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Photochemical Reactions as Key Steps in Organic Synthesis

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1. Introduction

Norbert Hoffmann studied Chemistry at the Technical University (RWTH) Aachen, Germany, and received his Ph.D. degree in 1992 under the supervision of Hans-Dieter Scharf. In 1993, he obtained a permanent research position at the CNRS (Chargé de Recherche) in Reims, France. In 2004, he was appointed Research Director in the CNRS. His research interests are in the field of organic photochemistry: electron transfer, photoinduced radical reactions, cycloadditions of aromatic compounds, and application of these reactions to organic synthesis. Further research activities concern the production of fine chemicals from biomass and synthesis of new organic semiconductor materials for microelectronics.

Since the beginning of scientific chemistry, chemists have been interested in light as an energy source to induce chemical reactions.[1] Absorbing light, molecules reach an electronically excited state. As a result, the distribution of electrons in the molecules is significantly different at these states when compared to the ground state. The chemical properties and more particularly the reactivity of the molecules also change, and the reaction spectrum of a family of compounds is considerably broadened. These phenomena may be fundamentally described by means of ground-state and excited-state potential-energy hypersurface topology.[2] In some instances, using photochemical steps significantly shortens a total synthesis, and frequently complex, polycyclic, or highly functionalized structures can be obtained from simple substrates. New product families or libraries difficult to achieve with ground-state reactions are thus available, opening new perspectives in the search of biologically active compounds.

Photochemical substrate activation often occurs without additional reagents, which diminishes formation of byproducts. Due to this fact, photochemical reactions become particularly interesting in the context of green chemistry. Some of these reactions can be carried out with visible light or sunlight as a renewable energy source. These possibilities were considered by Giacomo Ciamician almost a century ago when he stated in 1912:[3] *On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been*

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mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is. In the same paper, he also defined several principles of green chemistry.[4]

Using light as a reagent also facilitates transformations inside supramolecular structures or crystals. Such fragile structures are not decomposed by aggressive reagents or heating. These transformations are often carried out in order to control the stereoselectivity of photochemical reactions by a conformation-demanding environment. Such concepts have successfully been applied to organic synthesis.

Catalysis can also be performed in photochemical reactions. In those transformations possessing a quantum yield higher than 1, the reagent "light" is applied in substoichiometric amounts. In photosensitized reactions, stable sensitizers are used in small quantities and aspects of homogeneous and heterogeneous catalysis can be studied using soluble and insoluble sensitizers. Many of these compounds are organic, which opens this domain to organocatalytic reactions.[5] Irradiation with UV or visible light frequently improves the yields of metallocatalyzed reactions. For instance, ligand-exchange steps are often accelerated, and irradiation with light has become part of the standard reaction conditions.

One important item in organic synthesis is protecting-group manipulation. Although well established in biochemistry or microbiology, photochemically removable protecting groups is still rarely used in organic synthesis. These groups are particularly interesting since they do not need acidic, basic, or metal-assisted activation for cleavage and are removed under particularly mild conditions.

Irradiation is also used to initiate radical chain processes under mild conditions. Thus, particularly complex radical reactions such as certain radical tandem or multicomponent transformations have become possible.

After a period of stagnation, activity in the field of organic photochemical reactions and their application to synthesis has started to grow again in academic and industrial research. Many previous reactions as well as basic concepts of organic photochemistry have been outlined in books.[6−8] This review briefly discusses research activities in organic photochemistry from 2000 to 2006, demonstrating the high utility of these reactions for organic synthesis.

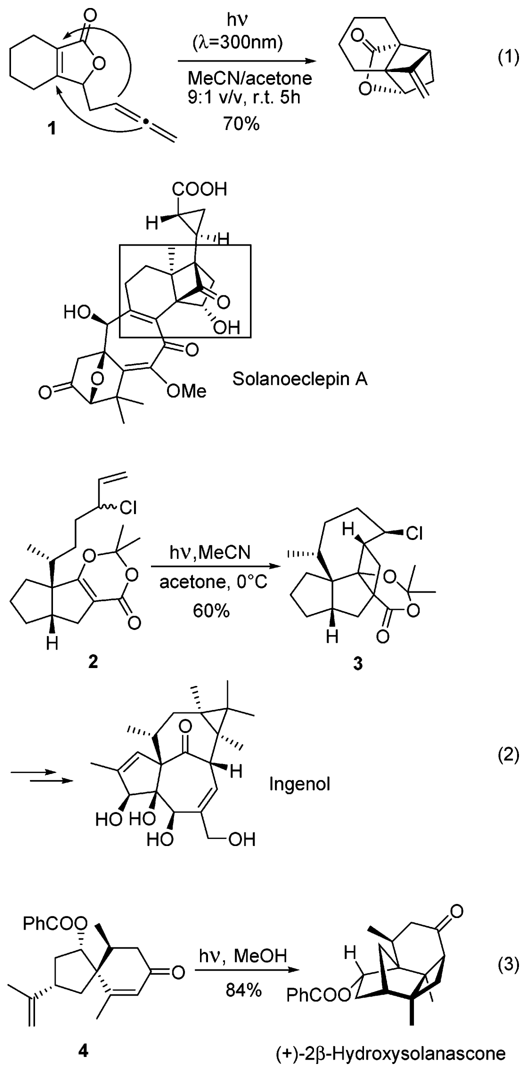
2. Photocycloadditions

2.1. [2 + 2] Cycloadditions

2.1.1. Formation of Cyclobutanes

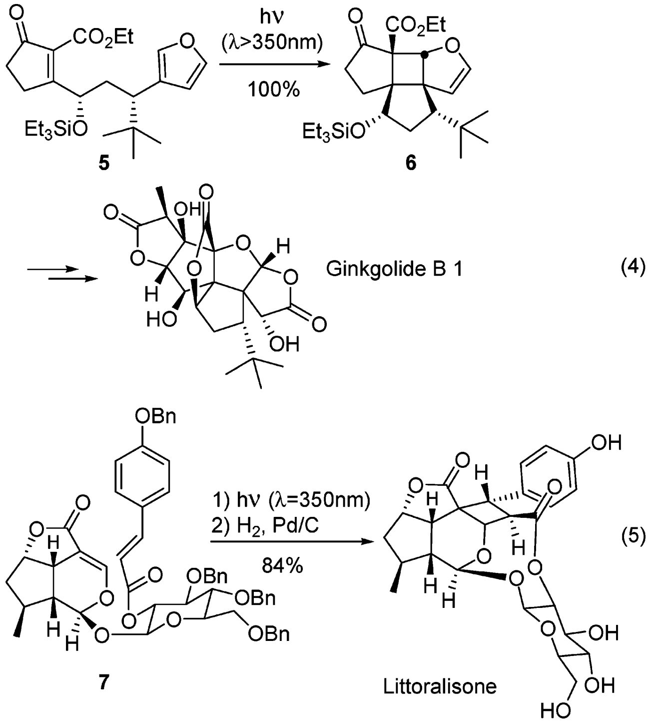
Among photochemical reactions, the [2 + 2] photocycloaddition of α,β-unsaturated ketones or esters to alkenes, alkynes, or allenes leading to cyclobutanes[9] is certainly the most applied reaction in organic synthesis.[10−14] With α,β-unsaturated ketones, the reaction can be induced by simple light absorption. In contrast, a sensitized reaction is preferred in the case of α,β-unsaturated esters. The transformation is then frequently performed with acetone as solvent and sensitizer. In many cases, the unsaturated carbonyl compounds react at the $^3\pi\pi^*$ state with alkenes and 1,4-biradical intermediates are generated. Their behavior significantly affects the outcome of the reactions,[11] particularly influencing the stereo- and regioselectivity. Numerous mechanistic investigations have been performed in the past. This research will not be reviewed here since most of the actual work in this field focuses on synthetic applications. As shown in the following examples, complex structures are accessible in only one step without using expensive and/or toxic reagents. This considerably simplifies the total synthesis of complex molecules such as natural products.

Scheme 1



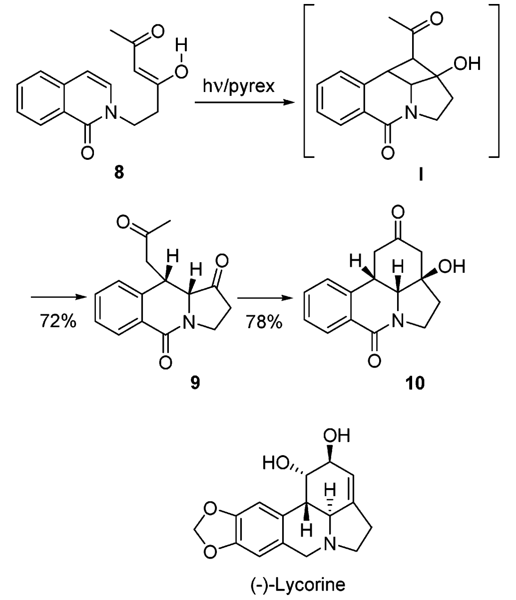
The sensitized [2 + 2] photocycloaddition of various α,β-unsaturated lactones such as **1** has been studied in the context of an application to the total synthesis of solaneclepin A (Scheme 1, eq 1).[15] As indicated by the arrows, only the crossed adduct was isolated. In one step, the tricyclic fragment containing a cyclobutane unit was obtained with the required relative configuration. In a comparable approach, the dioxyenone **2** was transformed into **3** via a [2 + 2] photocycloaddition (Scheme 1, eq 2).[16] The reaction efficiency is substrate dependent, and the yield was significantly increased by the presence of a chlorine atom in the allylic position of the alkene side chain. Due to a longer tether, and in contrast to the transformation of **1**, only the straight adduct was formed. Compound **3** was then used as an intermediate in the first total synthesis of ingenol.[17] It should be pointed out that this strategy is particularly efficient for building the trans-fused [4.4.1]bicyclic undecane core structure. The cyclohexenone derivative **4** was efficiently transformed into (+)-2β-hydroxysolanscone, the aglycone of phytoalexine, a compound possessing antibacterial activity (Scheme 1, eq 3).[18] In contrast to the previous examples, this transformation starts with light absorption of the substrate in the absence of sensitizers.

Scheme 2



A [2 + 2] photocycloaddition was also used as the key step in the synthesis of ginkgolide B 1 (Scheme 2, eq 4).[19] This natural product possesses a propellane core structure, and photochemical reactions have frequently been applied for the synthesis of such derivatives.[20] Cyclobutane **6** was obtained in quantitative yield from the nonsensitized photocycloaddition of **5**. Under similar conditions, the cinnamic acid derivative **7** was transformed in high yields via a [2 + 2] photocycloaddition followed by hydrogenation into littoralisone (Scheme 2, eq 5).[21] The reaction also occurs but less efficiently with visible light, which may indicate that the photochemical generation of the cyclobutane ring is part of the biosynthesis of this compound.[22] Currently, the acetone-sensitized [2 + 2] photocycloaddition is studied as a key step in the synthesis of bielschowskysin, a diterpene possessing a [9.3.0.0^{2,3}] tetradecane ring system with 11 stereocenters.[23]

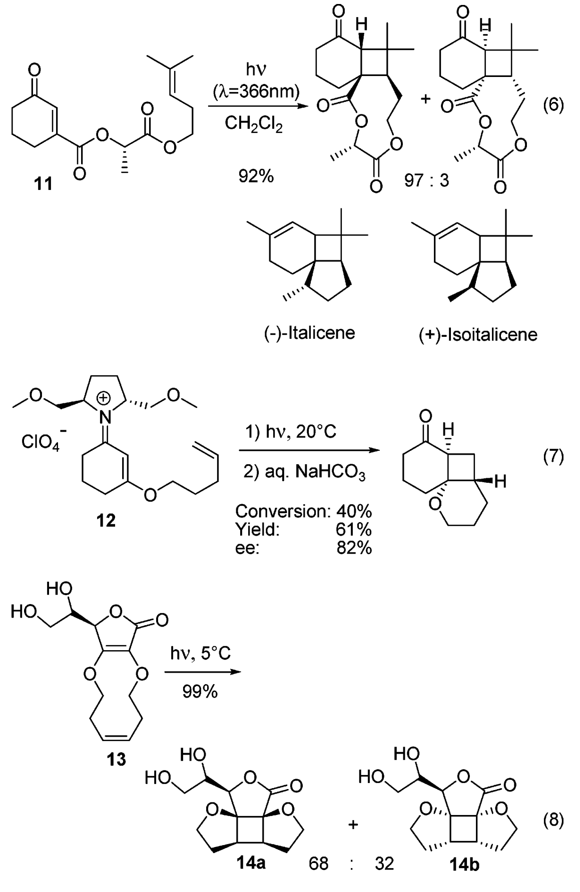
Scheme 3



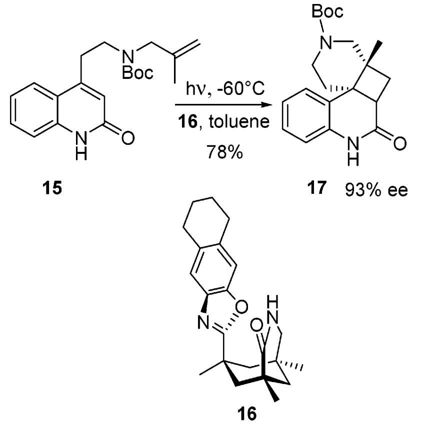
A versatile variant of the [2 + 2] photocycloaddition in synthetic applications is the de Mayo reaction. A recent example is presented in Scheme 3. In its enol form, a β-diketone reacts as an α,β-unsaturated ketone with an alkene. This step is followed by a retro-aldol reaction. In compound **8**, the mono-enolized β-diketone chromophore adds to the enamine part of the isoquinolone moiety and the tetracyclic aldol **I** is obtained as an intermediate.[24] Due to ring strain, the latter is immediately transformed into **9**. After an intramolecular aldol reaction, the more stable tetracyclic hydroxyketone **10** is isolated. Compound **10** possess the galathane skeleton which is encountered in lycorine alkaloids isolated from *Amaryllidaceae*.[25] In the context of a synthetic strategy, it can be interesting to temporarily prevent the retro-aldol step of the de Mayo reaction by protection of the hydroxyl group as shown for compound **2** in Scheme 1 (eq 2).[16] In such cases, transformations on other parts of the molecule can be performed which are incompatible with the retro-aldol product. Such a strategy was applied to reactions of dioxinones.[26] The reaction has also been performed with a boron derivative of a β-ketoimine.[27] A similar tandem [2 + 2] photocycloaddition-retro-Mannich reaction has been applied to the synthesis of nitrogen-containing heterocycles.[28]

In particular, the stereoselectivity of the [2 + 2] photocycloaddition[11,29,30] has been well documented due to its application to the synthesis of biologically active compounds. In the intramolecular reaction of **11**, enantioselectivity is achieved through the influence of a homochiral tether between the two reaction moieties (Scheme 4, eq 6).[31] Despite the fact that the chiral interaction is weak and far away from the reaction center (a convex system[32]), the

Scheme 4



Scheme 5



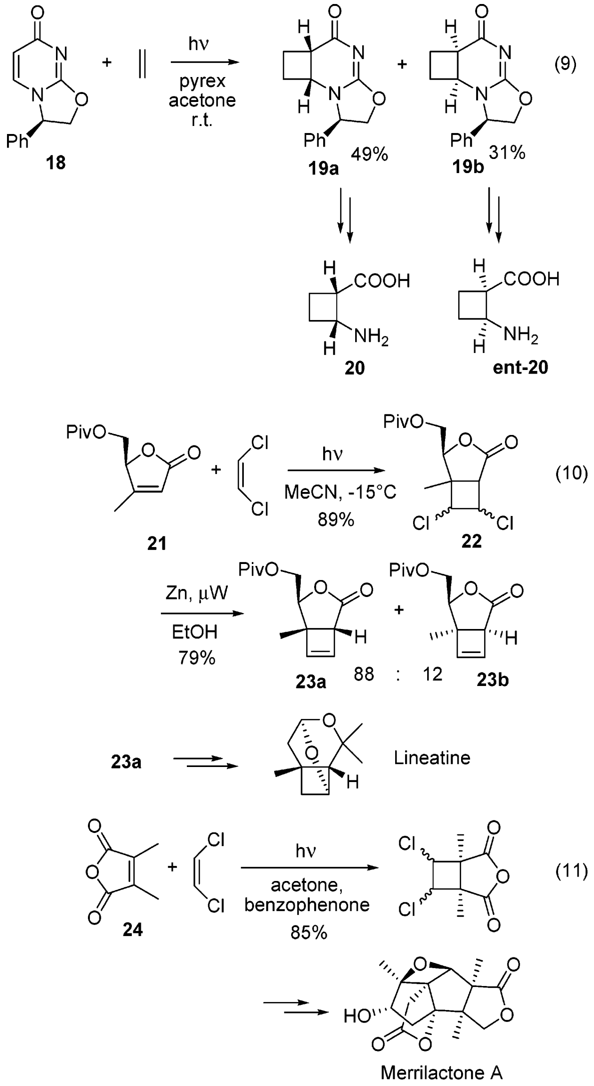
diastereoselectivity is high. The reaction can be applied to the asymmetric synthesis of the sesquiterpenes italicene and isoitalicene. These compounds have also been isolated from the essential oil of *Helicrysum* and are used as perfume and natural insecticides. For another recent example of macrocycle formation via a photosensitized [2 + 2] cycloaddition, see ref 33. Using a 1,4-naphthoquinone derivative carrying a smaller unsaturated side chain, the intramolecular cycloaddition was applied to the synthesis of elecanacin.[34] A [2 + 2] photocycloaddition was also carried out with enantiomerically pure α,β-unsaturated iminium salts such as the pyrrolidinium derivative **12** (Scheme 4, eq 7).[35] A transannular [2 + 2] photocycloaddition was performed with the ascorbic acid derivative **13** leading to the tetracyclic derivative **14a**,**b** (Scheme 4, eq 8).[36] In this case, the efficiency of the reaction depends on an appropriate chain length.

As previously mentioned, photochemical reactions have frequently been performed in supramolecular structures since the reaction conditions are particularly mild. In the case of an intramolecular [2 + 2] photocycloaddition, stereoselectivity can be induced inside such a host/guest structure. For example, the quinolone derivative **15** was complexed with the template structure **16** (Scheme 5).[37] Photocycloaddition yielded the cyclobutane derivative **17** with high enantioselectivity. For a comparable but less selective system, see ref 38. Numerous intra- and intermolecular photochemical reactions have been performed under analogous conditions using host structures such as **16**.[39,40]

β-Alkoxy- or β-amino-substituted α,β-unsaturated lactones, considered to possess only low photochemical reactivity, have recently been transformed with high yields.[41,42]

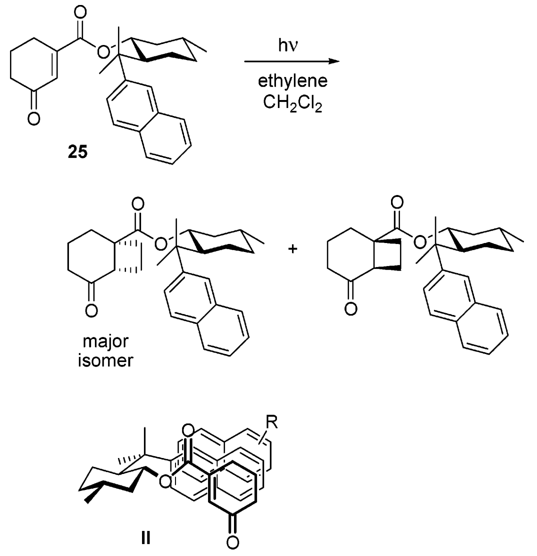
Intermolecular [2 + 2] photocycloadditions have also been studied and represent a facile and versatile access to cyclobutane derivatives. For example, the enantiomerically pure uracil derivative **18** reacted via a sensitized [2 + 2] photocycloaddition with ethylene to yield the corresponding cyclobutanes **19a** and **19b** (Scheme 6, eq 9).[43] The diastereoselectivity of this reaction was low,[44] but the stereoisomers were easily separated and then transformed into the β-amino acids **20** and **ent-20**. Similar products resulting from intra- or intermolecular [2 + 2] photocycloaddition have frequently been applied to the synthesis of β-amino acids.[42,45] When incorporated in a peptide structure, such β-amino acids have a significant influence on the secondary and tertiary structure of these compounds. In particular, 2-aminocyclobutane-1-carboxylic acid moieties rigidify a peptide structure in such a way that a helix secondary structure is induced.[46] In this context, the acyclic β-amino acid of a rhodopeptin derivative was replaced by a cyclobutane analog, prepared via [2 + 2] photocycloaddition of ethylene to a corresponding uracil derivative (compare to eq 9, Scheme 6).[47] Rhodopeptins are cyclic lipopeptides isolated from *Rhodococcus sp.* Mer-N 1033 possessing antifungal activities.

Scheme 6



In another example, 1,2-dichloroethylene was added to the furanone **21** (Scheme 6, eq 10).[48,49] The resulting mixture of diastereomers **22** was then dechlorinated to yield the cyclobutenes **23a**,**b**. The isomers **23a**,**b** have also been obtained by direct [2 + 2] photocycloaddition with acetylene, but this addition is significantly less efficient.[50] The isomer **23a** was then transformed into lineatine, the aggregation pheromone produced by the female ambrosia beetle (*Trypodendron lineatum*). The same strategy was recently applied to the synthesis of amino acids possessing a 2-azabicyclohexane skeleton and synthesis of the corresponding amino alcohols.[51] A further application concerns the synthesis of cyclobutane-fused nucleosides.[52] Addition of 1,2-dichloroethylene to dimethylmaleic acid anhydride **24** followed by dechlorination has also been applied to the total synthesis of the neurotropic sesquiterpene merrilactone A (Scheme 6, eq 11).[53] For a different application of the same reaction sequence to the synthesis of merrilactone A, see ref 54. Further detailed studies have been performed on this photocycloaddition.[55] Merrilactone A belongs to the family of propellane-containing natural products, and photochemical

Table 1. Influence of Naphthalene Derivatives on the Diastereoselectivity of the [2 + 2] Photocycloaddition of the Cyclic Enone 25 with Ethylene

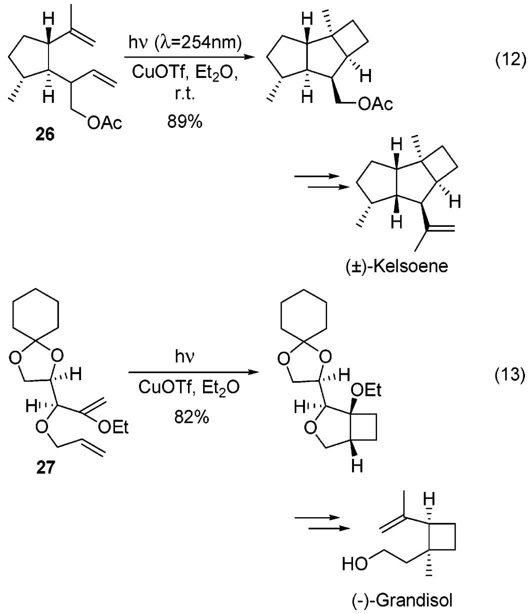


additive (equiv)	*T* (°C)	yield (%)	diastereomer excess (%)
	−78	89	56
naphthalene (5)	−78	95	70
1-cyanonaphthalene (10)	−78	85	81
2-cyanonaphthalene (10)	−78	99	79
1-methoxynaphthalene (10)	−78	95	77
1-phenylnaphthalene (10)	−78	95	83

reactions have been frequently applied to the synthesis of such compounds (see also Scheme 8, section 2.1.2).[20]

High stereoselectivities with chiral auxiliaries have been obtained using different techniques of double induction.[56] In these cases, chiral information is located on both substrates. Recently, a novel technique was developed in order to increase the diastereoselectivity of these reactions. It is often hard to induce high stereoselectivities in the intermolecular [2 + 2] photocycloaddition of enones. The reaction of enones such as **25** with alkenes is less stereoselective when a chiral auxiliary is used (Table 1).[57] With no additive, the stereoselectivity of the reaction of **25** with ethylene is low. However, in the presence of an excess of a naphthalene derivative, reaction diastereoselectivity significantly increased.[58] The authors explain this observation by formation of the exciplex **II**. An exciplex is a complex formed by a molecule in the ground state and a molecule in the excited state. The interaction is generally established by conjugated π systems. In such a structure, a conformation is stabilized which orients the cyclohexenone moiety to give a favorable diastereodifferentiation. Grafting the substrate on a polymer may also improve the diastereoselectivity.[59]

Scheme 7



Numerous photochemical reactions have been conducted in the liquid crystal phase, and the maximal observed stereoselectivity in a cholesteric phase was 1.1%.[60] Significant progress was recently achieved with a [2 + 2] photocycloaddition in a homochiral cholesteric phase.[61] A diastereoselectivity of 14% was obtained, while only 8% was detected for the same reaction in an isotropic phase.[61]

