metal complexes as templates. The correct choice of new developmental procedure opens up a wealth of new direction. It is hoped that interest in this area will continue to ensure the flow of new ideas and reactions, particularly in the area of organic synthesis.

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IX. References

(1) Mattay, J., Ed. *Top. Curr. Chem.* **1990**, *156*; **1990**, *158*; **1991**, *159*; **1992**, *163*.
(2) Fox, M.-A., Chanon, M., Eds. *Photoinduced Electron Transfer*; Elsevier: Amsterdam, 1988; Part A–D.
(3) (a) Mattay, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 825. (b) Mattay, J.; Vondenhof, M. *Top. Curr. Chem.* **1991**, *159*, 219.
(4) Mattay, J. *Synthesis* **1989**, 233. Mattay, J. *Nachr. Chem., Tech. Lab.* **1988**, *36*, 376.
(5) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.
(6) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978.
(7) Becker, H. G. O. *Einführung in die Photochemie*, 2nd ed.; Deutscher Verlag der Wissenschaften: Berlin, 1991.
(8) Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry*; Blackwell: Oxford, U.K., 1991.
(9) Fox, M.-A. *Adv. Photochem.* Wiley, New York **1986**, *13*, 237.
(10) (a) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (b) Weller, A. *Z. Phys. Chem. (Munich)* **1982**, *133*, 93. (c) Weller, A. *Z. Phys. Chem. (Munich)* **1982**, *130*, 129.
(11) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3794. Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290.
(12) Fainberg, A. H.; Winstein, S. J. *J. Am. Chem. Soc.* **1956**, *78*, 2767.
(13) Ciamician, G.; Silber, P. *Chem. Ber.* **1908**, *41*, 1928.
(14) Padwa, A., Ed. *1,3 Dipolar Chemistry*; Wiley: New York, 1984.
(15) Trost, B. M., Ed. *Comprehensive Organic Synthesis*; Pergamon: Oxford, U.K., 1991; Vol. 5.
(16) Cossy, J.; Carrupt, P.-A.; Vogel, P. In *The Chemistry of Double-bonded Functional Groups*; Patai, S., Ed.; Wiley: New York, 1989; Suppl. A. Vol. 2, Part 2, p 1369.
(17) Becker, D.; Haddad, N. In *Organic Photochemistry*; Padwa, A., Ed.; Dekker: New York, 1989; Vol. 10, p 1.
(18) Laarhoven, W. H. In *Organic Photochemistry*; Padwa, A., Ed.; Dekker: New York, 1989; Vol. 10, p 163.
(19) Wender, P. A. In *Organic Photochemistry*; Padwa, A., Ed.; Dekker: New York, 1989; Vol. 10, p 357. Wender, P. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, U.K., 1991; Vol. 5, p 645.
(20) Crimmins, M. T. *Chem. Rev.* **1988**, *88*, 1453.
(21) Katritzky, A. R.; Dennis, N. *Chem. Rev.* **1989**, *89*, 827.
(22) Bauld, N. J. *Tetrahedron* **1989**, *45*, 5307.
(23) Welker, M. E. *Chem. Rev.* **1992**, *92*, 97.
(24) Huisgen, R. *Naturwiss. Rundsch.* **1961**, *14*, 63.
(25) Huisgen, R. *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 781.
(26) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 633.
(27) (a) Huisgen, R. *Proc. Chem. Soc.* **1961**, 357. (b) Huisgen, R.; Gotthardt, H.; Bayer, B. O. *Chem. Ber.* **1970**, *103*, 2370. (c) Bunge, K. H.; Huisgen, R.; Raab, R.; Sturm, H.-J. *Chem. Ber.* **1972**, *105*, 1307.
(28) Padwa, A.; Dharan, M.; Smolanoff, J.; Wetmore, S. I. *J. Am. Chem. Soc.* **1973**, *95*, 1945.
(29) (a) Padwa, A. In *Synthetic Organic Photochemistry*; Horspool, W., Ed.; Plenum: New York, 1984; p 313. (b) Heimgartner, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 234. (c) Trozzolo, A. *Chem. Rev.* **1993**, in press.
(30) Padwa, A.; Dharan, M.; Smolanoff, J.; Wetmore, S. I. *J. Am. Chem. Soc.* **1973**, *95*, 1954.