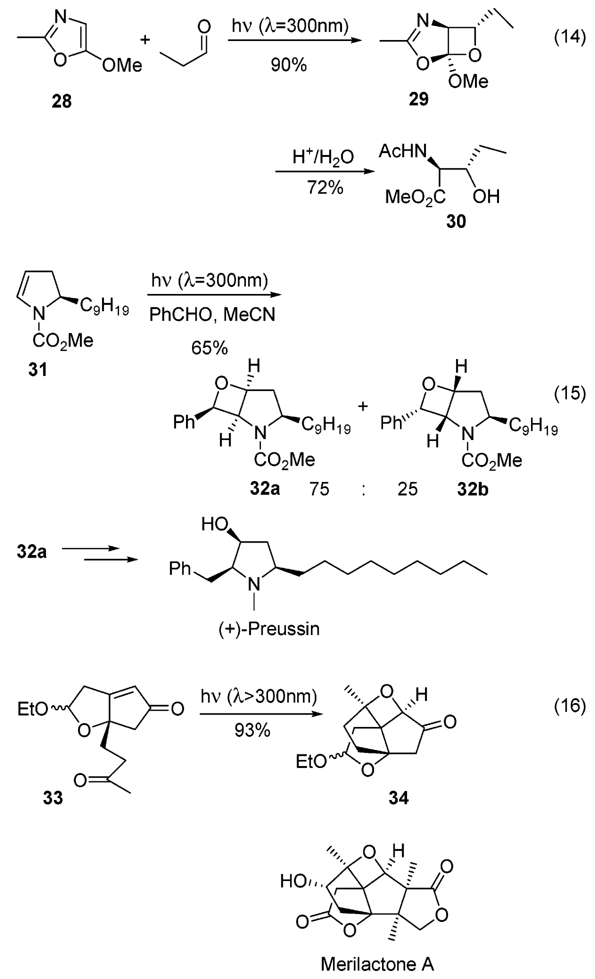
High enantiomeric excesses in the intermolecular [2 + 2] photocycloaddition (photodimerization) of coumarin derivatives have been observed when the reaction was carried out in homochiral crystals.[62]

The copper-catalyzed intramolecular [2 + 2] photocycloaddition with two alkenes is a frequently used reaction in organic synthesis.[11,63] In these reactions, complex formation enables the reaction partners to approach each other. Furthermore, the photophysical properties change, and two absorption bands of the complex are observed. It is not clear whether a MLCT (metal to ligand charge transfer) or a LMCT (ligand to metal charge transfer) excitation leads to formation of cyclobutanes.[63,64] Two examples are shown in Scheme 7. (±)-Kelsoene was synthesized from the diene **26** (Scheme 7, eq 12).[65] This sesquiterpene was also obtained using the corresponding addition of ethylene to an α,β-unsaturated ketone.[66] The copper-catalyzed [2 + 2] photocycloaddition is very versatile and has often been applied to asymmetric synthesis. For instance, (−)-grandisol, a component of the aggregation pheromone of the male boll weevil (*Anthonomus grandis*) was obtained from compound **27** with a copper-catalyzed [2 + 2] photocycloaddition as the key step of the synthesis (Scheme 7, eq 13).[67]

2.1.2. Formation of Four-Membered Heterocycles

Mechanistic aspects of the [2 + 2] photocycloaddition with a ketone and an alkene (the Paternò-Büchi reaction) and its application to organic synthesis are currently being investigated.[13,14,68] The products of this reaction are oxetanes, which are versatile intermediates for synthesis. For example, the alkoxyoxazole **28** readily reacted with propionaldehyde (Scheme 8, eq 14).[69] Product **29** was then transformed into the *erythro*-α-amino-β-hydroxy acid derivative **30**. Systematic studies on photochemical reactions between different oxazoles and dicarbonyl compounds have been carried out.[70] As part of the synthesis of (+)-preussin, the reaction of dihydropyrrol **31** and benzaldehyde gave oxetanes **32a,b**, where the relative configuration of the oxetane ring was completely controlled (Scheme 8, eq 15).[71] However, the chiral induction resulting from the chiral center carrying the *n*-nonyl substituent was moderate. The reaction was highly selective as far as regioisomers or exo/endo isomers (orientation of the phenyl substituent) were concerned. As in the case of the [2 + 2] photocycloaddition of α,β-unsaturated carbonyl compounds with alkenes (see above), the intramolecular version of the Paternò-Büchi reaction has been applied

Scheme 8

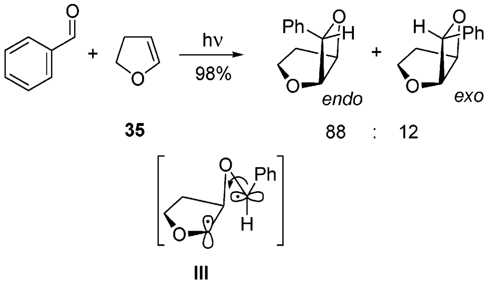


to organic synthesis. Compound **33** was efficiently transformed into the oxetane **34** (Scheme 8, eq 16).[72] This compound represents the core structure of merrilactone A, a natural product isolated from *Illicium mirrillianum* A. In the context of a screening for non-peptide neurotropic compounds, this natural product was reported to promote neurite outgrowth in fetal rat cortical neurons.

In recent years, many investigations have dealt with the stereoselectivity of this reaction with particular attention being paid to the temperature dependence of the diastereoselectivity and the mechanism of the stereoselection.[73] In this way, the role of the biradical intermediate for stereoselectivity was elucidated. Different mechanistic aspects of the regioselectivity and implication of single electron transfer have also been systematically studied.[74]

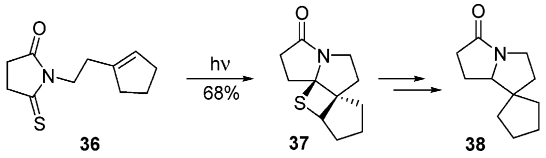
Recently, organochemical, physicochemical, and theoretical studies have been carried out on the exo/endo selectivity of the Paternò-Büchi reaction.[75] While not only being of interest in this reaction context, these results contribute to a general understanding of the behavior of biradical intermediates.[76] In the reaction of aromatic aldehydes with dihydrofuran **35**, formation of oxetanes possessing an endo configuration is favored even in examples where the corresponding exo isomer is much less sterically hindered (Scheme 9).[75,77] This behavior can be explained by steric interactions in the triplet biradical intermediate **III**. These interactions are minimized in the depicted conformation. The perpendicular orientation of the two radical-carrying orbitals favor spin–orbit coupling during the cyclization in order to accelerate intersystem crossing (triplet → singlet) in this reaction step. This is essential since the final products possess singlet multiplicity. The selectivity is increased because biradicals in unfavorable conformations may readily undergo cleavage to yield the starting compounds. Recently, a thorough theoretical investigation was performed on the cyclization step of the Paternò-Büchi reaction.[78,79] Other reaction parameters such as temperature, solvent viscosity, different steric and electronic interactions, as well as the spin multiplicity have been systematically studied.[75,80]

Scheme 9



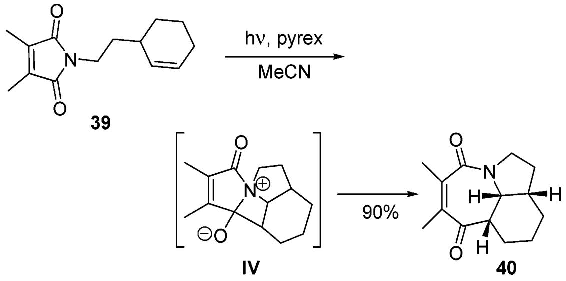
The Paternò-Büchi reaction can also be performed with thiocarbonyl compounds.[81] Thioketones undergo photochemical reaction from the $^3n\pi^*$ and long-lived $^1\pi\pi^*$ (S_2) state.[81,82] Thioamides, thiocarbamates, or thioimides preferentially react from the $n\pi^*$ state.[83−85] In the case of thioamides or thioimides, the thiethanes which are initially formed are not always stable. In this way, nitrogen-containing heterocycles have been obtained after their rearrangement.[86] For instance, upon irradiation, the thiosuccinimide **36** underwent a thio analogous Paternò-Büchi reaction leading to **37** (Scheme 10).[83] This compound was transformed into the spirocyclic pyrrolicidine derivative **38**.

Scheme 10



In compound **39**, an intramolecular [2 + 2] photocycloaddition is observed between a maleimide moiety and an alkene (Scheme 11).[87] Due to ring strain and steric hindrance, addition occurs with the C═N bond (**IV**). The double-bond character of the latter bond can be explained by the high contribution of the corresponding mesomeric structure in amide or imide functions. The rearrangement leads to the tricycle **40** in high yields. This motif is found as a core structure in various alkaloids such as neotuberostemonine, stenine, and tuberostemonine (Figure 1).[88] The reaction also provides a versatile approach to bi- or tricyclic derivatives

Scheme 11



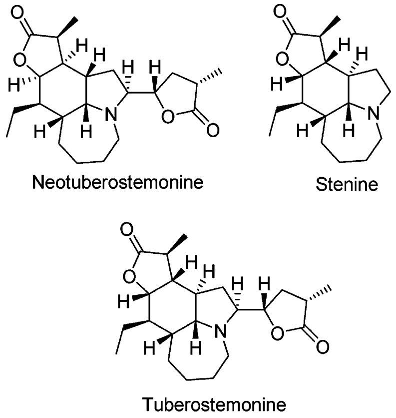


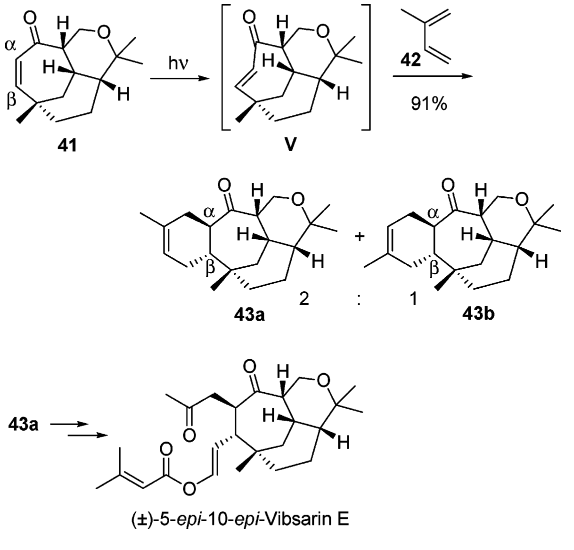
Figure 1.

of perhydroazaazulene.[89] The transformation has also been performed in a photochemical continuous flow reactor.[90] After a run of 24 h, 175 g of a corresponding azaazulendione derivative was obtained (yield = 80%).

2.2. [4 + 2] Cycloadditions of Photochemically Generated Strained Alkenes

[4 + 2] Cycloadditions (Diels−Alder reactions) are mainly observed in the ground state. The high reactivity is explained by means of orbital symmetry according to the Woodward−Hoffmann rules for concerted reactions.[91] Consequently, these types of concerted reactions should be unfavorable in the excited state. Indeed, photochemical [4 + 2] cycloaddition reactions are less frequent. In many cases, these reactions are not concerted and various intermediates are involved. In contrast to these cycloadditions, [2 + 2] photocycloadditions involving α,*β*-unsaturated ketones and alkenes are frequently observed and start in the electronically exited state of the enone chromophore (section 2.1.1). In the following example, the α,*β*-unsaturated ketone moiety of **41** undergoes photochemical cis/trans isomerization leading to intermediate **V**, which is no longer electronically excited but highly strained (Scheme 12).[92] According to Woodward−Hoffmann rules,[91] it may undergo a [4 + 2] suprafacial cycloaddition with a diene (Diels−Alder reaction). Thus, the two regioisomeric trans adducts **43a**,**b** were obtained via addition of isoprene **42**. It should be noted that in a Diels−Alder reaction the cis isomer **41** is much less reactive, probably due to the increased thermodynamic stability of this isomer. Steric hindrance in **41** also contributes to the low reactivity. Compound **43a** was transformed into (±)-5-*epi*-10-*epi*-vibsarin E. This strategy also enabled the entry of a substituent in the *β* position of **41** in the sterically more hindered diastereotopic half space.

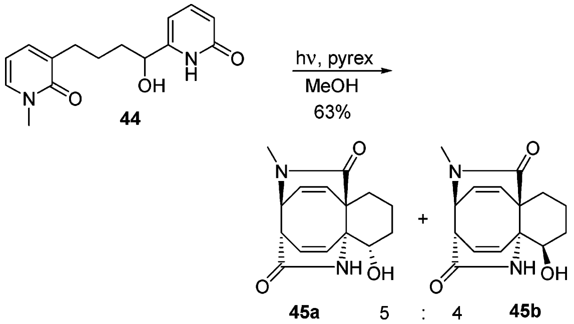
Scheme 12



2.3. [4 + 4] Cycloadditions

Although rare in the ground state, [4 + 4] cycloadditions are frequently observed in the excited state. In an intramolecular reaction, the two pyridone moieties of **44** react with each other, leading to the cyclooctadiene derivatives **45a**,**b** (Scheme 13).[93] Various other examples have been published.[94] The reaction also provides an approach to tricyclic derivatives of cyclooctane.[95] This motif is encountered in several natural products such as fusicoccin A, ophiobolin A, or ceroplastol (Figure 2). The intermolecular version of this reaction has also been performed.[96] This reaction was also carried out in the solid state.[97] Use of more electron-rich heterocyclic moieties such as furans has also been studied.[98]

Scheme 13



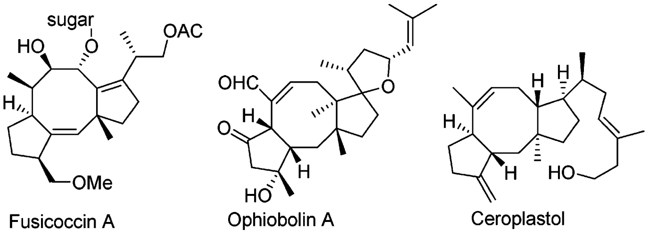


Figure 2.

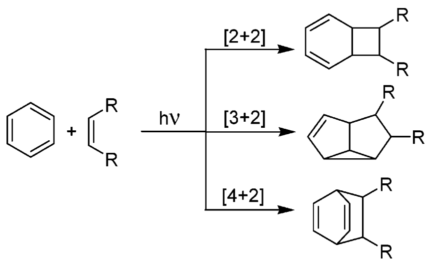
2.4. Photocycloadditions of Aromatic Compounds

2.4.1. Benzene Derivatives

Most ground-state reactions of aromatic compounds are characterized by the fact that aromaticity is reestablished in the final products. For instance, electrophilic substitution is the most characteristic reactivity for these compounds. At the exited state, however, these molecules possess a strong tendency to lose aromaticity. The most characteristic photochemical reactions of aromatic compounds are cycloadditions with alkenes.[99,100] Three modes can be distinguished: [2 + 2] (*ortho*-photocycloaddition), [3 + 2] (*meta*-photocycloaddition), and [4 + 2] (*para*-photocycloaddition or photo-Diels−Alder reaction) (Scheme 14). Numerous applications in organic synthesis have been described.

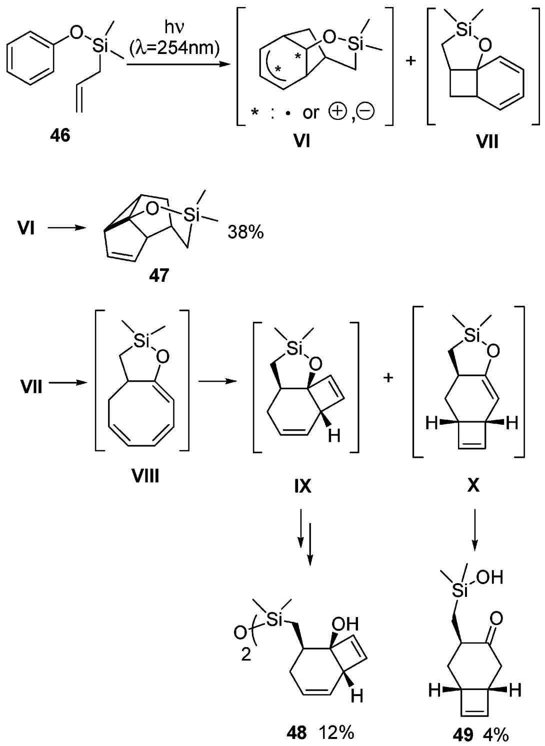
Among these reaction modes, [3 + 2] photocycloaddition has been studied the most.[101] However, recent work has shown that this cycloaddition competes with the [2 + 2]

Scheme 14



photocycloaddition.[102] Often the products of the latter reaction are less stable. Due to the availability of efficient separation techniques, characterization of these products has become possible. The silylated phenol derivative **46** reacts via both a [3 + 2] and a [2 + 2] photocycloaddition to yield intermediates **VI** and **VII**, respectively (Scheme 15).[103]

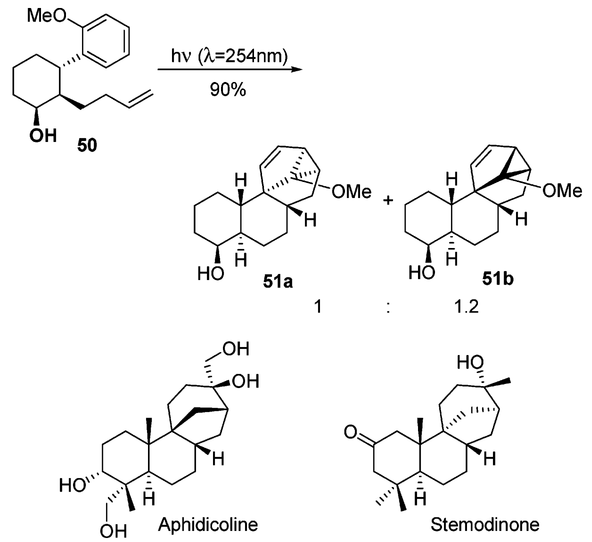
Scheme 15



Intermediate **VI** was transformed into the tetracyclic compound **47** by a cyclopropanation step. Since the reaction occurs in the singlet state, this intermediate also possesses a zwitterionic character. Intermediate **VII** resulting from [2 + 2] addition generates **VIII** via a pericyclic reaction. Contraction of the cyclooctatriene moiety leads to the cyclobutene intermediates **IX** and **X**. The final products of this reaction are obtained by hydrolysis (**49**) or hydrolysis followed by dimerization (**48**).

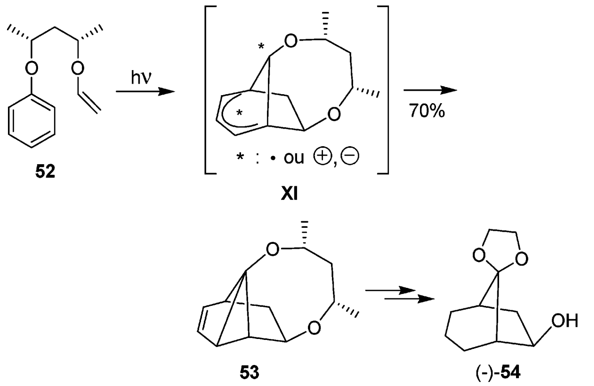
Compound **50** only undergoes [3 + 2] photocycloaddition (Scheme 16).[104] The adducts **51a**,**b** were isolated in high yields, and these structures resemble aphidicoline and stemodinone. Several analogues of these compounds possess anticancer activity or can be used against leishmanial parasites. Recently, intramolecular [3 + 2] photocycloadditions with bicyclic benzene derivatives have been published.[105] The transformation topology of the different isomers of the [3 + 2] photocycloaddition has been reviewed.[100] For other possible applications to organic synthesis, see ref 106.

Scheme 16



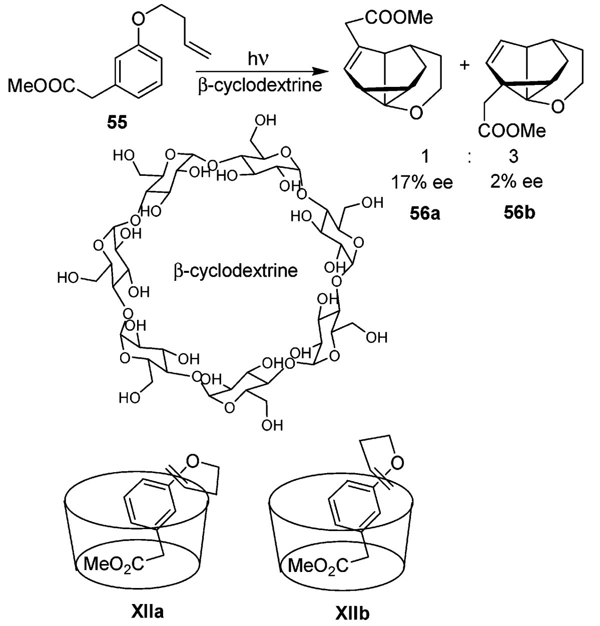
Chiral induction has also been studied for the [3 + 2] photocycloaddition. In compound **52**, the two reaction partners (phenol and vinyl ether) are linked together by a homochiral tether (Scheme 17).[107] Addition occurs stereospecifically, and intermediate **XI** is formed. As the reaction takes place at the singlet state, the intermediate **XI** may be viewed as either a biradical or a zwitterion. After regioselective formation of a cyclopropane ring, product **53** is isolated and then transformed into the enantiopure alcohol (−)-**54**. Several other examples have also been described.[108] A further approach deals with chiral induction inside a supramolecular structure. As previously indicated, photochemical reactions are especially suitable for such reaction media since they can be carried out under particularly mild conditions. Neither high temperatures nor aggressive reagents, which may destroy the supramolecular assembly, are needed for such transformations. Inside β-cyclodextrin, the phenol derivative **55** was transformed into the regioisomeric products **56a**,**b** of a [3 + 2] photocycloaddition (Scheme 18).[109] The difference in enantiomeric excess between **56a** and **56b** is explained by the fact that the interaction with the homochiral matrix is different for the two transition states **XIIa** and **XIIb**. During the formation of isomer **56a** from intermediate **XIIa** this interaction is stronger and induces a higher enantioselectivity. Numerous photochemical reactions are currently being studied that employ cyclodextrins.[110−112]

Scheme 17



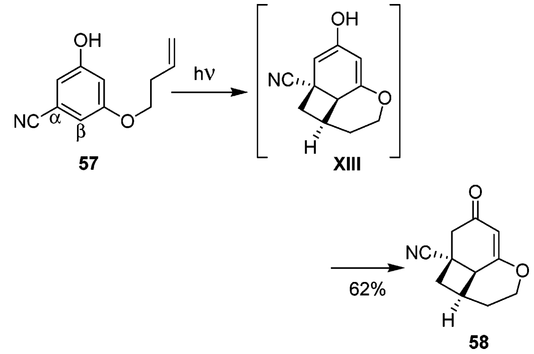
The presence of electron-withdrawing substituents favors the [2 + 2] photocycloaddition compared to the [3 + 2]

Scheme 18



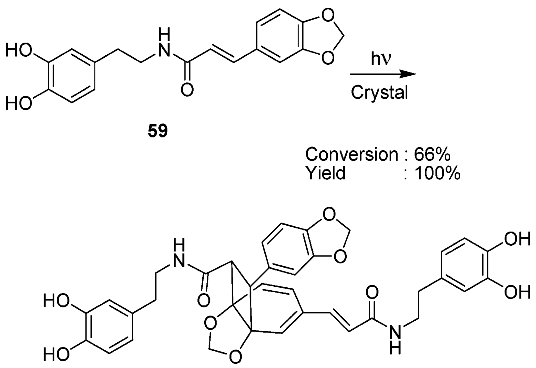
one.[113,114] For instance, the presence of a nitrile group in the resorcinol derivative **57** favored a [2 + 2] cycloaddition in the α,*β* position of this substituent (Scheme 19).[115] A cyclohexane-1,3-dione derivative **58** was obtained by spontaneous rearrangement of the intermediate **XIII**. Such products may be used as intermediates in the synthesis of a new generation of herbicides. For other recent examples of this reaction, see ref 116. The same reaction was also stereoselectively performed.[114]