(31) Padwa, A.; Smolanoff, J.; Tremper, A. *J. Am. Chem. Soc.* **1975**, *97*, 4682. Padwa, A.; Rasmussen, J. K.; Tremper, A. *J. Am. Chem. Soc.* **1976**, *98*, 2605.

(32) Orahovats, A.; Heimgartner, H.; Schmid, H.; Heinzelmann, W. *Helv. Chim. Acta* **1975**, *58*, 2677.

(33) Padwa, A.; Rosenthal, R. J.; Dent, W.; Filho, P.; Turro, N. J.; Hrovat, D. A.; Gould, I. R. *J. Org. Chem.* **1984**, *49*, 3174.

(34) Naito, I.; Morihara, H.; Ishida, A.; Takamuku, S.; Isomura, K.; Taniguchi, H. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2757.

(35) (a) Giezendanner, H.; Märky, M.; Jackson, B.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1972**, *55*, 745. (b) Jakis, N.; Märky, M.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1972**, *55*, 748. (c) Giezendanner, H.; Heimgartner, H.; Jackson, B.; Winkler, T.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1973**, *56*, 2611.

(36) Gerber, U.; Heimgartner, H.; Schmid, H.; Hansen, H.-J. *Heterocycles* **1977**, *6*, 143.

(37) Orahovats, A.; Heimgartner, H.; Schmid, H.; Heinzelmann, W. *Helv. Chim. Acta* **1974**, *57*, 2626.

(38) Müller, F.; Mattay, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1336.

(39) Müller, F.; Steenken, S.; Mattay, J. Unpublished results.

(40) Würthwein, E. U. Ab-initio-calculation (UMP 2/6-31G* basic set). Private communication.

(41) Müller, F.; Mattay, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 209.

(42) Müller, F.; Karwe, A.; Mattay, J. *J. Org. Chem.* **1992**, *57*, 6080.

(43) Mattay, J. *J. Photochem.* **1987**, *37*, 167.

(44) Gilbert, A. *Pure Appl. Chem.* **1980**, *52*, 2669.

(45) Cornelisse, J. *Chem. Rev.* **1993**, in press.

(46) Mattay, J. *Tetrahedron* **1985**, *41*, 2393.

(47) Mattay, J. *Tetrahedron* **1985**, *41*, 2405.

(48) Gilbert, A.; Taylor, G. N.; bin Samsudin, M. W. *J. Chem. Soc., Perkin Trans. 1* **1980**, 869. Mattay, J.; Leismann, H.; Scharf, H.-D. *Chem. Ber.* **1979**, *112*, 577.

(49) Mattay, J.; Runsink, J.; Heckendorn, R.; Winkler, T. *Tetrahedron* **1987**, *43*, 5781.

(50) (a) Berridge, J. C.; Forrester, J.; Foulger, B. E.; Gilbert, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2425. (b) Gilbert, A.; Rodwell, P. W. *J. Chem. Soc., Perkin Trans. 1* **1990**, 931.

(51) van der Hart, J. A.; Mulder, J. C.; Cornelisse, J. *J. Photochem. Photobiol. A* **1991**, *61*, 3.

(52) Mattay, J.; Rumbach, Th.; Runsink, J. *J. Org. Chem.* **1990**, *55*, 5691.

(53) (a) Wender, P. A.; Howbert, J. J. *J. Am. Chem. Soc.* **1981**, *107*, 688. (b) Wender, P. A.; v. Geldern, T. W.; Levine, B. H. *J. Am. Chem. Soc.* **1988**, *110*, 4858.

(54) d'Alessandro, N.; Mella, M.; Fasani, E.; Toma, L.; Albini, A. *Tetrahedron* **1991**, *47*, 5043.

(55) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 758.

(56) Reference 8, Chapter 6.7.2. and references cited therein.

(57) (a) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133. (b) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Dekker: New York, 1983; Vol. 6, p 233.

(58) Kuwata, S.; Shigemitsu, Y.; Odaira, Y. *J. Org. Chem.* **1973**, *38*, 3803.