Scheme 19



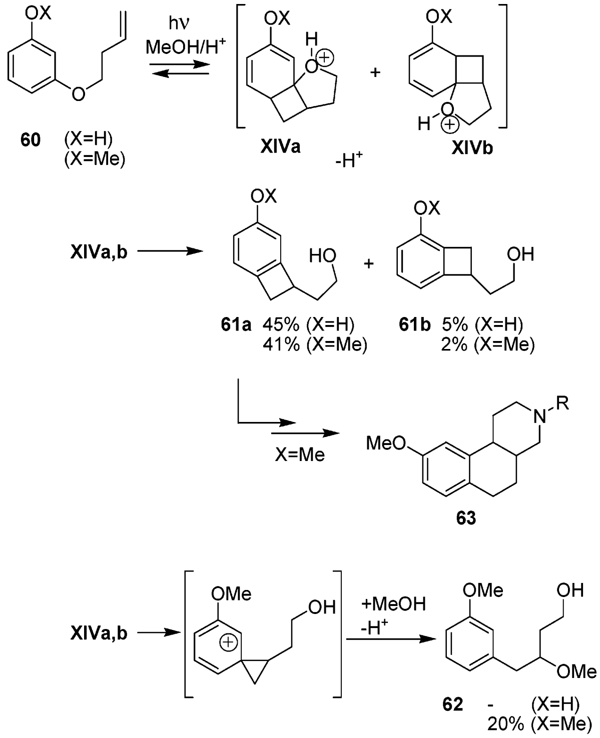
The orientation of the substrate in a crystal may direct the reaction pathway. For instance, dimerization of the cinnamic derivative **59** proceeds via a [2 + 2] photocycloaddition of an alkene moiety to a benzene ring.[117] When irradiated in solution, no photocycloaddition of **59** is observed (Scheme 20). The [2 + 2] photocycloaddition is also frequently observed with naphthalene derivatives.[118−120]

Scheme 20



As indicated above, primary adducts of [2 + 2] photocycloadditions with benzene derivatives are frequently unstable. However, when the reaction is performed in an acidic medium, these reaction adducts can be transformed into stable final products via acid-catalyzed reactions. The resorcinol derivatives **60** yielded adducts **XIVa** and **XIVb** (Scheme 21).[121] These intermediates rearranged to benzocyclobutenes **61a**,**b** or, depending on the substitution, monocyclic compounds such as **62**. Benzocyclobutenes are interesting substrates in organic synthesis. For instance, **61a** has been transformed into the nitrogen-containing tricyclic compound **63**, which possesses an affinity to dopamine receptors. A comparable reaction was also performed with naphthalene derivatives.[122] The effects of an acidic reaction medium have been observed for numerous photochemical reactions.[123]

Scheme 21

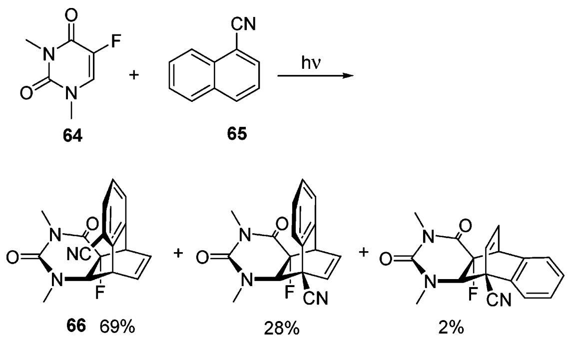


Numerous efforts have been made to understand the reaction mechanism of photocycloadditions of aromatic compounds.[99,100,101,113,122,124] In this context, the gas-phase reactivity of 5-phenyl-1-pentene was studied in order to describe the behavior of different intermediates such as biradicals or exciplexes.[125] Pure theoretical studies complete this approach.[126]

2.4.2. Condensed Aromatic Compounds

In contrast to the benzene aromatics, [4 + 2] or [4 + 4] photocycloadditions are often observed with polycondensed aromatic compounds. The [4 + 2] cycloaddition (photo-Diels−Alder reaction) is frequently observed with naphthalene derivatives.[118−120] In contrast to their ground-state counterparts, this cycloaddition is not concerted. Recently, the fluorouracil derivative **64** was added to 1-cyanonaph-

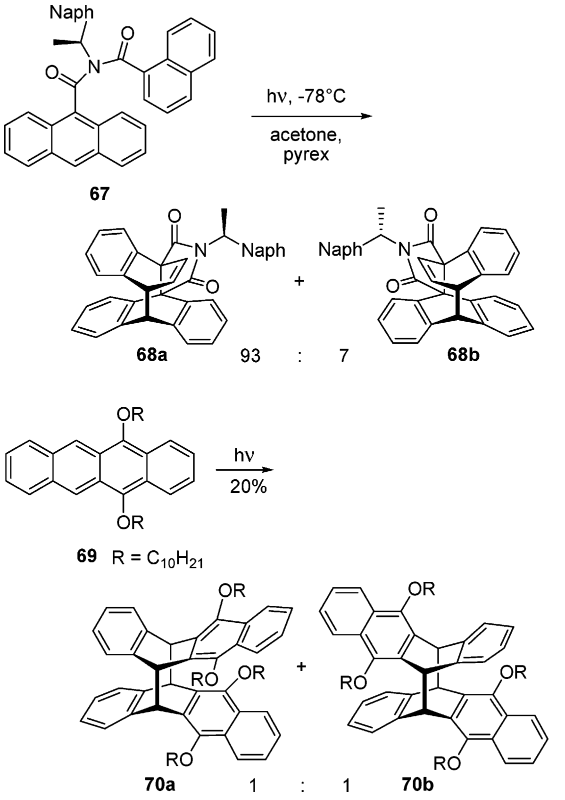
Scheme 22



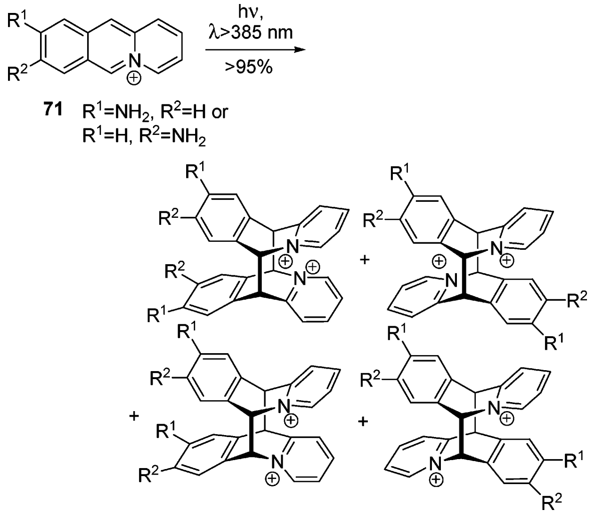
thalene **65** (Scheme 22).[127] A similar reaction was also observed with an unsubstituted naphthalene.[128] Interestingly, most of the adducts resulted from addition to the nonactivated benzo moiety (**66**). Mechanistic details involving various intermediates, among them [2 + 2] adducts, have been discussed for such reactions.[119,129]

A large variety of these reactions with anthracene derivatives is known.[112,119,120,130,131] Irradiation of the enantiomerically pure anthracene derivative **67** yielded the adducts **68a**,**b** with high diastereoselectivity via [4 + 4] photocycloaddition (Scheme 23).[132] The reaction has also been performed in crystals.[132,133] As already mentioned, the crystal structure considerably influences the outcome of these reactions. This was shown for the regioselectivity of the [4 + 4] dimerization of anthracene derivatives.[134] Comparable reactions can also be performed with benzene derivatives.[135] The tetracene derivative **69** reacted in the same way to yield two regioisomers of the adduct **70a**,**b** (Scheme 23).[136] Heterocyclic analogues such as acridicinium salts **71** also react via [4 + 4] photocycloaddition, and the adducts can be used as materials possessing nonlinear optic (NLO) or photorefractive properties (Scheme 24).[137] A similar dimerization via [4 + 4] photocycloaddition of a 2,7-diazaanthracene derivative has been reported.[138]

Scheme 23



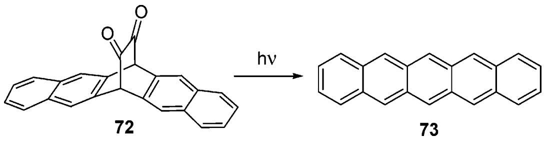
Scheme 24



Recently, an intramolecular [3 + 2] photocycloaddition of an alkene moiety to a naphthalene ring was described.[139] In this case, competitive [2 + 2] photocycloaddition is faster, and at the beginning of the reaction the corresponding adducts are the main components in the product mixture. However, their formation is reversible, and the [2 + 3] adducts progressively become preponderant since they possess a higher photostability.

A reversed [4 + 4] photocycloaddition was used for the release of pentacene **73**, a technique used for fabrication of organic thin-film transistors (OTFT) (Scheme 25). The low solubility of **73** significantly complicates its deposition in suitable quantities. Soluble precursors are therefore needed. After deposition, for instance on a wafer, pentacene is regenerated by a chemical reaction. In the present case, α-diketone **72**, which is fairly soluble in toluene, was irradiated at $\lambda > 390$ nm under argon atmosphere in order to generate pentacene **73** (Scheme 25).[140] The presence of oxygen must be avoided in order to prevent photooxygenation[141] (see also section 8). The same reaction has been performed to release heptacene[142] or an air-stable anthracene derivative.[143]

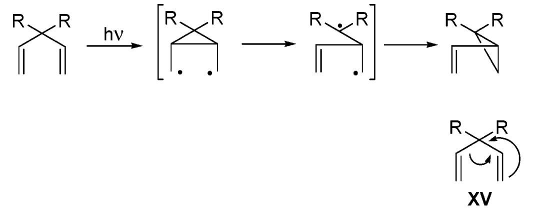
Scheme 25



3. Photochemical Rearrangements

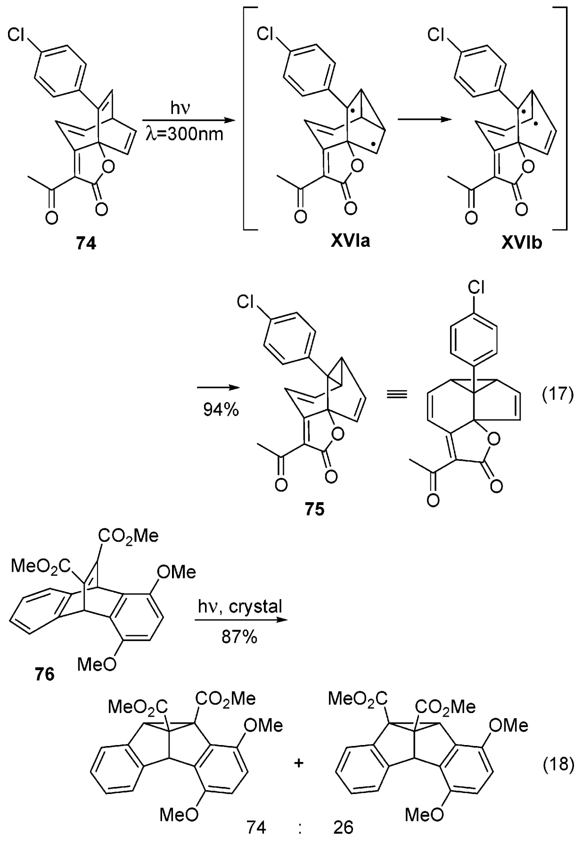
Starting from relatively simple substrates, photochemical rearrangements have been used to synthesize complex, mainly cyclic, products.[6-8] For the reactions presented below, mechanistic aspects and applications to organic synthesis have been particularly well investigated. One example is the di-π-methane rearrangement[144] whose mechanism is shown in Scheme 26.[8] The biradical character is accentuated, which in the case of a triplet sensitization is particularly relevant. The reaction can also be induced by direct absorption. Under these conditions, a reaction at the singlet state is also possible. Therefore, a concerted mechanism as indicated by structure

Scheme 26



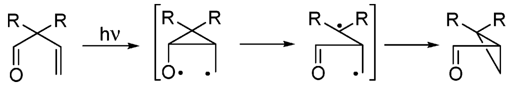
XV should also be considered. Compound **74** is transformed into **75** by direct light absorption (Scheme 27, eq 17).[145] In the first step, the 1,4-biradical intermediate **XVIa** containing a cyclopropane is formed. Cleavage of one of the σ bonds of the cyclopropane moiety leads to the 1,3-biradical and formation of one π bond in intermediate **XVIb**. Radical recombination yields the final product. On the basis of the published results of this example, it cannot be decided whether the reaction possesses a triplet or singlet mechanism. The di-π-methane rearrangement is frequently described with barrelene derivatives.[146] Transformation of the dibenzobarrelene **76** has been carried out in a crystal (Scheme 27, eq 18).[147] The reaction also occurs with heterocyclic aromatic compounds[148] or in ionic liquids.[149]

Scheme 27

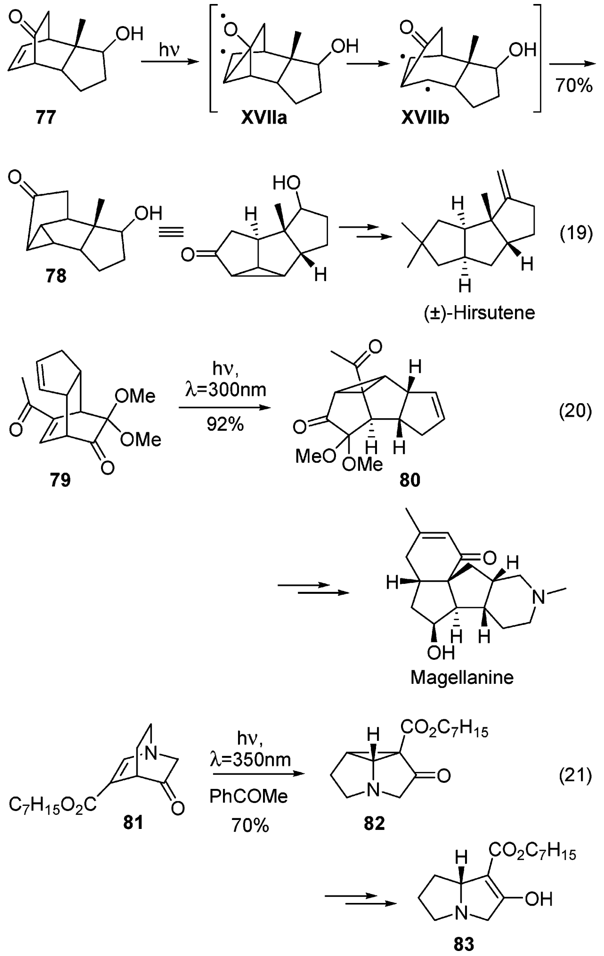


A heteroatom variant of this reaction also exists. The oxa-di-π-methane rearrangement has been studied, and numerous applications to synthesis have been described.[150] The mechanism is depicted in Scheme 28. In this case, the C═O double bond is regenerated in the final product. For example, the tricyclic β,γ-unsaturated ketone **77** is transformed into **78** via the intermediates **XVIIa** and **XVIIb** (Scheme 29, eq 19). The linear triquinane (±)-hirsutene has been synthesized from **78**.[151] For a similar synthesis, see ref 152. The tricyclic ketone **79** was efficiently transformed into **80** (Scheme 29, eq 20),[153] which was used as a key intermediate in the synthesis of the tetracyclic alkaloid magellanine. A tricyclic derivative of **79** was also subjected to an oxa-di-π-methane rearrangement.[154] The resulting photoproduct is currently used as a key intermediate in the asymmetric synthesis of the linear triquinanes (+)-hisutic acid and (−)-complicatic acid. The oxa-di-π-methane rearrangement has also been performed with heterocycles such as **81**, which was transformed into **82** in a photosensitized reaction (Scheme 29, eq 21).[155] Compound **82** was then transformed into the pyrrolizidine derivative **83**. As in many other cases, the oxa-di-π-methane rearrangement can be performed inside supramolecular structures. In this case, the reaction was performed in zeolite cavities.[156] A di-π-methane rearrangement with corresponding imines of β,γ-unsaturated ketones is also possible.[157] Currently, these aza-di-π-methane rearrangements are also carried out under electron-transfer conditions.[158]

Scheme 28

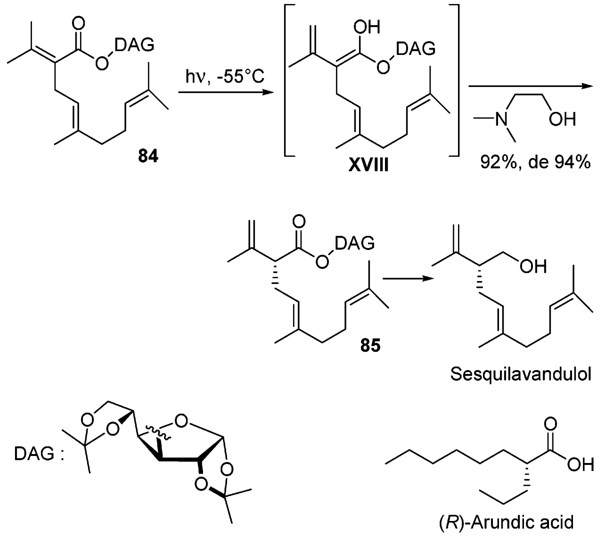


Scheme 29



Although possible in the ground state, deconjugation reactions can conveniently be performed under photochemical conditions. The stereoselectivity of the photodeconjugation of α,β-unsaturated carbonyl compounds and its application to organic synthesis have been particularly well

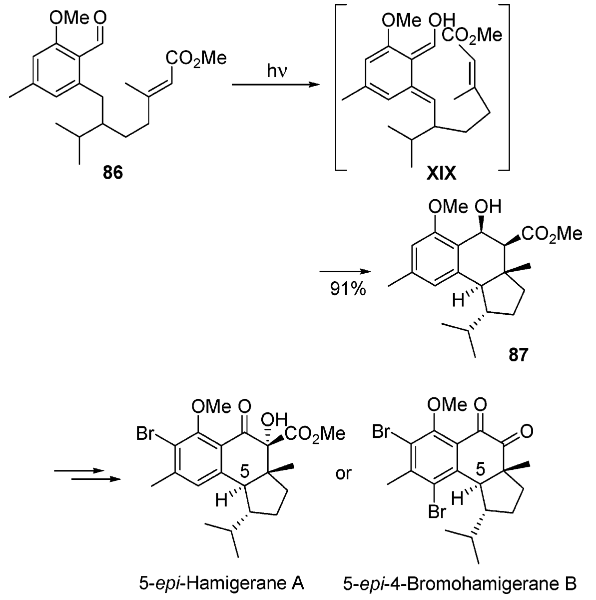
Scheme 30



investigated. For example, the α,*β*-unsaturated ester **84** was transformed with high yields and high diastereoselectivity into the corresponding *β*,*γ*-unsaturated derivative **85** (Scheme 30).[159] Chiral induction occurred during the protonation of intermediate **XVIII**. The reaction was applied to the synthesis of sesquilavandulol. The same strategy was chosen for the synthesis of (*R*)-arundic acid.[160] This compound possesses neuroprotective properties and may play a role in the treatment of Alzheimer's disease. Enantioselectivity was also induced catalytically using homochiral amino alcohols as protonating reagents.[161] In this case, detailed mechanistic studies were carried out. For other examples, see refs 162−164.

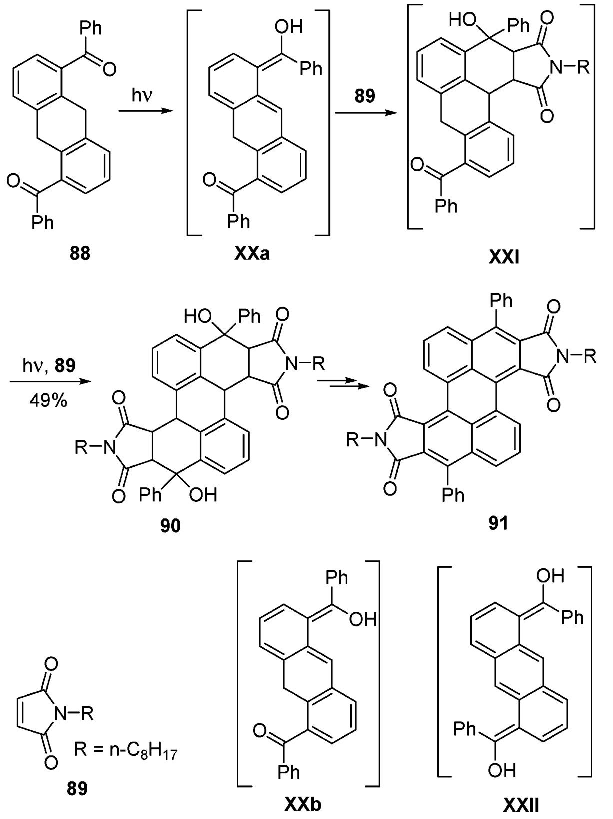
In a similar way, hydrogen abstraction by an aromatic aldehyde function in the benzylic position of a side chain leads to a photoenol or, more precisely, a hydroxyquinodimethane derivative. Thus, the salicylic aldehyde derivative **86** afforded intermediate **XIX**, which was trapped in an intramolecular Diels−Alder reaction (Scheme 31).[165] Compound **87** possessing five stereocenters was then transformed into 5-*epi*-hamigerane and 5-*epi*-4-bromohamigerane B. Several other examples of this reaction, used in hamigerane syntheses, have been published.[166] In the synthesis of polycyclic compounds, *o*-quinodimethane intermediates have frequently been generated from the corresponding precursors, proving once again the efficiency of the strategy.[167]

Scheme 31



The same reaction was applied to the synthesis *Z*-shaped perylene bisimide derivatives. Perylene bisimides have been used in the fields of electron-transfer processes, liquid crystals and other supramolecular assemblies, photovoltaics, fluorescent sensors, or organic semiconductors. Upon irradiation, the diketone **88** was transformed into the enol **XXa** (Scheme 32).[168] The maleimide derivative **89** was added via a Diels−Alder reaction (**XXI**). In a second reaction sequence, the bisadduct **90** was prepared. The proposed mechanism is more probable than the mechanism involving the bisenolintermediate **XXII**.[169] In principle, both cis/trans isomers **XXa** and **XXb** are generated from **88**. However, it has frequently been observed that only intermediates of type **XXa** undergo intermolecular cyclization while intermediates such as **XXb** rapidly tautomerize.[164,170,171] Formal dehydration led to the fully conjugated *Z*-shaped perylene bisimide derivative **91**. The reaction was applied to the synthesis of an anthracene-based chemical sensor.[172] Phenanthrene and benzo[*e*]pyrene bisimides have been obtained in the same way.[173] Reaction of a variety of bis(*o*-methylphenyl)phenyl ketone derivatives in combination with acrylates has been applied to the production of copolymer blends.[174]

Scheme 32



o-Quinomethanes or *o*-quinomethides, which are heteroatom analogues of quinodimethanes, can be mildly generated by photolysis of *o*-hydroxybenzyl alcohols.[175] The reaction can also be performed with the corresponding Mannich bases.[176] Nucleophiles such as amines or α-aminoesters

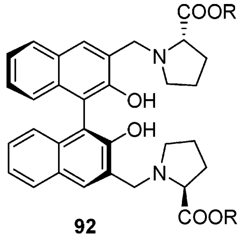
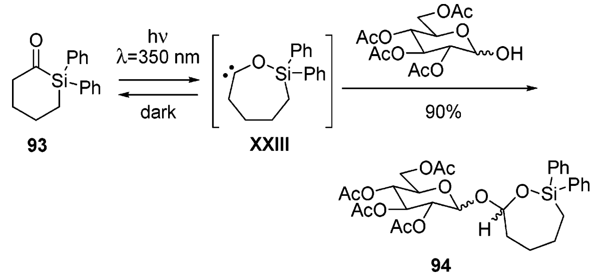


Figure 3.

readily add to these intermediates. This strategy was applied to the synthesis of enantiomerically pure BINOL ligands such as **92** (Figure 3) carrying L-proline substituents.[177] SimilarBINOL derivatives were used for photoinduced cross linking of DNA.[178]

Rearrangements involving C−X bonds may be accelerated by light absorption. This has been shown for the Brook rearrangement of acylsilanes.[179] Under photochemical conditions, the acylsilane **93** is in equilibrium with the silyloxycarbene **XXIII** (Scheme 33).[180] These intermediates react with a variety of functional groups. In the present case, addition occurs with an anomeric hydroxyl group of a carbohydrate, leading to an acetal such as **94**. For mechanistic details, see ref 181. Addition was also performed with acyclic acylsilanes and on different carbohydrate hydroxyl functions. Some of these products may serve as photoreleasable anticancer prodrugs. The photochemically induced Brook rearrangement was applied to the synthesis of nucleosides.[182] Photoinduced migration of silyl groups to oxygen have also been observed at longer distances. Recently, such 1,5 shifts were studied in aromatic systems.[183,184]

Scheme 33

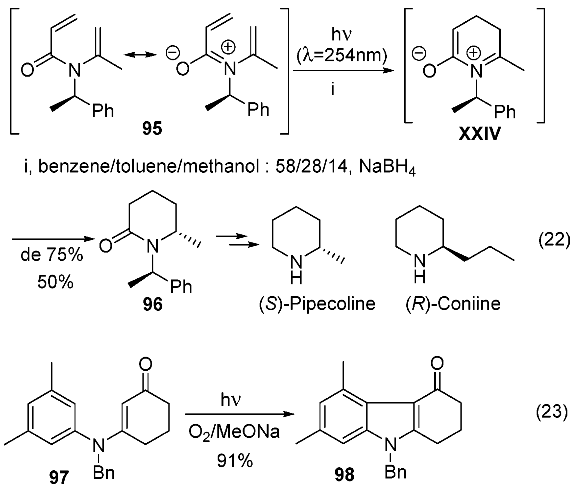


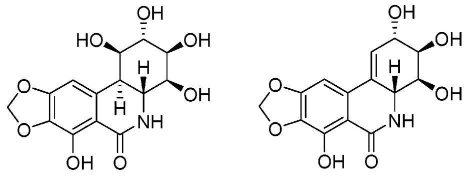
4. Cyclizations

4.1. Pericyclizations

Investigation of pericyclization reactions, in particular, their stereoselectivity, contributed significantly to formulation of the Woodward−Hoffmann rules for concerted reactions.[91] Pericyclizations are valuable tools in organic synthesis,[185] and photochemical transformations of this type have been used for the synthesis of carbocyclic[186] and heterocyclic compounds.[187] Synthesis of (*S*)-pipecoline, for example, was carried out by photochemical cyclization of the enantiomerically pure acrylamide derivative **95** (Scheme 34, eq 22).[188] The presence of $NaBH_4$ in the reaction mixture caused reduction of the imonium function of **XXIV** (or an O-protonated intermediate), and lactam **96** was isolated. This product was easily transformed into the desired target molecule. An identical strategy was applied to the synthesis of (*S*)- and (*R*)-coniine. Cyclization of a benzamide derivative was used as the key step in the synthesis of (+)-narciclasine and (+)-pancratistatin (Figure 4).[189] These alkaloids have been isolated from the roots of *Pancratium littorale* and possess antitumor activity. Photocyclization of vinylogous anilides such as **97** lead to tricyclic indoles (**98**) when carried out in the presence of air oxygen (Scheme 34, eq 23).[190]

Scheme 34



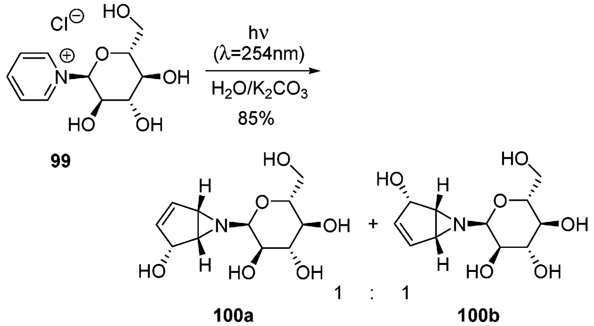


(+)-Pancratistatin (+)-Narciclasine

Figure 4.

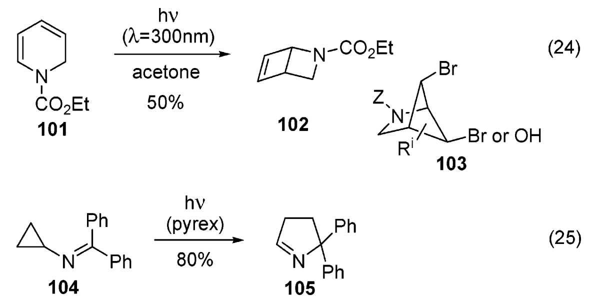
Irradiation of the *N*-glucosylpyridinium salt **99** yielded two diastereoisomers of the bicyclic aziridine **100a**,**b** in a ratio of 1:1 (Scheme 35).[191] No protection of the different hydroxyl functions was necessary to perform the photochemical transformation. The *O*-peracylated derivatives of these products were easily separated by diffusion−crystallization, thus making the reaction interesting for application to asymmetric synthesis. Further examples have been recently published.[192]

Scheme 35



In a sensitized reaction, the dihydropyridine derivative **101** was transformed into the constrained 2-azabicyclo[2.2.0]hex-5-ene **102** (Scheme 36, eq 24).[193] Such compounds were transformed into a large variety of 2-azabicyclo[2.1.1]hexane derivatives (**103**) of pharmaceutical interest. Various other reactions have been performed with 2-azabicyclo[2.2.0]hex-5-enes and 2-azabicyclo[2.2.0]hexanes.[194] The diene−amino

Scheme 36



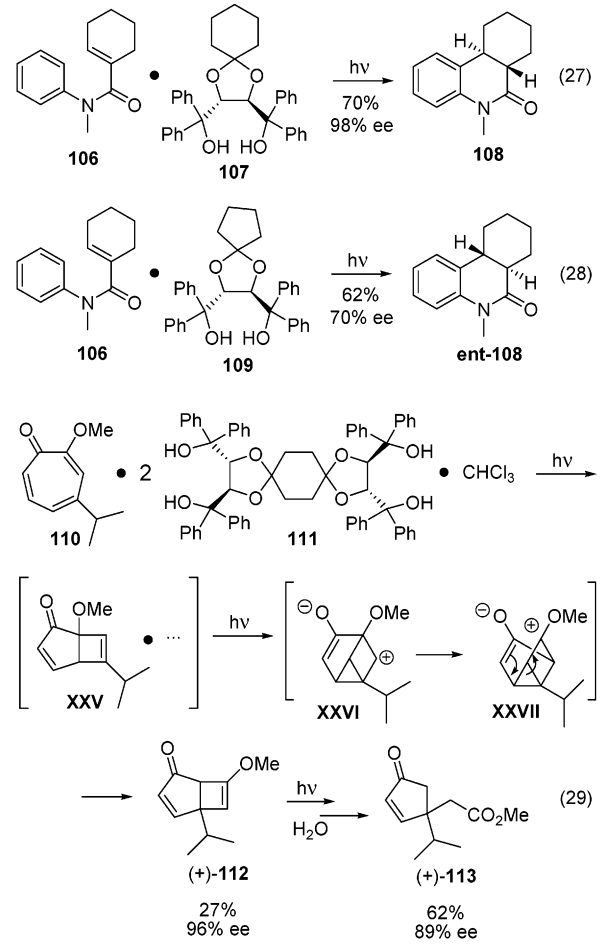
moiety is also present in 1-azabicyclo[4.2.1]nona-2,4-dienes, 1-azabicyclo[4.3.1]deca-2,4-dienes, and related structures. Similar photochemical rearrangements have been performed with such compounds.[195] The reactivity of the cyclopropane function resembles that of an alkene. This property is well illustrated in the transformation of cyclopropylimines such as **104** into pyrrolines (**105**) (Scheme 36, eq 25).[196] The reaction proceeds at the singlet state, and theoretical treatment reveals two conical intersections.[197] For further examples, see ref 198. The reaction is the aza analogue of the vinylcyclopropane rearrangement.[199]

Multistep rearrangements of polyenes and heterocycles have also been studied in a mechanistic context and for application to organic synthesis. For recent examples, see ref 200.

Currently, photochemical cyclizations are being studied inside confined structures such as crystals or zeolites in order to benefit from a limited of conformational mobility in these structures and optimize chiral induction.[201−206] For a variety of photochemical reactions in crystals, see ref 207. Photochemical reactions are more feasible than ground-state reactions in such media since high temperatures and aggressive reagents can be avoided. Beyond interest in the chemical transformations, these investigations also contribute to a better characterization of the crystal structures used and the molecular interactions inside them.

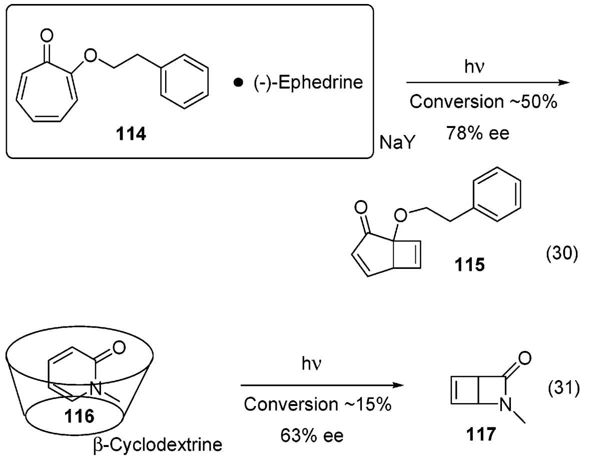
Tartaric acid derivatives of the TADDOL type (α,α,α′,α′-tetraaryl-2,2-dimethyl-1,3-dioxolane-4,5-dimethanol) are capable of forming cocrystals with a large variety of molecules.[208] Hydrogen bonds frequently contribute to the stability of such structures, and numerous cocrystals with substances possessing a chromophore have been obtained. The anilide **106** cocrystallizes with the TADDOL **107** possessing a cyclohexanone acetal function (Scheme 37, eq 27).[209] Irradiation of these crystals yielded the cyclization product **108** with high enantiomeric excess. Using the TADDOL **109** possessing the same configuration at the tartaric acid moiety but with a cyclopentanone acetal instead of a cyclohexanone one, **ent-108** was isolated with good enantiomeric excess (Scheme 37, eq 28). Photocyclization reactions are easily performed with tropolone ethers. Inside a crystal with two TADDOL molecules (**111**) and one chloroform per substrate molecule, the tropolone derivative **110** was transformed into **XXV** (Scheme 37, eq 29).[210] Under the described reaction conditions, this product was not isolated. Absorption of a second photon afforded the final product (+)-**112** via intermediates **XXVI** and **XXVII**. This reaction step resembles the di-π-methane rearrangement, which was described in section 3. Addition of water to (+)-**112** leads to the second product (+)-**113**. In the corresponding reference, the stereochemistry is not indicated. This reaction can also be performed in zeolites.

Scheme 37



In contrast to the cocrystals with TADDOLs, the cavity is not chiral in the zeolite NaY, and substrate **114** is therefore coadsorbed with (−)-ephedrine (Scheme 38, eq 30).[211] No covalent interaction was established between the two molecules, and formation of one conformer with respect to its enantiomer was solely controlled by constraints of the environment. Due to a reduced irradiation time, **115** was obtained as the major reaction product. In Scheme 37, a similar product (**XXV**) was transformed in a consecutive reaction into **112**. The corresponding transformation of product **115** (Scheme 38, eq 30) is low. Inclusion in zeolites significantly enhances chiral induction via auxiliaries which are covalently linked to the substrate.[212] For a comparable

Scheme 38

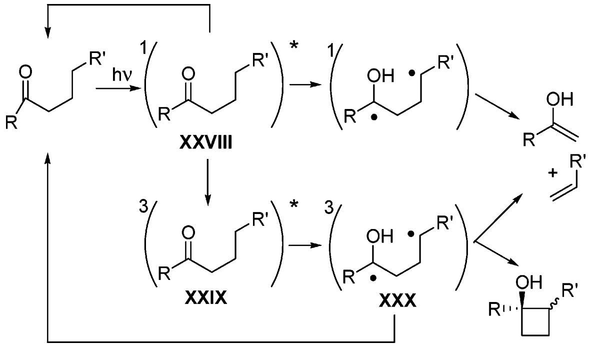


transformation in an inclusion complex with cyclodextrin, see ref 213. Numerous photochemical reactions have been carried out in such complexes with cyclodextrins.[110,112] In general, the enantiomeric excesses are lower than in cocrystals with TADDOLs. Photocyclization of pyridones such as **116** was performed in β-cyclodextrin.[214] The enantiomeric excess of 63% is one of the best obtained from inclusion complexes with cyclodextrins (Scheme 38, eq 31). Conversion is relatively low due to the reversibility of the reaction. When performed in TADDOL cocrystals, the same reaction yielded the cyclization product with enantiomeric excesses between 91% and 99.5%.[215] Products such as **117** are suitable precursors for the synthesis of β-lactams.

4.2. Norrish−Yang Reaction

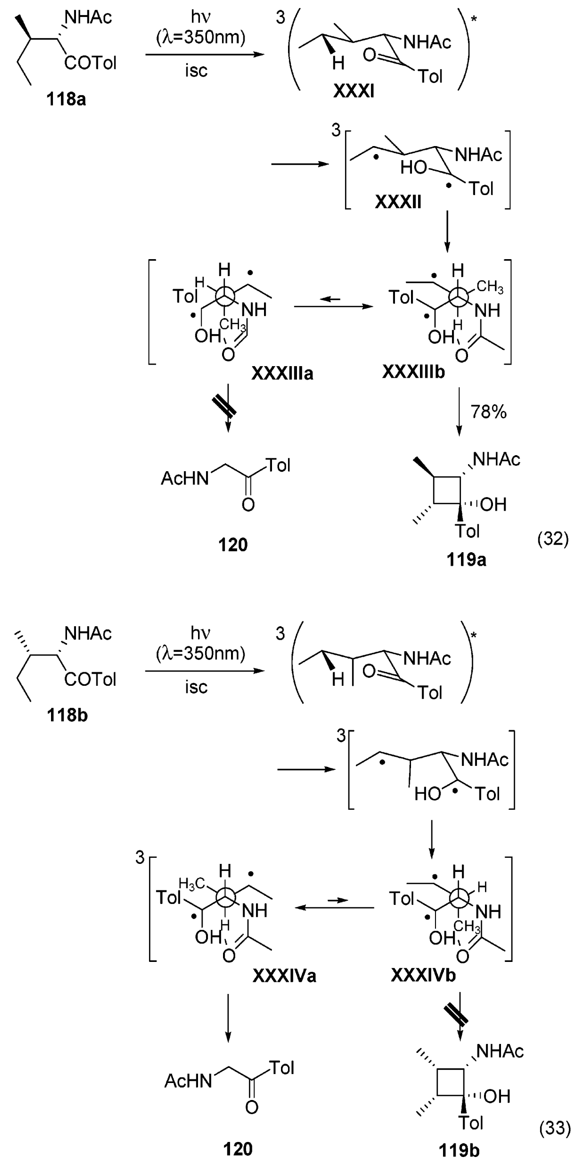
A photochemically excited ketone may abstract a hydrogen atom in the γ position of a substituent (Scheme 39).[170,216] This first step is then followed by either fragmentation (Norrish Type II reaction) or cyclization (Yang cyclization). Depending on structural factors, hydrogen abstraction may occur in other positions of the side chain. The reaction may take place in the $^1(n\pi)^*$ state **XXVIII** or the $^3(n\pi)^*$ state **XXIX**. Fragmentation is preferred at the singlet state, while cyclization is favored in the triplet state. Reversible steps have been detected in the excited singlet state and starting from the triplet biradical **XXX**. The competition between cyclization and fragmentation of **XXX** strongly depends on the nature of the substituents.

Scheme 39



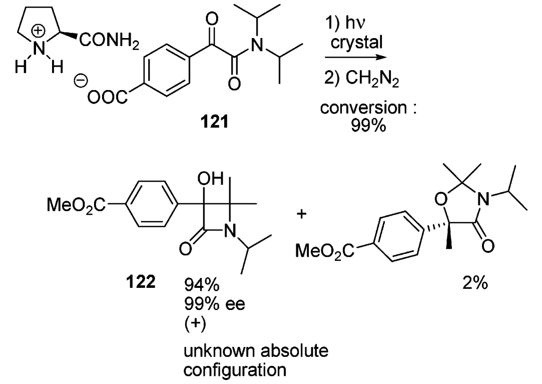
By electronic excitation and intersystem crossing (isc), the isoleucine derivative **118a** is transferred into its triplet state **XXXI** (Scheme 40, eq 32). Hydrogen abstraction from the γ position then yields the 1,4-biradical **XXXII**.[217] Two conformations, **XXXIIIa** and **XXXIIIb**, are in equilibrium. These two forms are stabilized by hydrogen bonds. Due to steric interactions, the conformational equilibrium is shifted to the right side, favoring **XXXIIIb**. This conformer undergoes cyclization, and the aminocyclobutanol derivative **119a** is obtained in high yield. The elimination product **120** is not observed. In the case of the epimeric leucine derivative **118b**, the corresponding conformational equilibrium between **XXXIVa** and **XXXIVb** is shifted to the left side, which orients the radical sites anti with respect to each other (Scheme 40, eq 33). Only the elimination product **120** is formed. In either the cyclization or the fragmentation of the 1,4-biradical, conformation requirements for high spin−orbit coupling must be fulfilled since the triplet intermediates are transformed into the final products at the singlet ground state.[76] A similar study with aromatic ketones has been published.[218] 1,4-Biradicals are also involved in many [2 + 2] photocycloadditions, which were discussed in section 2.1. The same considerations with respect to the reactivity of the biradical intermediates are made for these reactions. For a diastereoselective Norrish−Yang reaction using a chiral auxiliary, see ref 219. The reaction has also been performed in a host/guest structure.[40]

Scheme 40



To promote chiral induction, the Norrish−Yang cyclization can also be performed in crystals. The homochiral salt **121** was crystallized and irradiated leading to the β-lactam **122** in high yield and almost complete enantioselectivity (Scheme 41).[220] The Norrish−Yang reaction took place in the phenylglyoxylamide moiety. Similar reactions have been published.[221] Inside crystals, the rigid orientation of the molecules enables almost complete enantioselectivity. Instead of a homochiral ammonium salt, an enantiomerically pure alcohol can also be attached through an ester function and used for chiral induction in a crystalline structure.[222] The same reaction has been carried out in zeolites.[223] The substrates were coadsorbed with homochiral amines, and ee values up to 44% were observed.

Scheme 41

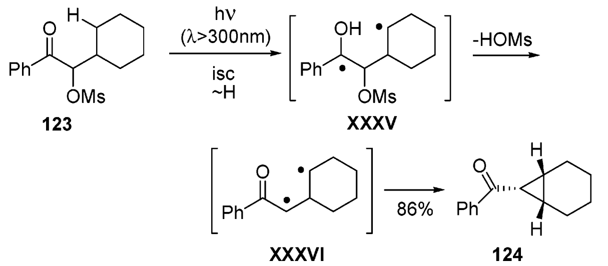


Under the same conditions, a retro-Claisen photorearrangement was carried out.[224] For additional examples, see ref 225. When crystallizing in chiral space groups,[204,226] achiral products may react with high enantioselectivity.[205,227]

Mechanisms with a two-step hydrogen abstraction process have frequently been discussed.[228] In this case, electron transfer occurs, which is followed by proton transfer (see section 6). In the presence of a hydrogen atom and a silyl or stannyl group at the reaction center of the radical cation, competition between deprotonation and desilylation or destannylation is possible.[229−231]

When a carbonyl compound is substituted in the α position, the reactivity is modified and cyclopropanes may be obtained. Irradiation of the cyclohexane derivative **123** led to the 1,4-biradical intermediate **XXXV** (Scheme 42).[232]

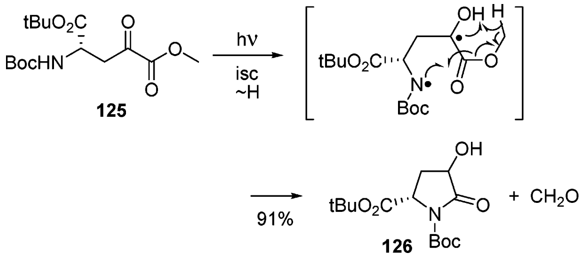
Scheme 42



Elimination of methanesulfonic acid becomes competitive with cyclization or fragmentation (compare Schemes 39 and 40), and the 1,3-biradical **XXXVI** is generated. Cyclization of this intermediate efficiently yields the cyclopropane derivative **124** as the final product. For further examples, see ref 233. The competitive elimination of sulfonic acid is also discussed in the context of long triplet lifetimes of the corresponding 1,4-biradicals.[234] This effect may be attributed to the hyperconjugative stabilization of one radical, which is established by an interaction of the radical carrying orbital with the σ^* orbital of the C−O bond of the OMs substituent. A comparable reaction involving hydrogen abstraction in a benzylic position was applied to the synthesis of indanone derivatives[235] such as the sesquiterpene Indane derivatives pterosine B or pterosine C.[236] Elimination of a carboxylate in the β position of an α-ketoamide lead to formation of oxazolidinones.[237] The same reaction with elimination of a phenol derivative has been performed.[238] In this way, formation of the corresponding β-lactam was inhibited (compare Scheme 40, eq 33).

Elimination at the stage of the 1,4-biradical intermediate was also observed when the α ketoester **125** was irradiated (Scheme 43).[239] First, hydrogen abstraction occurred at the nitrogen atom. In lieu of a 1,4-cyclization, addition of the aminyl radical to the methyl ester function took place. Elimination of formaldehyde via hydrogen transfer on the ketyl radical yielded the hydroxypyrrolidone **126**. Formation of product **126** might also be induced by hydrogen abstraction at the OCH$_3$ group. However, results of isotopic labeling experiments are in favor of the mechanism depicted in Scheme 43.

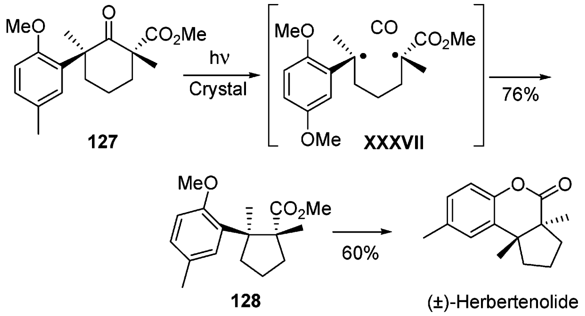
Scheme 43



5. Photochemical Extrusion of Small Molecules

Photochemically induced extrusion of small molecules has been frequently described.[240,241] Under UV irradiation, cyclic ketones can undergo double α-cleavage, releasing carbon monoxide and leading to α,ω-biradicals. These radicals can then recombine to generate rings lacking one carbon atom. Recently, such a reaction was performed inside a crystal with the racemic cyclohexanone derivative **127** (Scheme 44).[242]

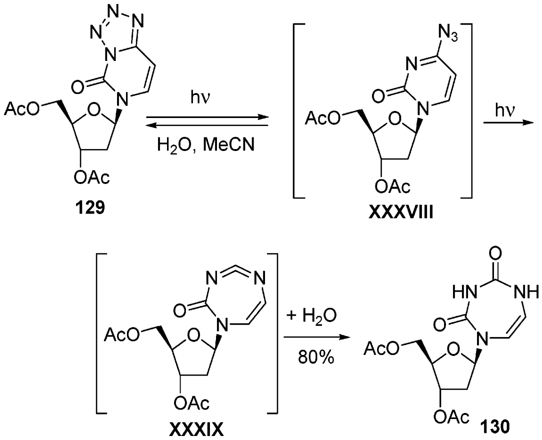
Scheme 44



After elimination of CO, the 1,5-biradical **XXXVII** was formed. Diastereoselective (de > 96%) radical recombination lead to the cyclopentane derivative **128** with 20−35% conversion. On this basis, the yield (or the selectivity) of the reaction was 76%. The solid-state photoreaction was applied to the total synthesis of (±)-herbertenolide obtained in one additional step. For similar reactions, see ref 243. Large-scale reactions are also possible. For example, irradiation of a colloidal suspension of 10 g of dicumylketone in 3.3 L of water led to 91% conversion in 19 h (conversion rate = 0.5 g/h).[244] Such reactions in solution are particularly suitable for the synthesis of cyclophanes.[245] For a recent example, see ref 246.

Nitrogen can be extruded from tetrazolo[1,5-*a*]pyridines (2-azidopyridines), leading to 1,3-diazepines.[247] This reaction was applied to the synthesis of a triazepindione nucleoside analogue (Scheme 45).[248] The tetrazolo[1,5-*a*]pyrimidin-5(6*H*)-one (4-azidouracil) derivative **129** is in photochemical equilibrium with the open azido form **XXXVIII**. In all probability, a nitrene sextet species is formed via elimination of N$_2$, which immediately undergoes ring expansion, leading to the intermediate **XXXIX**. Addition of water to the carbodiimide function affords the final product **130**.