(59) Mattay, J.; Vondenhof, M.; Denig, R. *Chem. Ber.* **1989**, *122*, 951.

(60) Evans, T. R.; Wake, R. W.; Jaenicke, O. In *The Exciplex*; Gordon, M., Ware, W. R., Eds.; Academic Press: New York 1975; p 345.

(61) Farid, S.; Shealer, S. E. *J. Chem. Soc., Chem. Commun.* **1973**, 677.

(62) (a) Yasuda, M.; Pac, C.; Nakasone, A.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 502. (b) Majima, T.; Pac, C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 4499.

(63) (a) Metzner, W.; Wendisch, D. *Liebigs Ann. Chem.* **1969**, *730*, 111. (b) McCullough, J. A. *Chem. Rev.* **1987**, *87*, 811.

(64) Nozaki, H.; Otani, I.; Noyori, R.; Kawanisi, M. *Tetrahedron* **1968**, *24*, 2192.

(65) Lewis, F. D.; Kojima, M. *J. Am. Chem. Soc.* **1988**, *110*, 8660, 8664.

(66) (a) Caldwell, R. A.; Smith, L. *J. Am. Chem. Soc.* **1974**, *96*, 2994. (b) Mizuno, K.; Pac, C.; Sakurai, H. *J. Am. Chem. Soc.* **1974**, *96*, 2993.

(67) (a) Lewis, F. D.; DeVoe, R. J. *Tetrahedron* **1982**, *38*, 1069. (b) Lewis, F. D.; DeVoe, R. J.; MacBlane, D. B. *J. Org. Chem.* **1982**, *47*, 1392.

(68) (a) Schuster, D. I. In *The Chemistry of Enones*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 623. (b) Schuster, D. I. *Chem. Rev.* **1993**, in press.

(69) (a) Hastings, D. J.; Weedon, A. C. *Tetrahedron Lett.* **1991**, *32*, 4107. (b) Hastings, D. J.; Weedon, A. C. *J. Org. Chem.* **1991**, *56*, 6326.

(70) (a) Hastings, D. J.; Weedon, A. C. *J. Am. Chem. Soc.* **1991**, *113*, 8525.

(71) Pienta, N. J.; McKimmey, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 5501.

(72) (a) Bischof, E. W. Dissertation, Aachen, 1991. (b) Bischof, E. W.; Mattay, J. *Tetrahedron Lett.* **1990**, *31*, 7134.

(73) (a) Bischof, E. W.; Mattay, J. *J. Photochem. Photobiol. A* **1992**, *63*, 249. (b) Mattay, J.; Banning, A.; Bischof, E. W.; Heidbreder, A.; Runsink, J. *Chem. Ber.* **1992**, *125*, 2119.

(74) Maruyama, K.; Imahori, H. *J. Chem. Soc., Perkin Trans. 2* **1990**, 257.

(75) Cruciani, G.; Rathjen, H.-J.; Margaretha, P. *Helv. Chim. Acta* **1990**, *73*, 856.

(76) (a) Carless, H. A. J. In *Synthetic Organic Photochemistry*; Horspool, W., Ed.; Plenum: New York, 1984; p 425; (b) Schreiber, S. W. *Science* **1985**, *227*, 858. (c) Jones, G. In *Organic Photochemistry*; Padwa, A., Ed.; Dekker: New York, 1981; Vol. 5, p 1.

(77) Buschmann, H.; Scharf, H. D.; Hoffmann, N.; Esser, P. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 477.

(78) Khan, N.; Morris, T. H.; Smith, E. H.; Walsh, R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 865.

(79) Bach, Th. *Tetrahedron Lett.* **1991**, *32*, 7037.

(80) Chung, W.-S.; Turro, N. J.; Srivastava, S.; le Noble, W. J. *J. Org. Chem.* **1991**, *56*, 5020.

(81) (a) Griesbeck, A. G.; Stadtmüller, S. *J. Am. Chem. Soc.* **1991**, *113*, 6923. (b) Griesbeck, A. G. Personal communication.

(82) (a) Mattay, J.; Gersdorf, J.; Leismann, H.; Steenken, S. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 249. (b) Mattay, J.; Gersdorf, J.; Buchkremer, K. *Chem. Ber.* **1987**, *120*, 307.