Scheme 45



6. Photochemical Electron Transfer

Under photochemical conditions, electron transfer becomes possible even when such a reaction is impossible in the ground state. In order to achieve exothermic electron transfer in the ground state, the energy of the highest occupied molecular orbital (HOMO) of the reductant must be superior to that of the lowest unoccupied molecular orbital (LUMO) of the oxidant. In the excited state, LUMO's (with respect to the ground state) are occupied by one electron. Both frontier orbitals become singly occupied (SOMO).[249] Electron-transfer processes which are endothermic at ground-state configurations are thus made possible (Scheme 46). Electron transfer can occur from the higher SOMO of the excited donor molecule into the LUMO of the acceptor (a) or from the HOMO of the donor in its ground state to the lower SOMO of the excited acceptor molecule (b). In the present case, an exothermic electron transfer in the ground state of both molecules is not possible. In the photoinduced electron transfer, the positive free enthalpy of the corresponding process in the ground state is compensated by the excitation energy. The free enthalpy of the process is given by the Rehm−Weller equation[250] (see also refs 124, 249, and 251)

$$\Delta G_{el}\ (\text{kcal mol}^{-1}) = 23.06\ [E(D^+/D) - E(A/A^-)] - \Delta G_{00} - w_p$$

where ΔG_{el} is the free enthalpy of the electron transfer and $E(D^+/D)$ and $E(A/A^-)$ are the corresponding redox potentials in eV. ΔG_{00} is the excitation energy of the donor or the acceptor molecule, and w_p is the attraction given by Coulomb's law. In polar solvents such as acetonitrile w_p possesses small values around 1.3 kcal mol^{-1}. Even if electron transfer at the ground state is endothermic ($\Delta G_{el} = 23.06\ [E(D^+/D) - E(A/A^-)] > 0$), the positive free enthalpy of the electron transfer can be compensated by the excitation energy ΔG_{00} of one of the reaction partners.

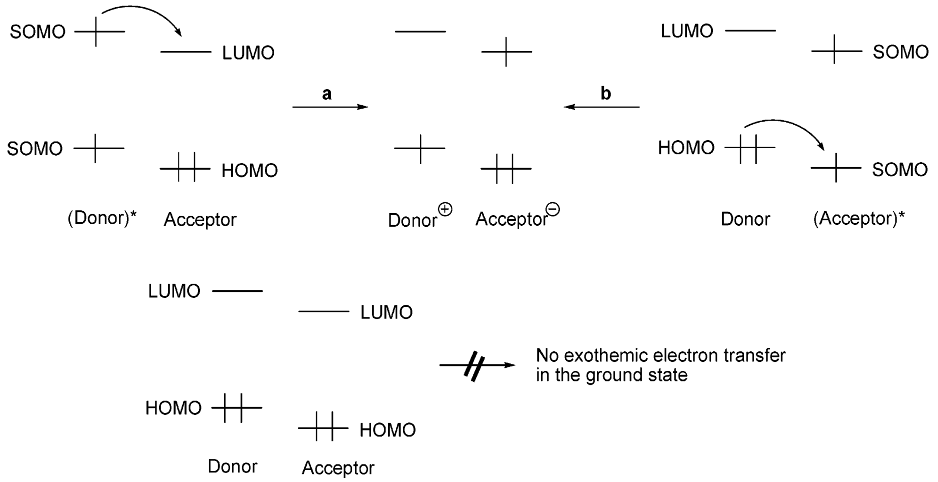
The kinetics of photoinduced electron transfers are described by the Marcus equation.[252] The consequences are considerable for the application of such photochemical reactions to organic syntheses as the redox chemistry of numerous compounds is significantly enriched when they are electronically excited. In the first step of such a reaction, a radical ion pair is generated possessing characteristic reactivities.[253] Frequently, proton exchange leads to neutral radicals. In the context of radical chemistry, these reactions are particularly valuable because they offer easy access to radical species without using toxic reagents such as tin derivatives.[254] Meanwhile, a large number of these reactions have been applied to organic synthesis.[124,255−259]

6.1. Photochemical Electron-Transfer Reactions with a Catalytic Sensitizer

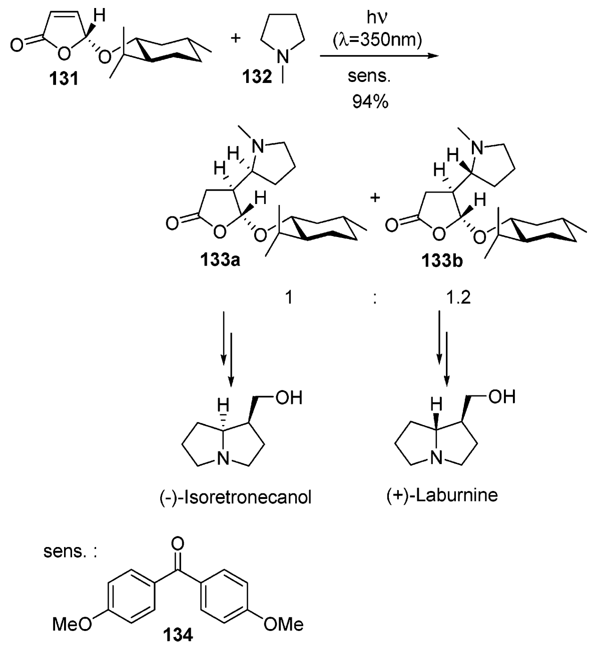
In photochemically sensitized reactions, light absorption not of the substrate but of the sensitizer leads to a chemical transformation. In the case of a photochemical electron transfer, the excited sensitizer can either abstract an electron or transfer an electron to one of the substrate molecules. The resulting radical ion of the substrate then undergoes chemical transformations (e.g., deprotonation). In several of these reactions, the sensitizer is consumed and therefore used in large amounts. Currently, such processes are optimized in order to regenerate the sensitizer during the photochemical transformation. The sensitizing compound is then only needed in a catalytic amount and, in some cases, can be readily recovered after the reaction. Under these conditions, the sensitizer fulfills the criteria of a catalyst. Since many of these compounds are organic, these transformations can be considered as being organocatalytic.[5]

The photoinduced radical addition of amines, in particular tertiary amines, to alkenes has been frequently studied. Only recently, however, has an efficient method been developed to perform this reaction in an intermolecular way. *N*-Methylpyrrolidine **132** was added to menthyloxyfuranone

Scheme 46



Scheme 47

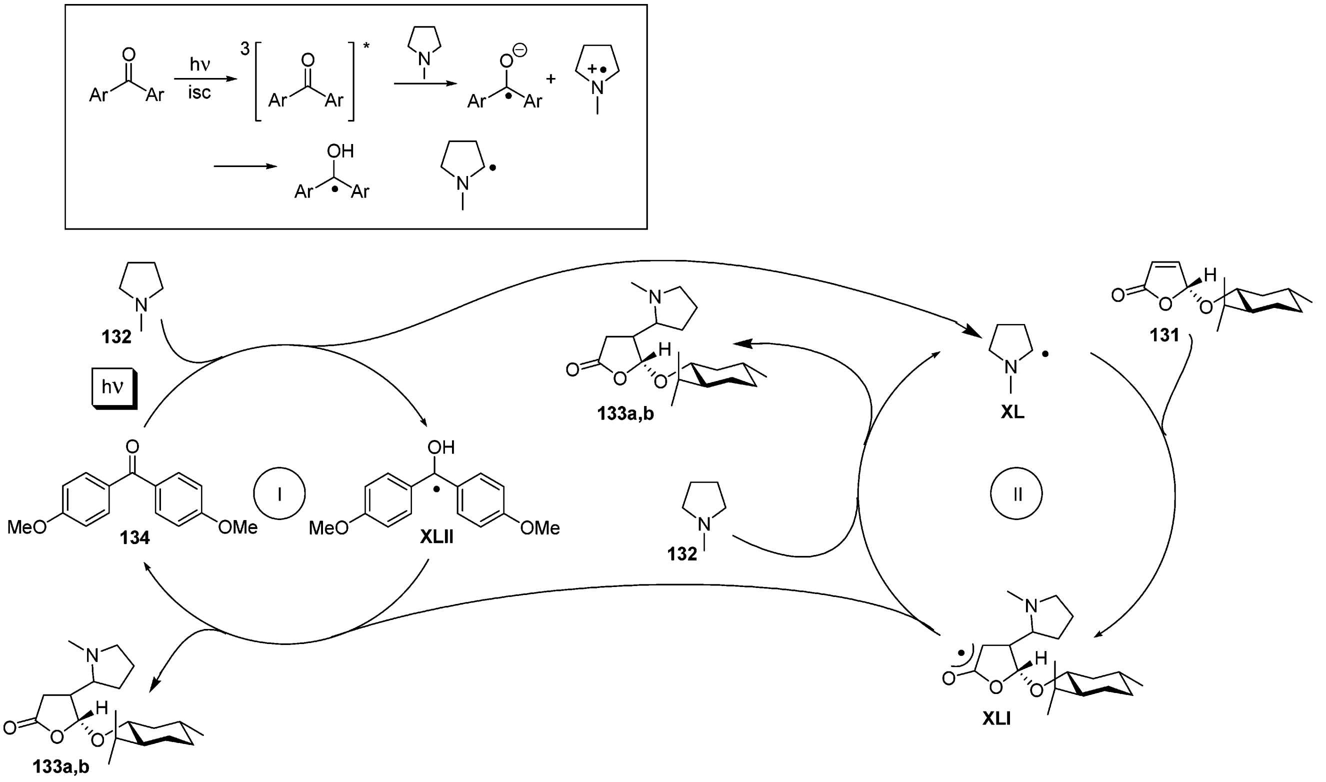


131 with yields > 90% (Scheme 47).[260] The adducts **133a**,**b** were transformed into the pyrrolizidine alkaloids (−)-isoretronecanol and (+)-laburnin. Aromatic ketones such as **134** possessing electron-donating substituents were used as sensitizers added in only catalytic amounts. No significant degradation was observed during the reaction. These results can be explained by the mechanism depicted in Scheme 48.[260,261] After excitation, the sensitizer **134** abstracts a hydrogen atom at the tertiary amine. The reaction takes place in two steps (see frame in Scheme 48). Electron transfer from the amine to the excited sensitizer is followed by a proton transfer in the same direction. The resulting α-aminoalkyl radical **XL** is nucleophilic and easily adds to electron-deficient alkenes such as **131**. For formation of α-aminoalkyl radicals, see refs 230, 259, 262, and 263. Polar effects considerably increase the efficiency of these radical reactions.[264] The resulting electrophilic oxoallyl radical **XLI** abstracts hydrogen at the tertiary amine, leading to the final product **133a**,**b** and a new α-aminoalkyl radical **XL** (cycle II). For the contribution of polar effects to hydrogen abstraction, see ref 265. Alternatively, **XLI** can react with the ketyl radical **XLII** to yield additional **133a**,**b** and regenerate the sensitizer (cycle I). This step is also a termination step of the radical chain process of cycle II. The electron-donor-substituted aromatic ketones can be considered as efficient homogeneous catalysts. The good results obtained can be explained by this mechanism. Particular physicochemical properties of the sensitizer have no significant influence. With regard to these properties, these compounds are not significantly different from classical sensitizers such as benzophenone.[266] For this reason, further reaction optimization was recently performed by modifying the complex interplay of the various radical intermediates. When thiocarbonyl compounds were added to the reaction mixture, tertiary amines of otherwise low reactivity, in particular acyclic amines, were efficiently transformed.[267] Thiocarbonyl compounds reversibly trap radical intermediates, thus giving them extra stability.[268]

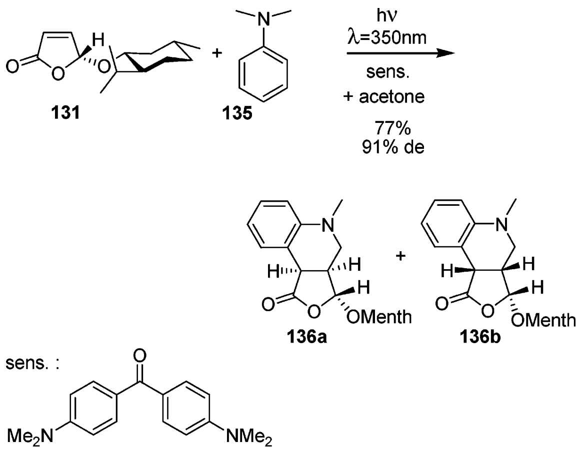
The reaction was also carried out under heterogeneous photocatalysis using inorganic semiconductors such as TiO_2 or ZnS as sensitizers.[269]

Using the same type of aromatic ketones as sensitizers, a radical tandem reaction was performed with aromatic tertiary amines such as **135** (Scheme 49).[261,270] Tetrahydroquinoline derivatives such as **136a**,**b** were isolated with high diastereoselectivity. The radical addition occurred preferentially anti with respect to the menthyloxy substituent, and **136a** was obtained as the major product. This family of compounds

Scheme 48



Scheme 49

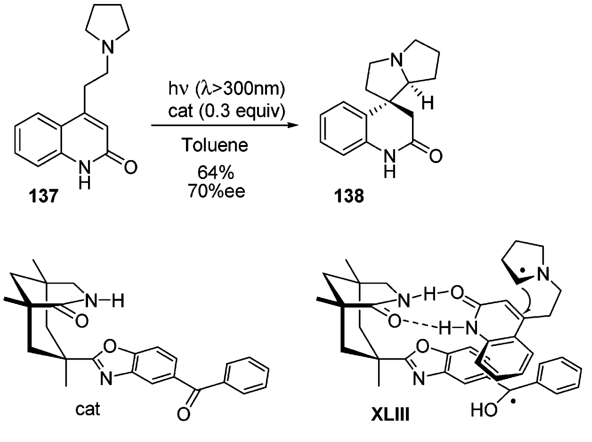


is particularly interesting due to its large variety of biological activity.[271] The same reaction was also performed using heterogeneous photocatalysis with inorganic semiconductors.[272] In this case, the stereoselectivity was lower (de up to 68%).

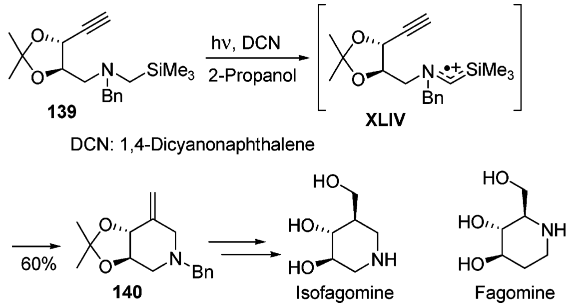
It is important to note that these methods do not require any activation of the tertiary amine by a functional group (e.g., a leaving group) or use of a reagent (e.g., for performing a metalation) in order to create a C−C bond. This fact, as well as other characteristics associated with homogeneous and heterogeneous catalysis, considerably reduce waste and place this method in the field of green chemistry. Many other electron-transfer reactions with tertiary amines have been described.[273]

Recently, electron-donor-substituted ketones were attached to a chiral derivative of Kemps acid (Scheme 50). The system was used to induce the intramolecular radical addition of tertiary amines to electron-deficient double bonds[274] analogous to the intermolecular reaction described in Scheme 47. The quinolinone derivative **137** was transformed into the spirocyclic compound **138** via complexation of the substrate (**XLIII**). It should be emphasized that enantioselectivity was catalytically induced for the first time in this type of photochemical electron-transfer reaction. The catalytic/sensitizing system had to be carefully optimized in order to fulfill reactivity requirements (compare to Scheme 48) as well as enantioselectivity (compare refs 37−40 and 58). Various other chiral sensitizers have been used to induce enantioselectivity in photochemical reactions.[275]

Scheme 50



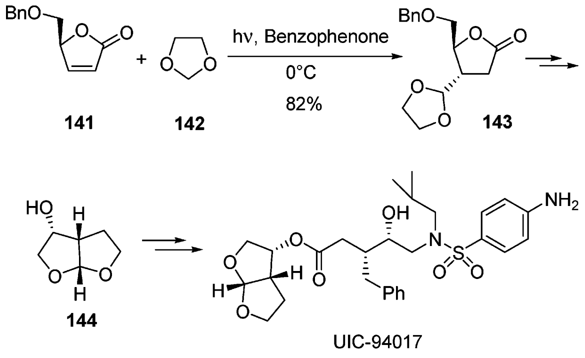
Scheme 51



The intramolecular addition of tertiary amines to alkynes or alkenes was applied to the synthesis of polyhydroxy piperidine and azasugar derivatives, several of which are glycosidase inhibitors. For example, an intramolecular radical addition was performed with compound **139** (Scheme 51).[276] A three-centered radical cation **XLIV** was discussed as being the reactive intermediate.[277] The influence of the silyl substituent on the tertiary amine has been studied in detail in these reactions.[229−231] The reaction was performed with similar derivatives possessing different substituents at the trimethylsilylmethylamino moiety.[278] The cyclization product **140** was then transformed into the branched chain aminosugar isofagomine which is a structural analogue of fagomine. For a similar approach, see ref 279. The intramolecular addition to an alkene was also performed.[280] For a review article on these reactions, see ref 281.

Secondary alcohols, ethers, and cyclic acetals can also be added to electron-deficient alkenes using similar reaction conditions. In a benzophenone-sensitized reaction the 1,3-dioxolane **142** was added to the furanone derivative **141** (Scheme 52).[282] The adduct **143** was isolated in high yield and high diastereoselectivity. For several recent examples and discussion of the mechanism, see refs 228, 283, and 284. An intramolecular version of the reaction has also been performed.[285] Compound **143** was then transformed into the bis-tetrahydrofuran **144**. Further transformations lead to UIC-94017 (now also named TMC-114). This latter compound is an efficient HIV protease inhibitor. In particular, the bis-tetrahydrofuran moiety contributes as a P_2 ligand.

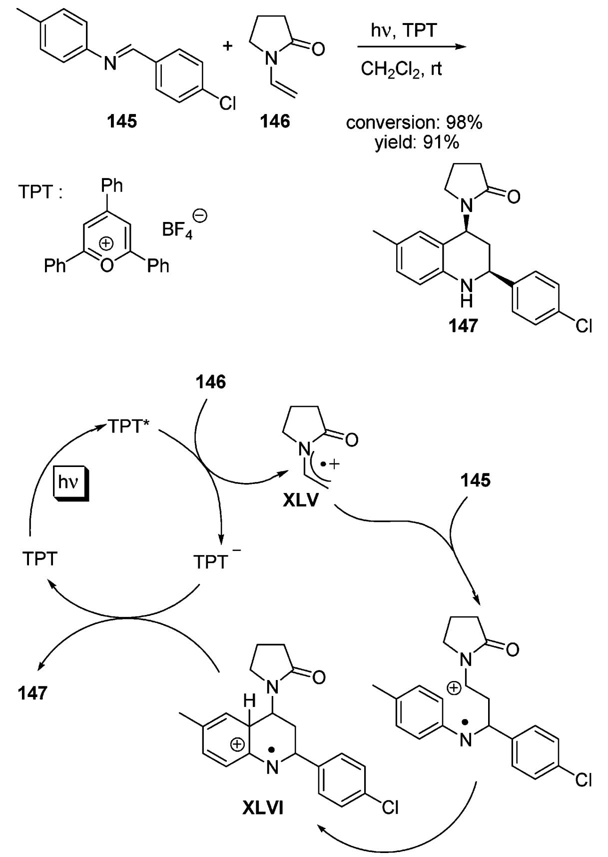
Scheme 52



The reaction in Scheme 52 resembles the addition of ketyl radicals to alkenes.[285] For a recent example, see ref 286. In this particular case, the radicals were obtained by partial photoreduction of the corresponding ketones.

A photoinduced electron transfer may also start a Diels−Alder reaction. Tetrahydroquinoline derivatives such as **147**

Scheme 53



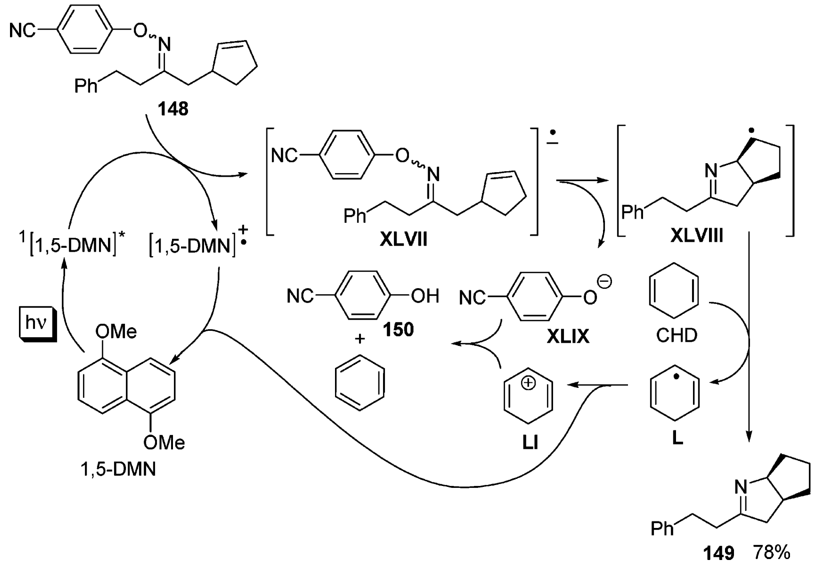
have been obtained from the corresponding aromatic imines (**145**) and vinylpyrrolidinone **146** (Scheme 53).[287] In the ground state this reaction is difficult because the aromaticity of the aniline moiety is suppressed (**XLVI**). Either strong oxidation or Lewis acids are then needed to perform the transformation. After photochemical excitation of the sensitizer TPT, electron transfer occurs from the alkene to TPT and the radical cation **XLV** is generated. The latter adds to the imine **145**, and after cyclization the bicyclic intermediate **XLVI** is obtained. A rearomatization step takes place in order to generate the final product **147**. In this step, an electron is transferred from the radical TPT$^-$ to **XLVI**, which regenerates the sensitizer. Compound **147** is obtained after tautomerization. This regeneration of the sensitizer, which is linked to the rearomatization step, is quite efficient. Due to this fact, only a small amount of TPT is needed. Using this efficient catalysis, the reaction was performed with a large variety of substrates with high yields. Various other cycloadditions can be performed under these reaction conditions.[258] A similar reaction was described with indole.[288] Intensive studies of the rearomatization step have been performed for the radical tandem addition cyclization reaction with aromatic amines (Scheme 49).[261,272]

As already indicated in Scheme 46, electron transfer can occur from an excited donor molecule to an acceptor. Such electron-donor molecules can also be used as sensitizers. The intramolecular radical addition of iminyl radicals was sensitized by 1,5-dimethoxynaphthalene (1,5-DMN) (Scheme 54).[289] Electron transfer first occurs from the singlet excited sensitizer to the oxime **148**. The resulting radical anion **XLVII** fragments to yield the cyclized radical **XLVIII** and the cyanophenolate **XLIX**. Hydrogen abstraction from cyclohexadiene (CHD) leads to the final product **149**. The resulting cyclohexadienyl radical **L** is oxidized by the radical cation of the sensitizer, leading to the corresponding cation **LI**. This reaction step regenerates the sensitizer. Therefore, 1,5-DMN is only needed in catalytic amounts. Proton exchange with **XLIX** finally yields 4-cyanophenol **150** and benzene. Further examples have been published.[290] Recently, methoxynaphthalene and dimethoxynaphthalene have been investigated as electron-donor sensitizers in photochemical transformations of oxetanes.[291]

1,6-Bisdimethylaminopyrene **151**, an electron-donating sensitizer, and 2-phenylbenzimidazoline **152**, a hydrogen donor, have been used in a similar way to perform photoreductions and photochemical electron-transfer-induced rearrangements (Figure 5).[292]

Electron-rich alkenes can be oxidized by photoinduced electron transfer. The resulting radical cation intermediate easily adds to other alkenes. This reaction was applied to the synthesis of polycyclic compounds by cascade reactions. The diastereomers of the silylated enol ethers **153** were oxidized by electron transfer (Scheme 55, eq 34).[293] The radical cation **LII** was added to an alkene, leading to rings

Scheme 54



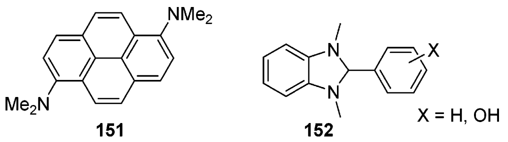
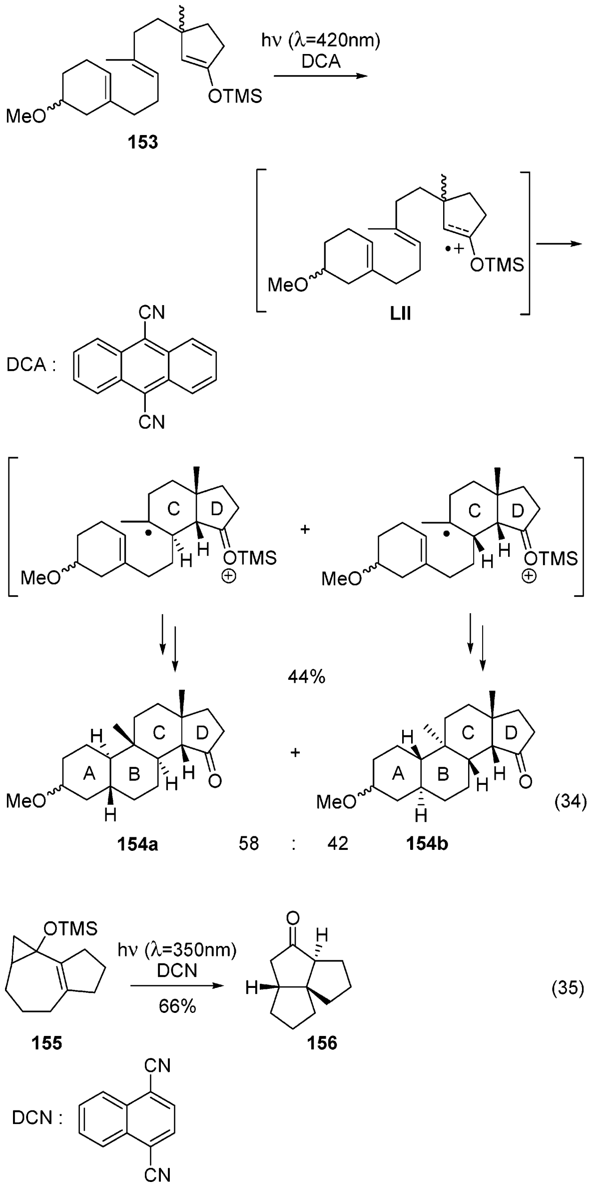


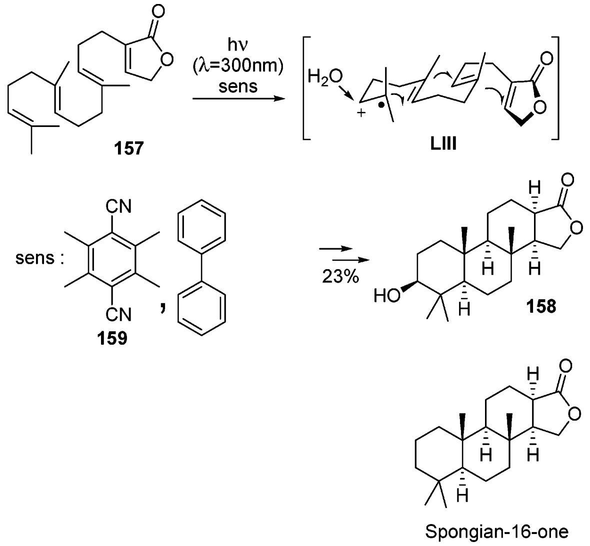
Figure 5.

C and D of a steroid system. The second cyclization occurs stereospecifically to establish ring B in the final products **154a**,**b**. Alkenes and cyclopropane derivatives possess similar reactivities. This analogy may also be observed in the formation of radical cations derived from these compounds.[294] Thus, the cyclopropane derivative **155** was transformed into the angular triquinane derivative **156** (Scheme 55, eq 35).[295] For similar reactions, see ref 296. Bicyclic cyclopropyl ketone derivatives have also yielded triquinane, propellane, and tetracyclic compounds.[297] In a cascade reaction, compound **157** was transformed via radical cation **LIII** into **158** (Scheme 56).[298] The primary sensitizer **159** and the cosensitizer (biphenyl) were used to start the reaction. For reaction mechanisms of such sensitizing systems, see refs 257 and 295. This procedure constitutes a biomimetic synthesis of hydroxylated analogues of spongian-16-one. This natural product was isolated from the marine sponge *Dictyodendrilla cavernosa*. The corresponding family of compounds possesses activities against leukemia cells and *Herpes simplex* type 1. For an asymmetric reaction of this type, see ref 299. Several other reactions have recently been described.[300]

Scheme 55

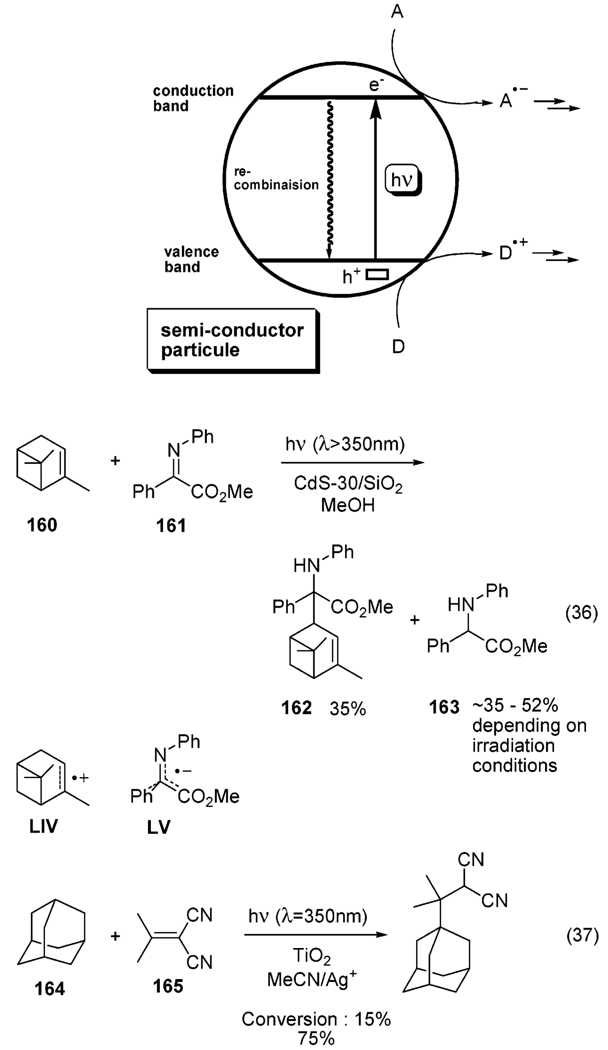


Scheme 56



Numerous research activities involve heterogeneous photocatalysis using semiconductors such as TiO_2 as sensitizers. This technique is frequently used to mineralize organic wastes in water in the presence of oxygen.[301] These reactions can be carried out with solar light. Other applications are in the field of solar light collector systems.[302] For reviews on applications in organic chemistry, see refs 303−305. In a semiconductor particle, an electron can be transferred from the valence band to the conductor band via light absorption (Scheme 57). The wavelength depends on the size of the band gap. For mechanistic questions, see, for example, ref 306. The allylic addition of pinene **160** to imine **161** leading to **162** has been carried out with CdS as sensitizer which was supported on silica (Scheme 57, eq 36).[307] The competitive formation of relatively high quantities of the reduction product **163** indicated that oxidation of **160** by electron transfer into the electron hole h^+ of the valence band (formation of the radical cation **LIV**) was accompanied by a reduction of **161** via electron transfer from the conduction band (formation of the radical anion **LV**). After deprotonation of **LIV** and protonation of **LV** at the surface of the semiconductor particle, radical recombination yielded the final product **162** (see also ref 304). Using TiO_2 as sensitizer in the presence of silver, adamantane **164** was added to isopropylidenemalonitrile **165** in a radical reaction (Scheme 57, eq 37).[308] The yield of this transformation was given with respect to a low conversion. It should be noted that activation of an alkane C−H bond was involved in the reaction. Formation of radicals by rupture of a C−Si instead of a C−H bond has also been investigated in this context.[309] The radical addition of adamantane or other cycloalkanes with alkenes or alkynes was carried out with homogeneous photocatalysis.[284,310,311] As previously mentioned, heterogeneous photocatalysis with inorganic semiconductors was also efficiently applied to the addition of tertiary amines to

Scheme 57

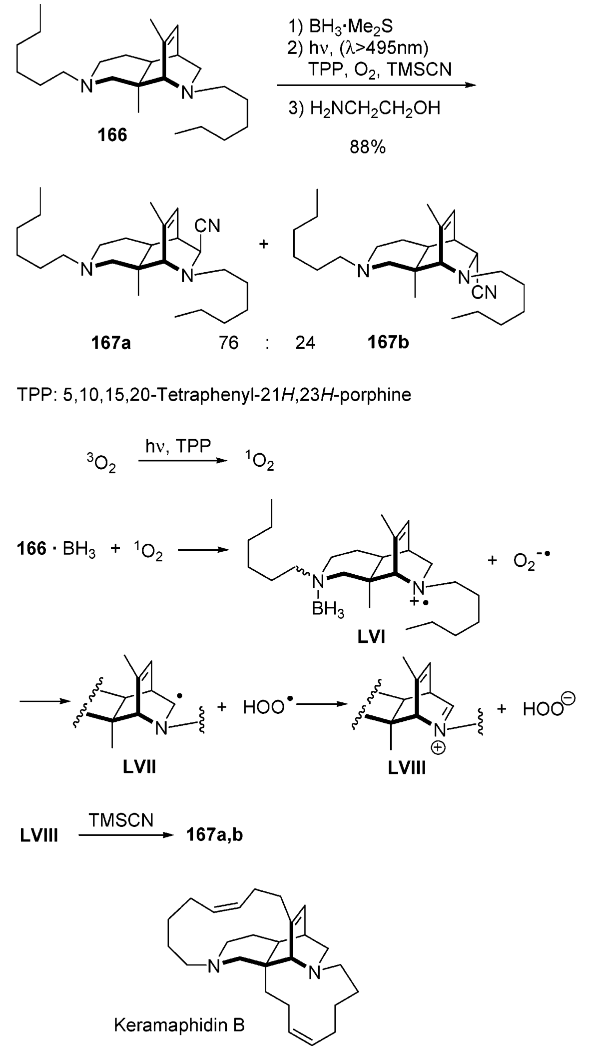


alkenes. Yields up to 98% were obtained for these transformations.[269,272]

Polyoxymetalates, especially polyoxotungstanates[312] such as $W_{10}O_{32}^{4-}$ or heteropolyoxometalates of Dawson type, are also capable of catalyzing these reactions. As for their photophysical properties, these compounds may be compared to inorganic semiconductors.[305,313] For the catalytic addition of alkanes, alcohols, ethers, or acetals to alkenes such as **165** (Scheme 57, eq 37) with these sensitizers, see ref 314.

Electron transfer also occurs with photochemically generated singlet oxygen (see section 8). In a three-step, one-pot procedure, the diamine **166** was transformed in high yield to the nitrile isomers **167a**,**b** (Scheme 58).[315] In the first step, the less sterically hindered amine function is selectively protected (**166**·BH_3). Electron transfer to singlet oxygen affords the radical cation **LVI**.[316] The resulting oxygen radical anion deprotonates the intermediate **LVI**, leading to the α-aminoalkyl radical **LVII** (compare to Scheme 48). The hydroperoxide radical performs a further oxidation, which affords the iminium **LVIII** ion. This intermediate undergoes addition of a cyanide ion from TMSCN (trimethylsilylcyanide). In the presence of ethanolamine, the stereoisomers **167a**,**b** are in equilibrium. These products are model structures of the alkaloid keramaphidine B. For further examples, see refs 316 and 317. These oxidation conditions have also been applied to the transformation of hydrazones.[318]

Scheme 58



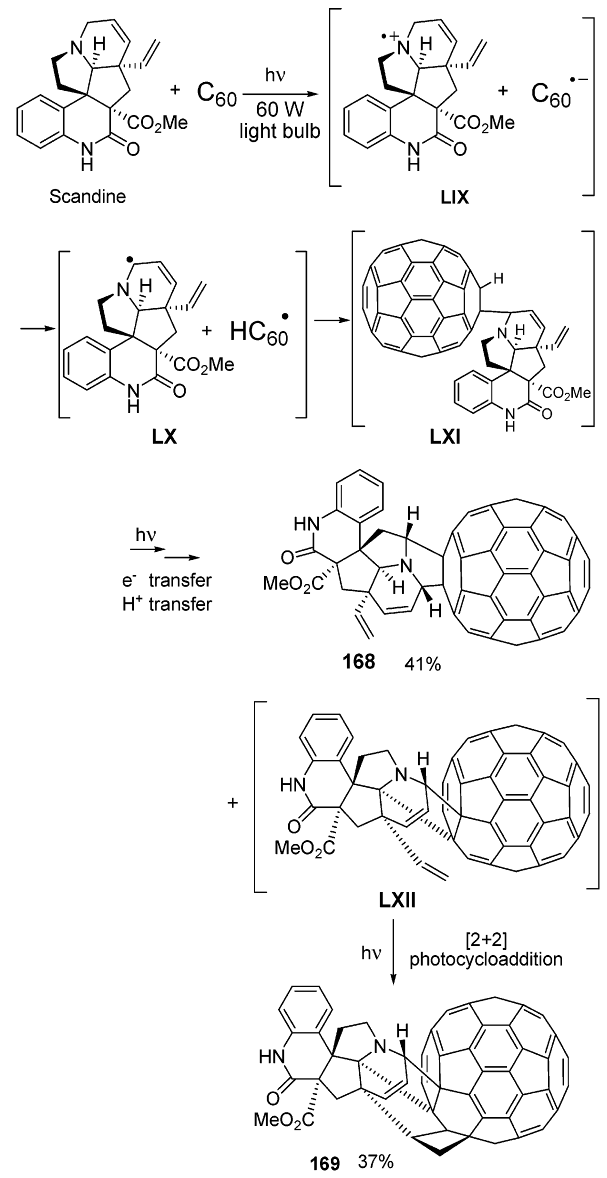
TPP: 5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine

6.2. Photochemical Electron-Transfer Reactions without Addition of a Sensitizer

In reactions discussed in the preceding section, photochemical electron transfer takes place between a substrate molecule and a sensitizer. The substrate radical ion is then transformed into the desired product. However, photochemically induced electron transfer can also occur between two substrate molecules. The resulting radical ion pair is then transformed into the final product. In this case, no mediating sensitizer is needed.

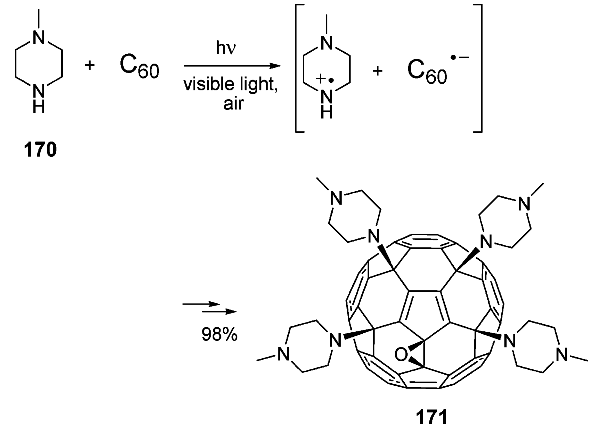
The generally mild conditions of photochemical reactions permit their application to the synthesis of complex structures such as fullerenes.[319,320] Photoinduced electron transfer has been applied to functionalization of these compounds, most frequently those of C_{60}. In most cases, C_{60} is involved as an electron acceptor. For properties of this fullerene, see refs 320 and 321. In a recent example, the alkaloid scandine is added to C_{60} (Scheme 59).[322] After excitation of the fullerene, electron transfer occurs from the alkaloid and a radical ion pair **LIX** and $C_{60}^{\bullet-}$ is generated. Proton transfer yields the neutral radicals **LX** and $HC_{60}^{\bullet}$. A first adduct **LXI** is obtained by radical coupling. A second C−C bond is formed between the alkaloid moiety and the fullerene via electron and proton transfer. Two regioisomers **168** and **LXII** result from this step. In the adduct **LXII**, the vinyl C=C double bond is near the C_{60} moiety. Under the reaction conditions, **LXII** is therefore transformed into the second final product **169** by

Scheme 59



a [2 + 2] photocycloaddition. (For other functionalizations via [2 + 2] photocycloaddition, see ref 323.) Recently, the same reaction was performed with C_{70}.[324] A [2 + 2] photocycloaddition with two fullerene moieties was also observed.[325] The same photochemical transformations have been carried out with $^{3}He@C_{60}$[322] (an atom of ^{3}He is included in C_{60}) as well as with $^{3}He@C_{70}$.[324] ^{3}He NMR is an efficient tool to determine the number and type of isomers which are formed during addition of asymmetric reagents to the fullerene. For an intensive investigation of the radical addition of triethylamine to C_{60}, see ref 326. Aromatic tertiary and secondary amines can also be added in the same way.[327] In the latter case, the radical cations were deprotonated at the nitrogen atom and aminyl radicals reacted with the fullerene. Four molecules of *N*-methylpiperazine **170** have thus been added to C_{60} (Scheme 60).[328] Air oxidation yields the final product **171**. In a pharmaceutical context, these compounds are interesting since they are capable of forming aggregates with DNA.[329] For similar compounds, see ref 330. A comparable addition of piperazine derivatives to the C_{70} fullerene was carried out.[331] For recent examples of photo-induced additions of various secondary amines to C_{60} fullerene, see ref 332.

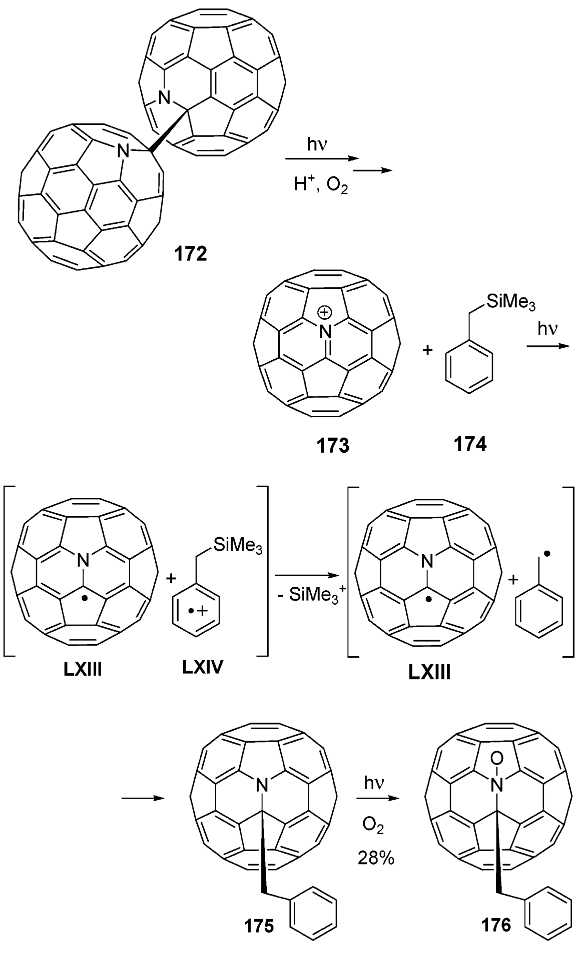
Scheme 60



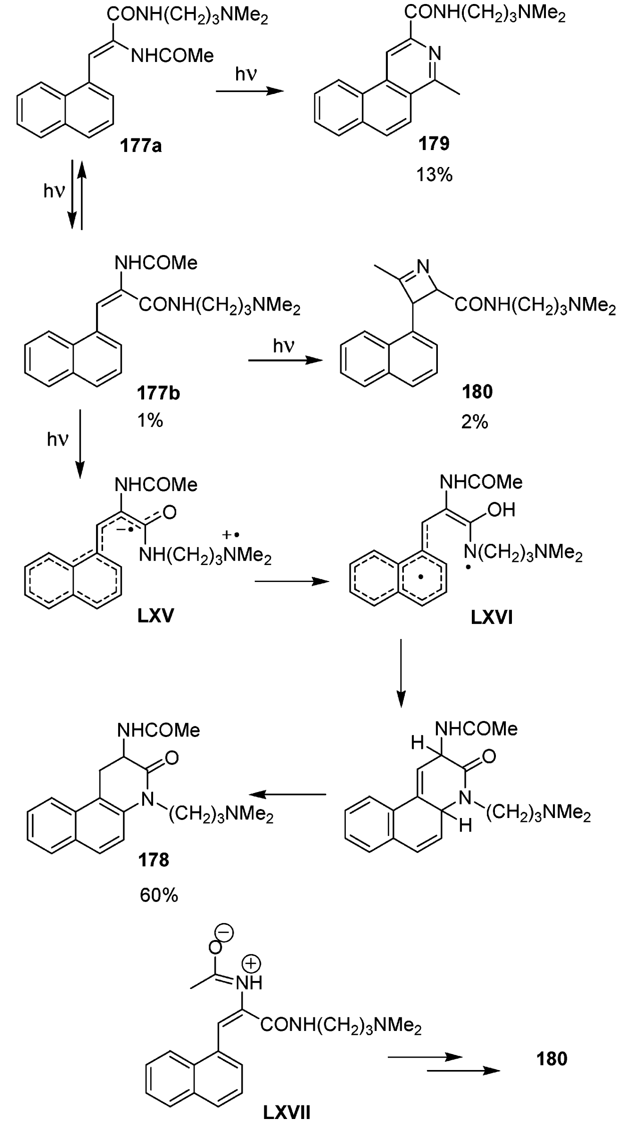
Aza[60]fullerenes, a family of C_{60} derivatives, have been frequently studied. These are radical species which resemble α-aminoalkyl radicals. The dimer fullerene derivative **172** represents a stable form (Scheme 61).[333] Under acidic and oxidative reaction conditions, these compounds can be cleaved into the corresponding iminium ions **173**. A photo-induced electron transfer from benzyltrimethylsilane **174** occurs, and radicals **LXIII** and **LXIV** are formed.[334] Desilylation of **LXIV** and radical recombination leads to compound **175**. Under the oxidative conditions, the latter is transformed into the final product **176**. Further examples of this reaction have been published.[335]

Carbon nanotubes represents a further allotropic modification of elemental carbon. For their derivatization, photochemical reactions are also used.[336]

Scheme 61



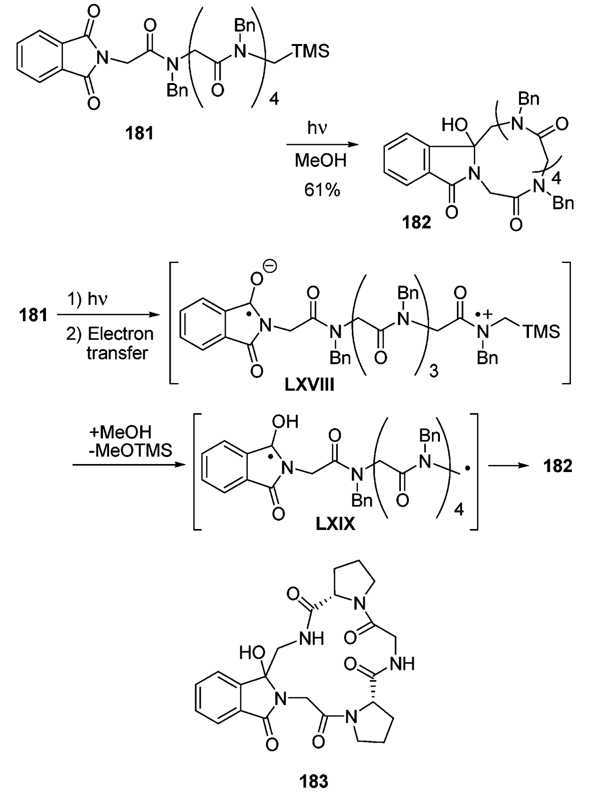
Scheme 62



In a series of naphthalene derivatives, cyclization was induced by a photochemical electron transfer. Intramolecular electron transfer in derivatives **177a** and **177b**, which are in photostationary equilibrium, lead to the radical ion pair **LXV** (Scheme 62).[337] After tautomerization and electron transfer from the naphthalene moiety to the outside ionized amine function, the intermediate **LXVI** was generated. Cyclization by radical recombination followed by a [1,7] sigmatropic rearrangement yielded the major product **178**. The two byproducts **179** and **180** were obtained by pericyclic reactions. It should be noted that formation of these products can be explained by mesomeric forms such as **LXVII**. In the presence of a tertiary amine, the same type of transformation can be started by an intermolecular single-electron transfer.[338] The chiral induction in these reactions has been studied using chiral auxiliaries.[339] Isoquinoline derivatives such as papaverine analogs have also been obtained from these reactions.[340]

Intramolecular electron transfer plays an important role in the photodegradation of drugs.[341] An electron transfer is also involved in the intramolecular addition of triazol-3-thiones with halogenated aromatic rings in order to form benzothiazines. In a basic medium, an electron is transferred onto the aromatic ring and thus causes the departure of a halide ion.[342]

Scheme 63

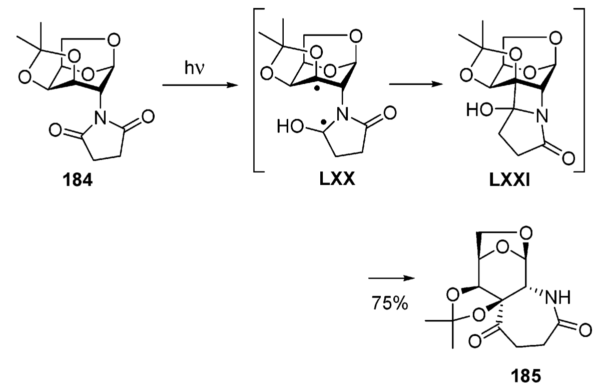


Photoinduced electron transfer is used to perform macrocyclization of polyfunctionalized substrates.[216,343] The reaction has been applied to the synthesis of cyclic oligopeptides. Starting from the phthalimide-substituted peptide derivative **181**, the cyclopeptide **182** was obtained in good yield (Scheme 63).[344] In these reactions, the phthalimide moiety is excited by either direct light absorption or sensitization. Intramolecular electron transfer leads to a radical ion pair **LXVIII**. The corresponding neutral radicals **LXIX** are generated by protonation of the aminoketyl radical anion of the phthalimide moiety and reaction with methanol used as solvent, enabling desilylation. The products resemble cyclopeptides, such as cyclosporine, which possess immunosuppressive activities. More complex structures such as **183** have been obtained by a similar reaction.[345] See also ref 231. The reaction has also been carried out with a corresponding 2,3-naphthalimide derivative.[346] This transformation was applied to the synthesis of lariat-type crown ethers, which proved to be sensitive sensors for Mg^{2+}, Cu^{2+}, and Ag^{+} ions.