(83) Mattay, J.; Gersdorf, J.; Freudensberg, U. *Tetrahedron Lett.* **1984**, *25*, 817.

(84) Gersdorf, J.; Mattay, J.; Görner, H. *J. Am. Chem. Soc.* **1987**, *109*, 1203.

(85) Mariano, P. S. In *Organic Photochemistry*; Padwa, A., Ed.; Dekker: New York, 1987; Vol. 9, p 1.

(86) (a) Koch, T. H.; Howard, K. A. *Tetrahedron Lett.* **1972**, *13*, 4035. (b) Howard, K. A.; Koch, T. H. *J. Am. Chem. Soc.* **1975**, *97*, 7288.

(87) (a) Mariano, P. S.; Stavinoha, J. L.; Pepe, G.; Meyer, Z. F. *J. Am. Chem. Soc.* **1978**, *100*, 7114. (b) Stavinhoa, J. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 3136.

(88) Stavinhoa, J. L.; Mariano, P. S.; Leone-Bay, A.; Swanson, R.; Bracken, C. *J. Am. Chem. Soc.* **1981**, *103*, 3148.

(89) (a) Ahmed-Schofield, R.; Mariano, P. S. *J. Org. Chem.* **1987**, *52*, 1478; **1985**, *50*, 5667.

(90) (a) Mazzocchi, P. H. In *Organic Photochemistry*; Padwa, A., Ed.; Dekker: New York, 1981; Vol. 5, p 421; (b) Coyle, J. D. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum Press: New York, 1984; p 259.

(91) (a) Mazzocchi, P. H.; Minamikawa, S.; Wilson, P. *J. Org. Chem.* **1985**, *50*, 2681. (b) Mazzocchi, P. H.; Fritz, G. *J. Am. Chem. Soc.* **1986**, *108*, 5362. (c) Kubo, Y.; Suto, M.; Arahi, T.; Mazzocchi, P. H.; Klingler, L.; Shook, D.; Somich, C. *J. Org. Chem.* **1986**, *51*, 4404. (d) Somich, C.; Mazzocchi, P. H.; Ammon, H. L. *J. Org. Chem.* **1987**, *52*, 3614. (e) Mazzocchi, P. H. *Heterocycles* **1988**, *27*, 1105.

(92) (a) Arnold, D. R.; Wong, P. C.; Maroulis, A. J.; Cambron, T. S. *Pure Appl. Chem.* **1980**, *52*, 2609. (b) Cantrell, T. S. *J. Org. Chem.* **1977**, *42*, 4238.

(93) (a) Pac, C. *Pure Appl. Chem.* **1986**, *58*, 1249. (b) Pac, C.; Fukunaga, T.; Go-An, Y.; Sakae, T.; Yanagida, S. *J. Photochem. Photobiol. A* **1987**, *41*, 37.

(94) (a) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1981**, *103*, 7210. (b) Roth, H. D. *Top. Curr. Chem.* **1992**, *163*. (c) Turro, N. J.; Cherry, W. R.; Mirbach, M. F.; Mirbach, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 7388.

(95) (a) Scharf, H. D.; Fleischbauer, J.; Leismann, H.; Ressler, I.; Schleker, W.; Weitz, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 652. (b) Hautala, R. R.; King, R. B.; Kutal, C. *Solar Energy: Chemical Conversion and Storage*; Humana Press: Clifton, 1979.

(96) Jones, G., II; Chiang, S. H.; Becker, W. G.; Welch, A. J. *J. Phys. Chem.* **1982**, *86*, 2805.

(97) Gassman, P. G.; Hershberger, J. W. *J. Org. Chem.* **1987**, *52*, 1337.

(98) (a) Hasegawa, E.; Okada, K.; Ikeda, H.; Yamashita, Y.; Mukai, T. *J. Org. Chem.* **1991**, *56*, 2170. (b) Yamashita, Y.; Ikeda, H.; Mukai, T. *J. Am. Chem. Soc.* **1987**, *109*, 6682.