Other functional groups such as thioethers[347] or succinimide may also act as an electron donor or an acceptor, respectively. For instance, the carbohydrate derivative **184** possessing a succinimide group was transferred via **LXX** and **LXXI** into the ketolactam **185** (Scheme 64).[348] For further examples, see ref 349.

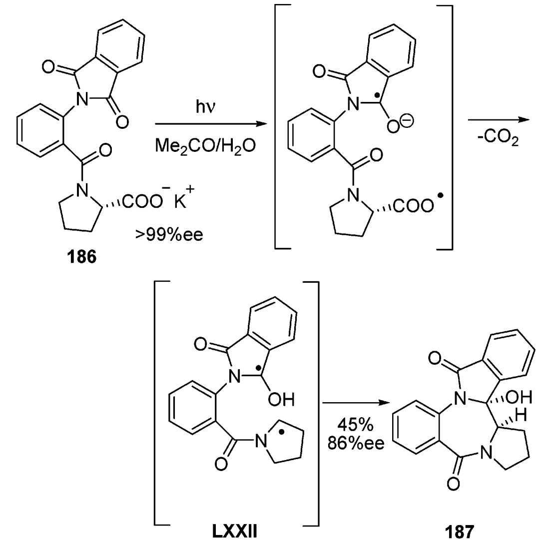
Chiral memory effects[350] have been observed with these reactions. The L-proline derivative **186** was transformed into the bislactam **187** with 86% of the chiral information preserved in the final product (Scheme 65).[351] In this case, electron transfer occurred between the carboxylate function and the phthalimide moiety which was directly excited to its triplet state (T_1) via acetone sensitization (energy transfer). For classification of this reaction it should be noted that no electron transfer occurs to or from the sensitizer. Thus, the reaction does not belong to reactions discussed in section 6.1. The configuration of the pyrrolidine moiety in **187** was

Scheme 64



inverted with respect to the substrate **186**. This result was explained by an enhanced rotation barrier around the central C−N bond of an atropisomer of intermediate **LXXII** before cyclization. The biradical also possesses triplet character. For a chiral memory effect in singlet reactions, see refs 84 and 352. For further examples, see refs 111 and 353.

Scheme 65

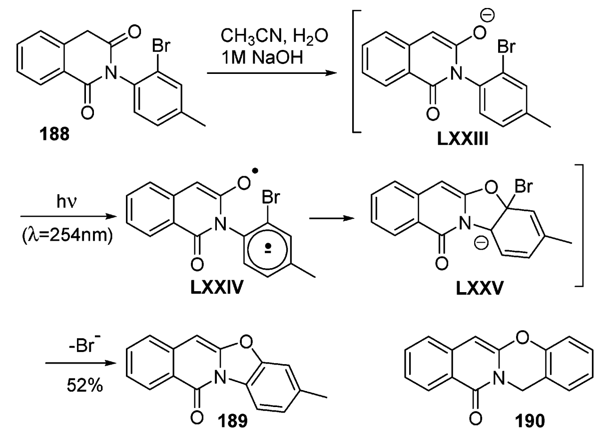


Other intermolecular[354] and intramolecular[345,355] electron-transfer reactions with carboxylates have been reported. Recently, formation of α-aminoalkyl radicals by decarboxylation of α-amino acids in the presence of diacetoxyiodobenzene was described.[356] The latter reaction is particularly efficient when the reaction medium is irradiated.

In a basic medium, an electron-transfer reaction was performed with tetrahydroisoquinoline-1,3-diones (benzo derivatives of glutaric imide that are homologues of phthalimides) such as **188** (Scheme 66).[357] In the basic medium, **188** is deprotonated (**LXXIII**). Photoinduced electron transfer leads to the anion biradical **LXXIV**. This biradical may also be discussed in the context of TICT states (twisted intramolecular charge transfer).[358] Intramolecular radical recombination (**LXXV**) and elimination of bromide leads to the final benzooxazoloisoquinolinone derivative **189**. Corresponding isoquinolinobenzoxazinone derivatives such as **190** are available in the same way. Since the reactivity in this case is lower, irradiation was performed in 3 M NaOH solution.

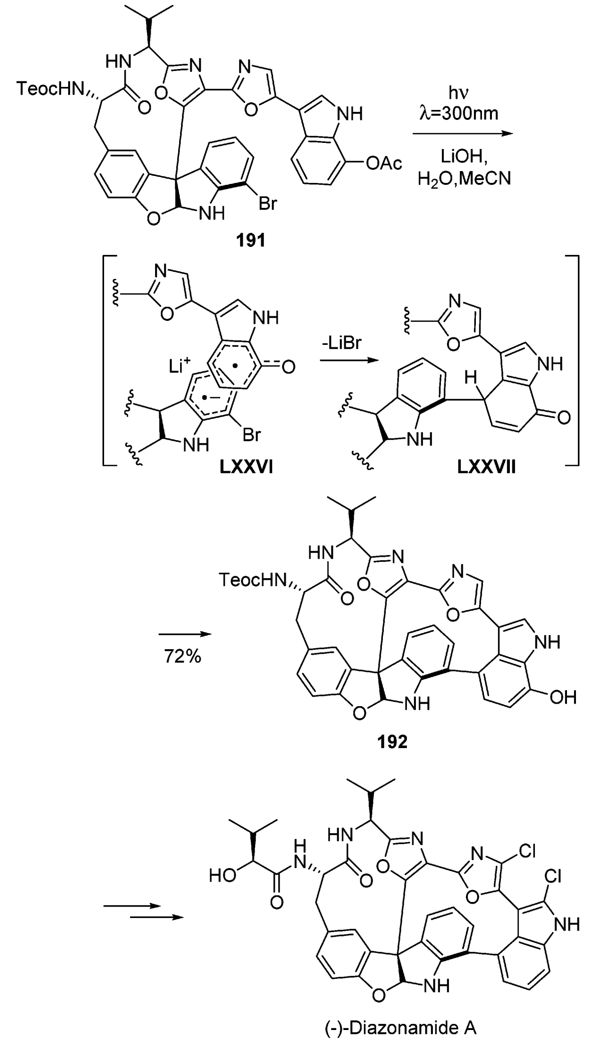
Benzothiazole-containing polycyclic compounds have been obtained in the same way from the transformation of corresponding thiourea substrates.[359] A similar reaction was performed in liquid ammonia as solvent and electron donor.[360] A photochemical $S_{RN}1$ mechanism was involved in this transformation, and the reaction was applied to the synthesis of aporphine and homoaprophine alkaloids.

Scheme 66

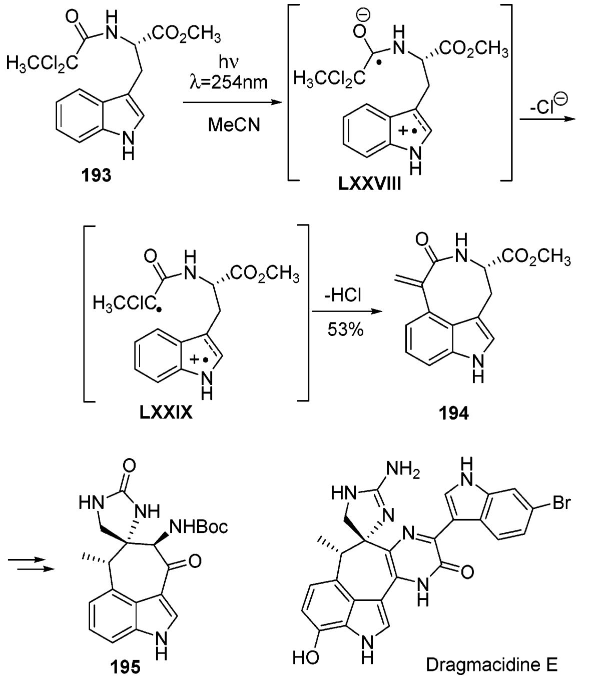


A photoinduced electron-transfer reaction was used as the key step of the synthesis of (−)-diazonamide A.[361] In compound **191**, an electron transfer occurs from the acetoxyindole moiety to the bromoindole group (Scheme 67). The intermediate **LXXVI** is formed by deacylation. Debromination and radical coupling yield **LXXVII**, which is trans-

Scheme 67



Scheme 68



formed into **192** in a rearomatization step. The presence of lithium hydroxide increases the polarity of the reaction mixture, which stabilizes the radical ion pair generated by the electron transfer. Furthermore, the radical ion in **LXXVI** is stabilized by Li$^+$. (−)-Diazonamide A is obtained in seven additional steps from **192**. Shortly after, a similar synthesis was published using the same photomacrocyclization step.[362] In this case, optimization details were described.

The transformation of **191** into **192** is also called a Witkop reaction. It is easily performed with choroacetamide derivatives such as **193** (Scheme 68).[363] The following mechanism can be proposed. After intramolecular photoinduced electron transfer, the radical ion pair **LXXVIII** is generated. Elimination of one chloride ion leads to **LXXIX**. Cyclization and elimination of HCl finally yields **194**. The latter compound was then transformed into the cycloheptane indole derivative **195**, which can be used as the key intermediate in the synthesis of dragmacidine E. This indole-derived metabolite was isolated from a *Spongosorites* sp. Such compounds are promising selective phosphatase inhibitors. For similar reactions, see refs 187, 258, 364, and 365. For a series of 2-halogenated imidazole derivatives, it was recently shown that photochemical methods of intramolecular radical addition to benzene rings are much more efficient than the corresponding ground-state transformations, for instance, Bu$_3$SnH/AIBN-mediated reactions.[366]

7. "Photo-Friedel–Crafts Reaction", Solar Photochemistry

In the context of green chemistry and development of sustainable chemical processes, use of sunlight as a renewable and costless energy is particularly interesting.[367,368] One of many examples is presented in Scheme 69. Addition of butyraldehyde to naphthoquinone **196** was carried out in high yields.[369,370] The resulting product **197** is a versatile synthon, for example, for the synthesis of tetracyclines. Even if the starting compounds are not similar to those used for a Friedel−Crafts reaction, the final products resemble the outcome of one. After 24 h of exposure to sunlight, 500 g of **196** in 80 L of a mixture of *tert*-butanol/acetone (3/1) were transformed. This solvent mixture was used for safety reasons (inflammability, toxicity,...) under conditions which are required for large-scale reactions in an industrial context. The reaction was carried out in the focal line of a circulation reactor (Figure 6). The reaction solution circulates in a system of parabolic mirrors. Solar technology is particularly adaptable to the reaction conditions needed for photo-oxygenation (see below). A large variety of appropriate solar plants for chemical transformations are, for instance, located at the European Solar Center at Almería (Spain) (Plataforma Solar de Almería).[371] For information about similar installations in the United States, see ref 372. New solar reactors have recently been developed in order to use diffuse sunlight for photochemical reactions.[373]

Scheme 69

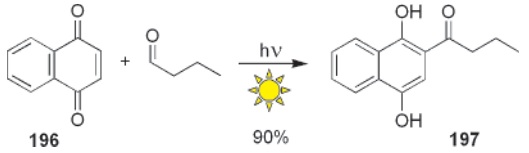


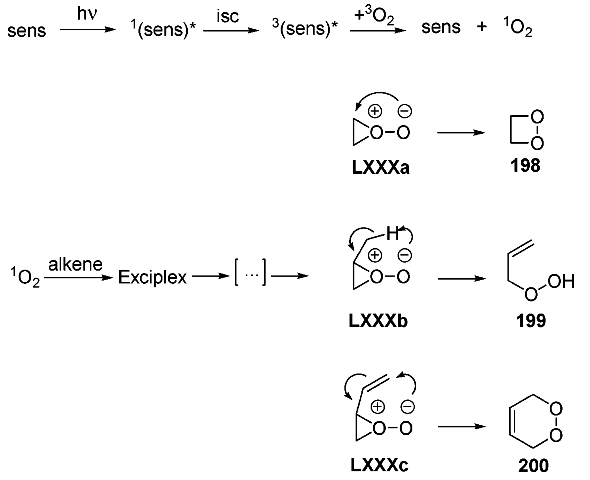
Figure 6. PROPHIS reactor (DLR (German Space Agency), Köln-Portz). (Reprinted with permission from ref 374. Copyright 2006 DLR, www.dlr.de.)

8. Photo-oxygenation

Due to the characteristic reactivity of singlet oxygen generated in these reactions, photo-oxygenation is a valuable complement of oxidation methods. In industry, the reaction is applied to production of perfumes and aromas by oxidation of terpenes or terpenols.[367] For recent patents, see ref 375. An economical evaluation of the industrial process using lamps or sunlight irradiation for a plant capacity of 100 t/a was performed for the photo-oxidation of citronellol to rose oxide.[368]

The high interest in photo-oxygenation results from the particular properties of singlet oxygen involved in these reactions. The singlet spin multiplicity significantly increases reactivity with respect to triplet (ground state) oxygen. In photo-oxygenation reactions, singlet oxygen is generated by

Scheme 70



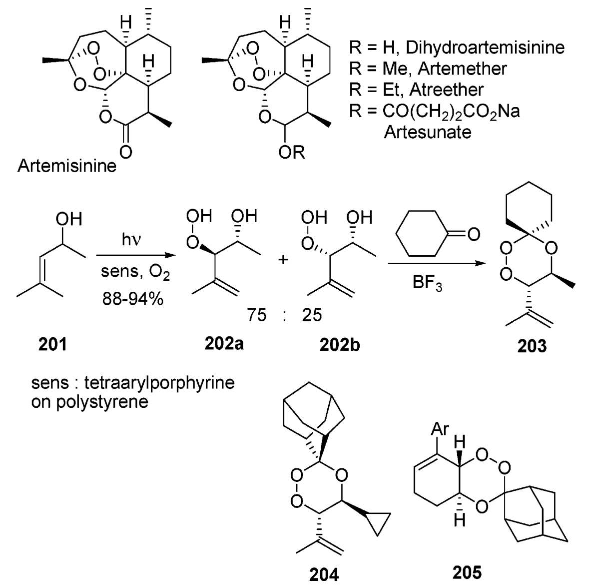
sensitization (Scheme 70).[376−378] Due to the low energy difference between these two species T_0 and S_1 (22.5 kcal·mol^{-1}), dyes can be used as a sensitizer possessing a low excitation energy. Consequently, photo-oxygenation can be carried out with visible light and, in particular, with sunlight (Figure 6).[367,368,379] Many research efforts concern optimization as well as the search for new sensitizers. In this context, fullerenes as unusual sensitizers have also been investigated, and it was found that the bisfullarene **172** (Scheme 61) is capable of sensitizing photo-oxygenation.[380] For other derivatives of the fullerene C_{60} in homogeneous photocatalysis, see ref 381, and for those in heterogeneous photocatalysis, see ref 382.

After excitation of the sensitizer and intersystem crossing (isc), energy transfer occurs from the sensitizer to the triplet oxygen and the sensitizer returns to its singlet ground state (Scheme 70). Most frequently, reactions between singlet oxygen and alkenes are used in organic synthesis. The first intermediate resulting from an interaction of singlet oxygen with an alkene is an exciplex (excited complex). Various other intermediates are discussed in the literature. The most significant ones used to explain final product formation are **LXXXa**−**c**. Three main reaction pathways result from this intermediate leading to dioxetanes **198**, hydroperoxides **199**, and endoperoxides **200**.

Photo-oxygenation products (e.g., endoperoxides) are also observed in electron-transfer reactions, for example, with semiconductors such as TiO_2.[383] In this case, $O_2^{\bullet-}$ is generated by electron transfer from the conduction band to triplet oxygen. The oxygen radical ion reacts with the radical cation, resulting from electron transfer from an alkene to the valence band of the excited semiconductor particle (compare with Scheme 57). Recent publications report however on the detection of singlet oxygen under these conditions.[384] Similar processes are also observed when the reactions are performed inside nanocavities of zeolites.[385]

In certain cases of homogeneous catalysis, two mechanisms are discussed: energy transfer and electron transfer. For recent physicochemical studies, see ref 386, and for an example, see ref 387.

Scheme 71

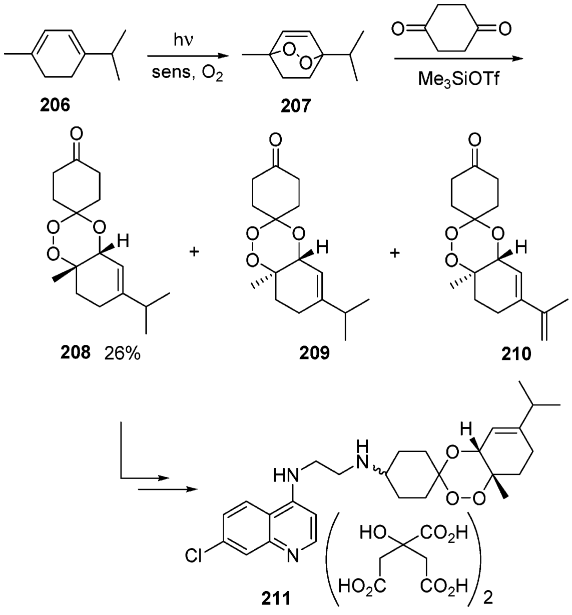


Recently, photo-oxygenation (in particular the ene reaction) was applied to the synthesis of artemisinine analogues (Scheme 71). These compounds originate from traditional Chinese medicine,[388] and certain derivatives possess antimalarial activity.[389] This activity is essentially linked to the 1,2,4-trioxane function. Many structural analogues have been synthesized. The ene reaction of singlet oxygen[377] followed by acetalization proved to be the most efficient method. The photo-oxygenation of the allylic alcohol **201** yields the diastereomeric hydroperoxides **202a**,**b** (Scheme 71).[390] This reaction was also performed with tetraarylporphyrines supported on polystyrene as a sensitizer.[391,392] This procedure can be discussed in the context of green chemistry because no solvent is necessary for the transformation. Various other methods of heterogeneous catalysis have been developed for photo-oxygenation of the same substrates.[382,393] The diastereoselectivity may be explained by the interaction of the hydroxyl group of **201** with singlet oxygen.[378,394] The final product **203** is obtained by acetalization with cyclohexanone. This compound possess a high in vitro antimalarial activity and only a slight cytotoxicity.[392,395] Almost the same activities have been detected for compound **204** synthesized in the same way. Compounds such as **205** have been obtained from arycylclohexenols[396] and also possess high antimalarial activity. Other examples resulting from an ene reaction of singlet oxygen with alkenes followed by acetalization have been published.[397] In this context, synthesis of 1,2,4-trioxepanes (seven-membered rings) and 1,2,4-trioxocanes (eight-membered rings) is worth mentioning.[398]

The formal [4 + 2] cycloaddition (leading to **200** in Scheme 70) was used as the key step in the synthesis of trioxanes. In this way, ascaridole **207** was synthesized by addition of singlet oxygen to terpinene **206** (Scheme 72). Trioxanes **208**, **209**, and **210** were obtained from **207** in a ratio of 78:10:12. Compound **208** was then transformed into **211**, possessing a high antimalarial activity, also due to the presence of the quinoline substituent.[399] See also ref 400. The photo-oxygenation of styrene derivatives in the presence of H_2O_2 was used for the synthesis of 1,2,5,6-tetraoxacycloalkanes with antimalarial activity.[401] These compounds are obtained by addition of H_2O_2 to intermediates of type **LXXXa**−**c** (Scheme 70).[402] Endoperoxides with antimalarial activity have also been obtained by photo-oxygenation of sesquiterpenes derived from perhydroazulene.[403]

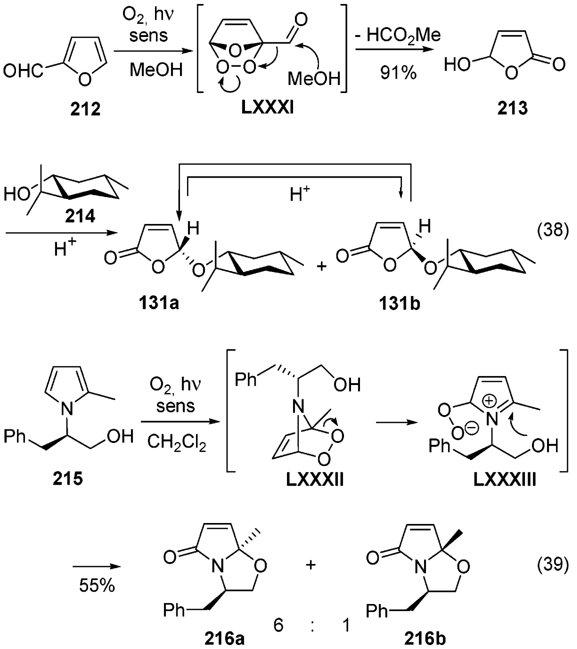
The photo-oxygenation of furan derivatives has been particularly well studied, and numerous applications to organic synthesis can be found in the literature. For instance, furfural **212** was oxidized, leading to the intermediate

Scheme 72



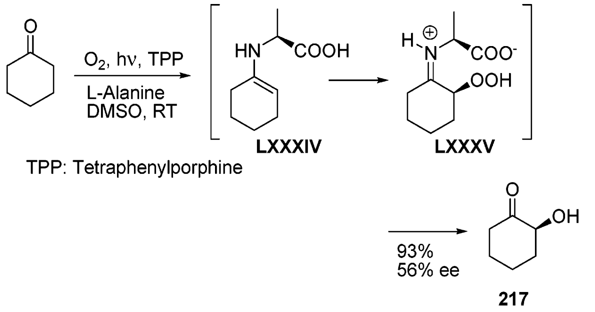
endoperoxide **LXXXI** (Scheme 73, eq 38). Reaction with methanol used as solvent lead to hydroxyfuranone **213** in high yield.[270,404] Acetalization with menthol **214** yielded two diastereomers of 5-menthyloxy-2[5*H*]-furanone **131a,b** (see also ref 405). The isomer **131a** crystallizes preferentially and can be easily separated, while isomer **131b** epimerizes in acidic conditions to yield **131a**. This compound is a versatile chiral synthon for organic synthesis since a minimum number of carbon atoms bear a maximum number of functional groups. Most of the reactions involving **131a** are highly diastereoselective, and the configuration of the chiral centers generated in the reactions can be predicted. Both enantiomers are easily accessible when the enantiomers of menthol **214** and **ent-214** are used in the acetalization step, which makes **131a** and **ent-131a** particularly attractive for application in asymmetric synthesis. Numerous examples have been described.[270,406] α,*β*-Unsaturated lactam derivatives have also been obtained by photo-oxygenation of pyrrole derivatives such as **215** (Scheme 73, eq 39).[407] In this example, the endoperoxide **LXXXII** is opened by intramolecular attack of an hydroxyl group (**LXXXIII**). The bicyclic lactams **216a**,**b** were obtained in high diastereoselectivity. The photo-oxygenation of chiral enecarbamates (carbamates derived from enamines) or tiglic acid amides carrying an oxazolidine chiral auxiliary can also be performed in high diastereoselectivity.[408]

Scheme 73



Recently, photo-oxygenation has been applied to the asymmetric synthesis of α-hydroxyketones or diols starting from ketones or aldehydes.[409] For these transformations, organocatalysis[5] with α-amino acids was used to induce enantioselectivity. In the presence of L-alanine, cyclohexanone was transformed into the corresponding enamine **LXXXIV** (Scheme 74).[410] Photo-oxygenation takes place, and the authors suggest formation of an iminium intermediate such as **LXXXV**. In the context of organocatalyzed aldol reactions with amino acid derivatives, these types of intermediates have been discussed. Under the reaction conditions, the hydroperoxide was reduced and the resulting hydroxyketone **217** isolated in high yields and with good enantiomeric excess. It should be mentioned that symmetric tricyclic endoperoxides obtained by photo-oxygenation can be transformed into cyclic *γ*-hydroxyenones with high enantioselectivity using organocatalysis[411] or organometallic catalysis.[412]