(99) (a) Diogo, H. P.; Dias, A. R.; Dhalla, A.; Minas da Piedade, M. E.; Begley, T. P. *J. Org. Chem.* **1991**, *56*, 7340. (b) Burdi, D.; Begley, T. P. *J. Am. Chem. Soc.* **1991**, *113*, 7768. (c) Cadet, J.; Vigny, P. In *Bioorganic Photochemistry*; Morrison, H., Ed.; Wiley: New York, 1990; p 1. (d) Myles, G. M.; Sancar, A. *Chem. Res. Toxicol.* **1989**, *2*, 197. (e) Hartmann, R. F.; Van Camp, J. R.; Rose, S. P. *J. Org. Chem.* **1987**, *52*, 2684.

(100) Aebischer, J. N.; Bally, T.; Roth, K.; Haselbach, E.; Gerson, F.; Qin, X.-Z. *J. Am. Chem. Soc.* **1989**, *111*, 7909.

(101) Haselbach, E.; Bally, T.; Gschwind, R.; Hemm, U.; Lanyiova, Z. *Chimia* **1979**, *33*, 405.

(102) Dass, C.; Sack, T. M.; Gross, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 5780.

(103) Kawamura, Y.; Thurnauer, M.; Schuster, G. B. *Tetrahedron* **1986**, *42*, 6195.

(104) Miyashi, T.; Wakamatsu, K.; Akiya, T.; Kikuchi, K.; Mukai, T. *J. Am. Chem. Soc.* **1987**, *109*, 5270.

(105) Takahashi, Y.; Kochi, J. K. *Chem. Ber.* **1988**, *121*, 253.

(106) (a) Linn, W. J.; Benson, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 3657. (b) Linn, W. J. *J. Am. Chem. Soc.* **1965**, *87*, 3665.

(107) (a) Ullman, E. F.; Milks, J. E. *J. Am. Chem. Soc.* **1964**, *86*, 3814. (b) Ullman, E. F.; Henderson, W. A. *J. Am. Chem. Soc.* **1964**, *86*, 5050.

(108) (a) Lee, G. A. *J. Org. Chem.* **1976**, *41*, 2656. (b) Lev, I. J.; Ishakawa, K.; Bhacca, N. S.; Griffin, G. W. *J. Org. Chem.* **1976**, *41*, 2654.

(109) Albini, A.; Arnold, D. R. *Can. J. Chem.* **1978**, *56*, 2985.

(110) (a) Clawson, P.; Lunn, P. M.; Whiting, D. A. *J. Chem. Soc., Chem. Commun.* 1984, 134. (b) Clawson, P.; Lunn, P. M.; Whiting, D. A. *J. Chem. Soc., Perkin Trans. 1* 1990, 153. (c) Clawson, P.; Lunn, P. M.; Whiting, D. A. *J. Chem. Soc., Perkin Trans. 1* 1990, 159.

(111) Clawson, P.; Whiting, D. A. *J. Chem. Soc., Perkin Trans. 1* 1990, 1193.

(112) Schaap, A. P.; Siddiqui, S.; Prasad, G.; Palomino, P.; Sandison, M. *Tetrahedron* 1985, *41*, 2229.

(113) Palomino, E.; Schaap, A. P.; Heeg, M. J. *Tetrahedron Lett.* 1989, *30*, 6801.

(114) Huisgen, R.; Scheer, W.; Huber, H. *J. Am. Chem. Soc.* 1967, *89*, 1753.

(115) Caër, V.; Laurent, A.; Laurent, E.; Tardivel, R.; Cebulska, Z.; Bartnik, R. *Nouv. J. Chim.* 1987, *11*, 351.

(116) (a) George, M. V.; Bhat, V. *Chem. Rev.* 1979, *79*, 447. (b) Schaap, A. P.; Siddiqui, S.; Gagnon, S. T.; Lopez, L. *J. Am. Chem. Soc.* 1983, *105*, 5149. (c) Schaap, A. P.; Siddiqui, S.; Prasad, G.; Rahman, A. F. M.; Oliver, J. P. *J. Am. Chem. Soc.* 1984, *106*, 6087. (d) Schaap, A. P.; Prasad, G.; Siddiqui, S. *Tetrahedron Lett.* 1984, *25*, 3035.

(117) Boche, G.; Walborsky, H. In *Cyclopropane Derived Reactive Intermediates*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1990; p 207.

(118) Gutsche, C. D.; Redmore, D. *Carbocyclic Ring Expansion Reactions*; Academic Press: New York, 1968.

(119) Padwa, A.; Blacklock, T. J.; Getman, D.; Hatanaka, N.; Loza, R. *J. Org. Chem.* 1978, *43*, 1481.

(120) (a) Dinnocenzo, J. P.; Schmittel, M. *J. Am. Chem. Soc.* 1987, *109*, 1561. (b) Dinnocenzo, J. P.; Coulon, D. A. *J. Am. Chem. Soc.* 1988, *110*, 2324. (c) Dinnocenzo, J. P.; Todd, M. P.; Simpson, T. R.; Gould, I. R. *J. Am. Chem. Soc.* 1990, *112*, 2462.

(121) (a) Prinzbach, H.; Eberbach, W. *Chem. Ber.* 1968, *101*, 4083. (b) Prinzbach, H.; Eberbach, W.; v. Veh, G. *Angew. Chem., Int. Ed. Engl.* 1965, *4*, 436.

(122) (a) Mizuno, K.; Kamiyama, N.; Otsuji, Y. *Chem. Lett.* 1983, 477. (b) Mizuno, K.; Kamiyama, N.; Otsuji, Y.; Ichinose, N.; Otsuji, Y. *Tetrahedron* 1985, *41*, 2207. (c) Ichinose, N.; Mizuno, K.; Tamai, T.; Otsuji, Y. *J. Org. Chem.* 1990, *55*, 4079.

(123) Kamata, M.; Furukawa, H.; Miyashi, T. *Tetrahedron Lett.* 1990, *31*, 681.

(124) (a) Gollnick, K.; Paulmann, U. *Tetrahedron Lett.* 1989, *30*, 4481. (b) Gollnick, K.; Weber, M. *Tetrahedron Lett.* 1990, *31*, 4585.

(125) Tomioka, H.; Kobayashi, D.; Hashimoto, A.; Murata, S. *Tetrahedron Lett.* 1989, *30*, 4685.

(126) Kamata, M.; Miyashi, T. *J. Chem. Soc., Chem. Commun.* 1989, 557.

(127) Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* 1973, *95*, 4080.

(128) Arnold, D. R.; Borg, R. M.; Albini, A. *J. Chem. Soc., Chem. Commun.* 1981, 138.

(129) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* 1986, *108*, 7356.

(130) Asanuma, T.; Gotoh, T.; Tsuchida, A.; Yamamoto, M.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* 1977, 485.

(131) Maroulis, A. J.; Arnold, D. R. *J. Chem. Soc., Chem. Commun.* 1979, 351.

(132) Bauld, N. L.; Bellville, D. J.; Harirchian, B.; Lorenz, K. T.; Pabon, R. A., Jr.; Reynolds, D. W.; Wirth, D. D.; Chiou, H.-S.; Marsh, B. K. *Acc. Chem. Res.* 1987, *20*, 371.

(133) Mattay, J.; Trampe, G.; Runsink, J. *Chem. Ber.* 1988, *121*, 1991.

(134) Mattay, J.; Vondenhof, M. *Chem. Ber.* 1990, *123*, 2457.

(135) Bellville, D. J.; Wirth, D. D.; Bauld, N. L. *J. Am. Chem. Soc.* 1981, *103*, 718.

(136) Calhoun, G. C.; Schuster, G. B. *J. Am. Chem. Soc.* 1984, *106*, 6870.

(137) Chung, W. S.; Turro, N. J.; Mertes, J.; Mattay, J. *J. Org. Chem.* 1989, *54*, 4881.

(138) Mlcoch, J.; Steckhan, E. *Angew. Chem., Int. Ed. Engl.* 1985, *24*, 412.

(139) Mattay, J.; Gersdorf, J.; Mertes, J. *J. Chem. Soc., Chem. Commun.* 1985, 1088.

(140) (a) Valentine, D.; Turro, N. S.; Hammond, G. S. *J. Am. Chem. Soc.* 1964, *86*, 5202. (b) Palmer, T. L.; Whitten, D. G.; Hammond, G. S. *J. Am. Chem. Soc.* 1970, *92*, 2861. (c) Schenk, G. O.; Mannsfeld, S. P.; Schomburg, G.; Krauch, C. H. *Z. Naturforsch.* 1964, *19B*, 18.

(141) Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* 1983, *105*, 2378.

(142) Wölfe, I.; Chan, S.; Schuster, G. B. *J. Org. Chem.* 1991, *56*, 7313.

(143) Mella, M.; Fasani, E.; Albini, A. *Tetrahedron* 1991, *47*, 3137.

(144) Harirchian, B.; Bauld, N. L. *J. Am. Chem. Soc.* 1989, *111*, 1826.

(145) Gieseler, A.; Steckhan, E.; Wiest, O.; Knoch, F. *J. Org. Chem.* 1991, *56*, 1405.

(146) Reynolds, P. W.; Harirchan, B.; Chiou, H.-S.; Marsh, B. K.; Bauld, N. L. *J. Phys. Org. Chem.* 1989, *2*, 57.

(147) Roth, H. D.; Schilling, M. L. M.; Abelt, C. *Tetrahedron* 1986, *42*, 6157.

(148) Pabon, R. A.; Bellville, D. A.; Bauld, N. L. *J. Am. Chem. Soc.* 1984, *106*, 2730.

(149) Kraft, K.; Koltzenburg, G. *Tetrahedron Lett.* 1967, 4357.

(150) (a) Yang, N. C.; Libman, J. *Tetrahedron Lett.* 1973, 1409. (b) Yang, N. C.; Yates, R. L.; Masnoui, J.; Shold, D. M.; Chiang, W. *Pure Appl. Chem.* 1979, *51*, 173. (c) Yang, N. C.; Gan, H.; Kim, S. S.; Masnovi, J. M.; Rafalko, P. W.; Ezell, E. F.; Lenz, G. R. *Tetrahedron Lett.* 1990, *31*, 3825.

(151) Gilbert, A. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum Press: New York, 1984; p 1.

(152) Yang, N. C.; Masnovi, J. M.; Chiang, W. *J. Am. Chem. Soc.* 1979, *101*, 6465.

(153) Gilbert, A.; Radwell, P. W. *J. Chem. Soc., Perkin Trans. 1* 1990, 931.

(154) Okamura, K.; Takamuka, S.; Sakurai, H. *J. Chem. Soc. Jpn., Ind. Chem. Sect.* 1969, *72*, 200.

(155) Rigby, J. H. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, U.K., 1991; Vol. 5, p 635.

(156) Wender, P. A.; Correia, C. R. D. *J. Am. Chem. Soc.* 1987, *109*, 2523.

(157) Becker, H. D. *Pure Appl. Chem.* 1982, *54*, 1589.

(158) Bonas-Laurent, H.; Castellan, A.; Desvergne, J. P. *Pure Appl. Chem.* 1980, *52*, 2633.

(159) Albini, A.; Fasani, E. *J. Am. Chem. Soc.* 1987, *109*, 811.

(160) Sieburth, S. McN.; Chen, J. *J. Am. Chem. Soc.* 1991, *113*, 8163.

(161) Rigby, J. H. Reference 155, p 617.

(162) (a) Özkar, S.; Kurz, H.; Neugebauer, D.; Kreiter, C. G. *J. Organomet. Chem.* 1978, *160*, 115. (b) Michels, E.; Sheldrick, W. S.; Kreiter, C. G. *Chem. Ber.* 1985, *118*, 964.

(163) Kreiter, C. G.; Kurz, H. *Chem. Ber.* 1983, *116*, 1494.

(164) (a) Rigby, J. H.; Ateeg, H. S. *J. Am. Chem. Soc.* 1990, *112*, 6442. (b) Rigby, J. H.; Henshilwood, J. A. *J. Am. Chem. Soc.* 1991, *113*, 5122.

(165) Salomon, R. G. *Tetrahedron* 1983, *39*, 485.

(166) (a) Hertel, R.; Mattay, J.; Runsink, J. *J. Am. Chem. Soc.* 1991, *113*, 657. (b) Langer, K.; Mattay, J.; Heidbreder, A.; Möller, M. *Liebigs Ann. Chem.* 1992, 257.