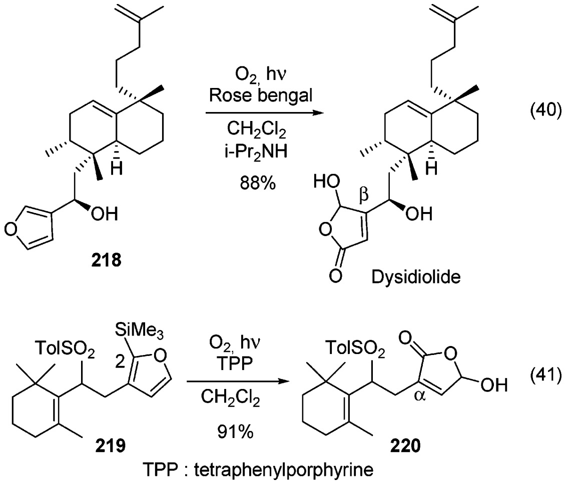
Scheme 74



TPP: Tetraphenylporphine

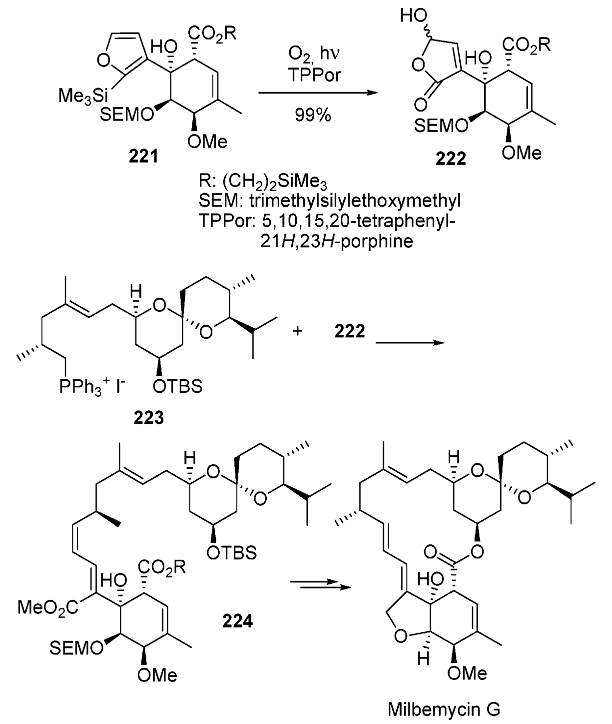
The structural element, 5-hydroxyfuranone, is found in several natural products and more specifically in sequiterpenes. Photo-oxygenation of a furan moiety is frequently applied to the synthesis of this element. For instance, **218** was oxidized to efficiently yield dysidiolide (Scheme 75, eq 40).[413] This compound as well as several of its derivatives are inhibitors of the protein phosphatase cdc25A and possess

Scheme 75



TPP : tetraphenylporphyrine

Scheme 76

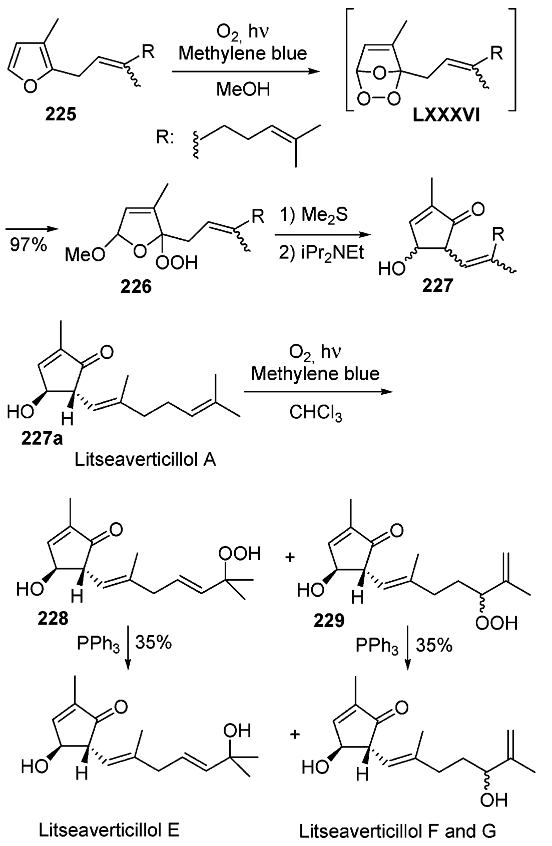


R: $(CH_2)_2SiMe_3$
SEM: trimethylsilylethoxymethyl
TPPor: 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine

anticancer activity.[414] In the present case, photo-oxygenation was also performed on the solid phase.[415] For a similar synthesis of dysidiolide, see ref 416. It is noteworthy that in most cases this oxidation is regioselective. For the hydroxyfuranone carrying the alkyl substituent the β position is favored. The regioselectivity is inverted when the furan carries a silyl substituent in position 2. For instance, **219** was oxidized in high yield to the hydroxyfuranone **220** (Scheme 75, eq 41).[417] For another recent example of the transformation of a silylated furan, see ref 418. These silylated furan derivatives have also been used as key intermediates in the synthesis of milbemycins (Scheme 76).[419] Compound **221** was oxidized in high yields to **222**. The lactol function of this compound is in equilibrium with the corresponding aldehyde. In a Wittig reaction, **222** can therefore be added to **223**, leading to the diene **224**, which was transformed into milbemycin G. This strategy is quite flexible. It was also applied to the synthesis of (6*R*)-6-hydroxy-3,4-dihydromilbemycin E.[420]

These reaction conditions also induce chemoselectivity. Despite the presence of an alkene double bond the latter is not oxidized, leading to a hydroperoxide via an ene reaction (see Scheme 70). Such selectivities have also been studied in biomimetic syntheses of various litseaverticillols. Furan **225** was selectively photo-oxidized in high yields, leading to the endoperoxide **LXXXVI** (Scheme 77).[421] No reaction took place at the alkene side chain. Under the reaction conditions, this intermediate opened via addition of methanol (**226**). After reduction of the hydroperoxide and treatment with base (aldol conditions), the hydroxycyclopentenone derivative **227** was isolated, and the stereoisomers were separated. The isomer **227a**, which possesses the structure of litseaverticillol A, was then selectively photo-oxidized (ene reaction) at the terminal alkene of the side chain (**228** and**229**). The regio- and chemoselectivity can be explained by steric and electronic effects. After reduction, three different members of the litseaverticillol family were obtained.

Scheme 77



Various natural products with the hydroxyfuranone moiety have been synthesized via photo-oxygenation of furans (Figure 7): cladocoranes A and B[422] and structural analogues,[423] acuminolide,[424] spongianolide A[424], luffolide,[425] (±)-toluccanolide,[426] (−)-cacospongionolide F,[427] and partial

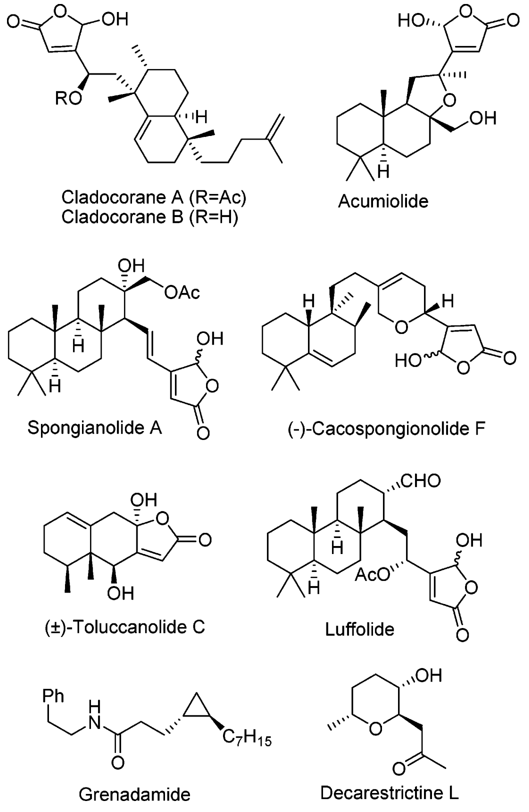
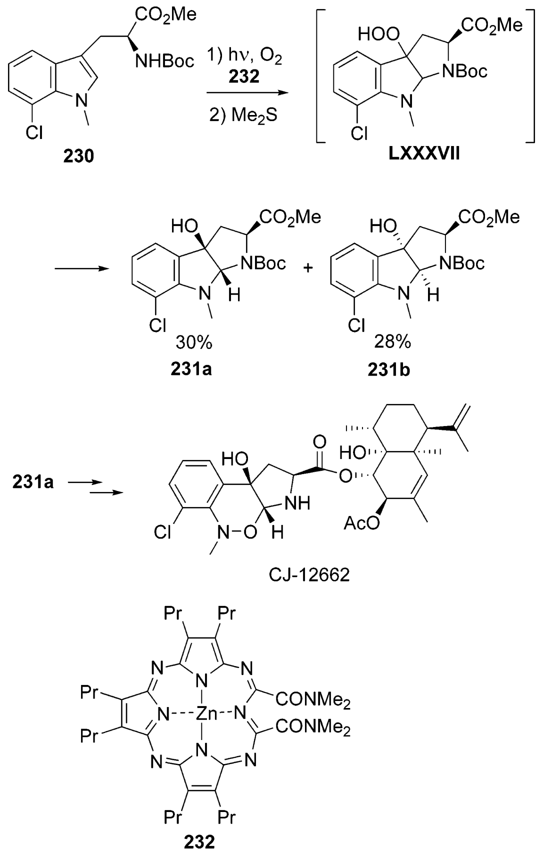


Figure 7.

structures.[428] Singlet oxygen addition to a diene leading to a 3,6-dihydro-1,2-dioxin intermediate (compare **200**, Scheme 70) was recently used as one key step in the first synthesis of natural grenadamide (Figure 7).[429] The compound was isolated from the marine cyanobacterium *Lyngbya majuscula* and possesses affinity to cannabinoid receptors. A regioisomeric hydroperoxide of **226** (Scheme 77) which resulted from the photo-oxygenation of the corresponding furan[430] was used for the synthesis of decarestrictine L (Figure 7).[431] This compound was isolated from *Penicillium simplicissiums*. It inhibits HMG-CoA reductase, which is involved in the biosynthesis of cholesterol. The same reaction was also applied to the synthesis of seven-membered oxocycles or 2,3-disubstituted tetrahydropyrans which are partial structures of complex polyether toxins such as hemibrevetoxin B, ciguatoxin, or brevetoxine A and B.[430,432]

Even electron-rich indole derivatives can be selectively oxidized. The tryptophane derivative **230** was oxidized leading to the diastereoisomeric hydroxypyrroloindole derivatives **231a,b** after in situ treatment with dimethyl sulfide (Scheme 78).[433] Under these reaction conditions the intermediate hydroperoxide **LXXXVII** was reduced to the corresponding alcohol. The secoporphyrazine **232** was used as an efficient sensitizer. The reaction conditions with this and similar sensitizers were systematically optimized.[434] By attaching the secoporphyrazines to polymers, their recycling was considerably improved.[435] In the present case, photo-oxygenation was used as the key step in the synthesis of the pyrrolobenzoxazine natural product CJ-12662.[433] The stereoisomer **231a** was also isolated from the fermentation broth of *Aspegillus fischeri* var. thermomutans ATCC 18618. Among other biological properties, it possesses considerable anthelmintic activity.

Scheme 78



The same photo-oxygenation of a tryptophane moiety was used as a key step in the synthesis of okaramine N.[436] The okaramines are a family of heptacyclic or octacyclic alkaloids which were isolated from the fungus *Penicillium simplicissum* (ATCC 90288).

9. Photochemical Reactions in Microstructured Reactors

Recently, microstructured reactors have become an important topic in industrial chemistry.[437] This technique is particularly useful for the investigation of fast or highly exothermic reactions facilitating isothermic reaction conduction and thus reducing formation of byproducts. Using microstructured reactors also increases safety. Several photochemical reactions can be found among the large number of processes already performed in these reactors. An assembly is shown in Figures 8[437] and 9.[438] This reactor is particularly suitable for performing photo-oxygenation reactions where a gas and a liquid phase are involved.[439] The photo-oxygenation of terpinene **206** to ascaridol **207** (see Scheme 72) has been carried out under these conditions.[440] The same technique was also efficient for other photochemical reactions. The [2 + 2] photocycloaddition of vinylacetate

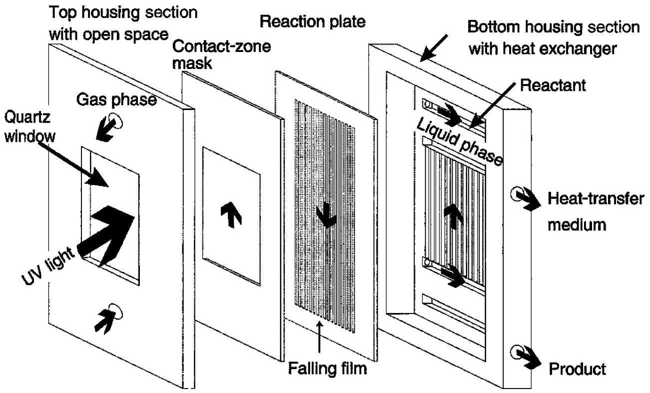


Figure 8. (Reprinted with permission from ref 437a. Copyright 2004 Wiley-VCH Verlag GmbH & CoKGaA, Weinheim.)

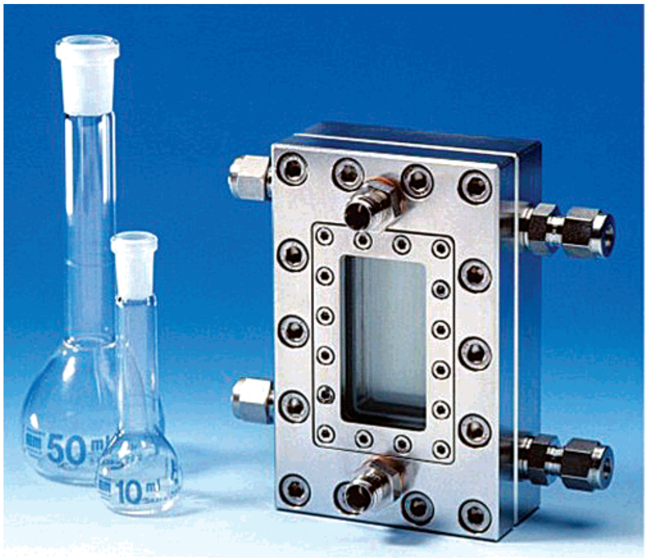


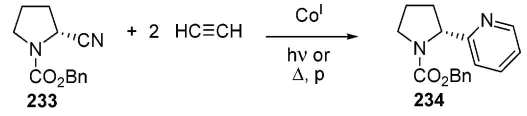
Figure 9. Falling film microreactor. (Reprinted with permission from www.imm-mainz.de. Copyright 2006 Institut fuer Mikrotechnik Mainz GmbH.)

to cyclohex-1-en-3-one has been conducted in a microstructured reactor. Compared to conventional experimental procedures, the reaction became more efficient, increasing the yield from 22% to 88%.[441] For an example of an intramolecular reaction, see ref 442. The Barton reaction (nitrite photolysis) was successfully carried out in a microreactor.[443] The transformation yielded a key steroid intermediate for an endothelin receptor antagonist. Heterogeneous photocatalysis with immobilized TiO_2 was performed under the same conditions.[444]

10. Photochemically Supported Organometallic Reactions

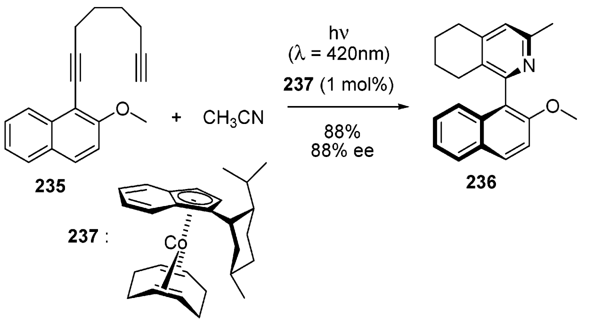
Metal-catalyzed reactions can frequently be accelerated by UV or visible light irradiation.[445,446] In the case of the [2 + 2 + 2] cycloaddition, the effect of irradiation was studied in detail in order to optimize the reaction. Using organometallic catalysis, in particular with cobalt complexes, pyridines can be synthesized from two molecules of acetylene and one nitrile molecule.[447] The reaction of the D-proline derivative **233** with acetylene yields the pyridine derivative **234** (Table 2).[448] Under photochemical conditions, only small amounts of the catalyst are necessary. The reaction can be carried out at room temperature and atmospheric pressure. These conditions are important due to particular safety requirements which are inherent to acetylene transformations. Moreover, the reaction is faster[449] and the yields are higher. Irradiation favors generation of the catalytic species from the precatalyst. It should also be noted that these mild conditions facilitate the transformation of enantiomerically pure nitriles such as **233**, which easily racemize under more drastic conditions.[450] The same mild conditions enable asymmetric catalysis of this reaction. The naphthalene derivative **235** was transformed in high yields and high enantioselectivity into the pyridine derivative **236** (Scheme 79).[451] In this case, using the cobalt complex **237**, an atropoisomer chirality is induced.

Table 2. Photochemical and Ground-State Reaction Conditions of the [2 + 2 + 2] Photocycloaddition of Acetylene to the Enantiomerically Pure Nitrile 233



method	conditions				yield (%)
	CpCo(cod) (mol %)	*T* (°C)	*p* (atm)	*t* (h)	
hν	0.5	25	1	4	90
ground state	3.2	110	14	22	82

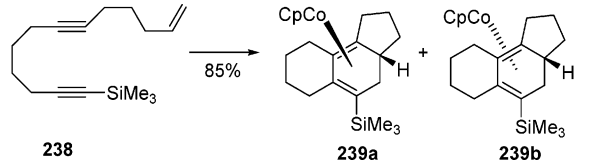
Scheme 79



The same reaction was applied to the synthesis of macrocycles,[452] cyclopropane containing oligocycles,[453] and silylated pyridines.[454] The latter products can be easily transformed into hydroxypyridines.

Different reaction conditions of the intramolecular [2 + 2 + 2] cyclization of two alkynes and one alkene have been investigated.[455] A thermal and a photochemical method were compared. Generally higher product yields were obtained with the photochemical method. In the case of compound **238**, a significant influence on the stereoselectivity was observed (Table 3). Applying the photochemical reaction conditions, isomer **239b** was the only reaction product. Under thermal reaction conditions, isomer **239a** was also obtained. The reaction can also be used for the synthesis of complex carbocyclic systems such as the steroid derivative **240** (Figure 10).[456] A large variety of similar reactions have been performed using light.[446] The [2 + 2 + 2] cycloaddition of three alkyne moieties was applied to the synthesis of polycyclic compounds such as **241**, which are similar to the taxane ring system.[457]

Table 3. Photochemical and Ground-State Reaction Conditions of the Intramolecular [2 + 2 + 2] Photocycloaddition of Acetylene and One Alkene Moiety



conditions	ratio **239a**/**239b**
$CpCo(CO)_2$ (1 equiv), toluene, *hν*	0/100
$CpCo(CO)_2$ (1 equiv), decane, D	46/54

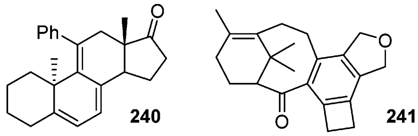
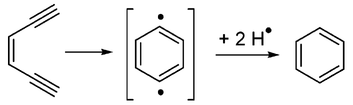


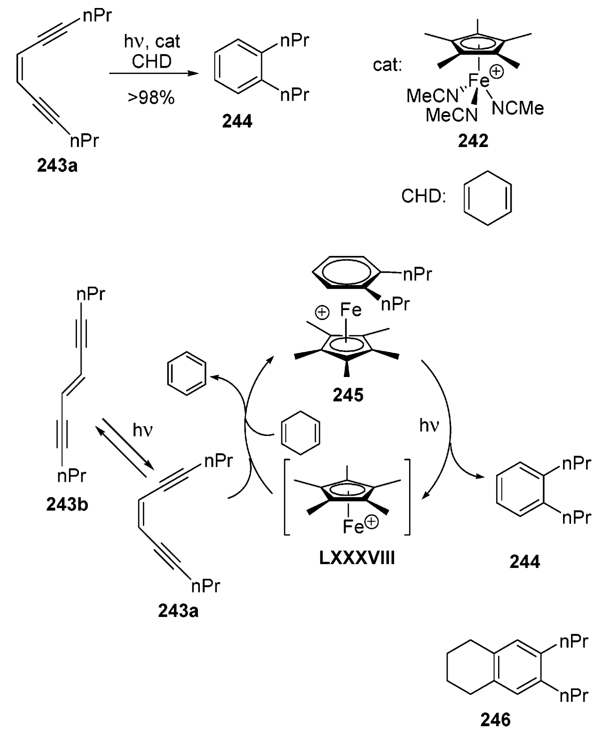
Figure 10.

The Bergman cyclization of enediyne derivatives (Scheme 80)[241,458,459] was carried out using photochemically supported metal catalysis. In general, acyclic derivatives and, in particular, trans isomers rarely undergo Bergman cycloaromatization.[460] Using the air-stable iron catalyst **242**, (*Z*)-dodeca-4,8-diyne-6-en **243a** was efficiently transformed into **244** (Scheme 81).[461] In a similar way, the corresponding trans derivative **243b** yielded the same product. In the proposed mechanism, compound **245**, which was also isolated, was photochemically decomplexed, leading to the intermediate **LXXXVIII**. This intermediate then reacted with the substrate **243a**. The Bergman reaction takes place in the coordination sphere of the complex. The 1,4-biradical is saturated by hydrogen abstraction from cyclohexadiene (CHD), and the cis/trans isomers **243a**,**b** are in photostationary equilibrium. In this way, transformation of the trans isomer becomes possible. Product **246** was obtained under the same conditions.

Scheme 80



Scheme 81



Several other conditions[459] have been applied to perform the photochemical Bergman cyclization. The products **247**,[460] **248**,[462] and **249**[463] have recently been isolated from such transformations (Figure 11).

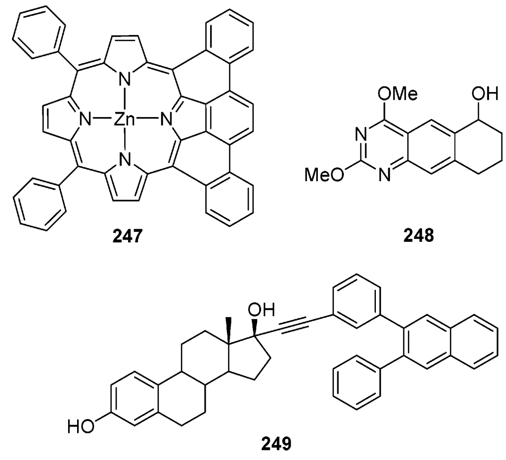
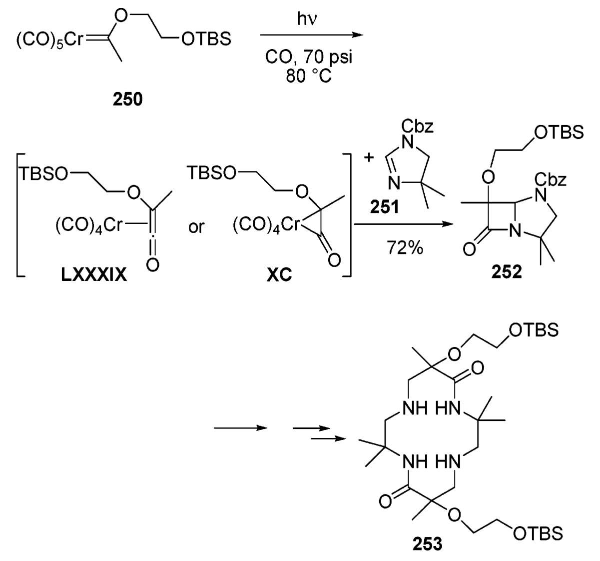


Figure 11.

Numerous photochemical transformations have been described with Fischer-type carbene complexes.[464−466] Many of them are obtained from transition group VI metals.[467,468] For example, the carbene complex **250** is transformed into the ketene intermediate **LXXXIX**, which is bonded to a chromium atom (Scheme 82).[469] Formation of the chromacyclopropanone intermediate **XC** was also discussed.[464,465] The *β*-lactam **252** was formed in a cycloaddition of the imidazoline **251** to **LXXXIX**. The bislactam **253**, obtained from reaction of two molecules of **252**, was used for the synthesis of lanthanide ligands such as **254** and **255** (Figure 12). The corresponding Gd^{3+} complexes can be used as magnetic imaging contrast agents. A similar approach to this type of compound was previously described.[470] The same reaction was systematically applied to the synthesis of amino acids and peptides.[465] It has also been frequently performed with alkenes. For a recent application to the asymmetric synthesis of aminocyclopentenols, see ref 471.

Scheme 82



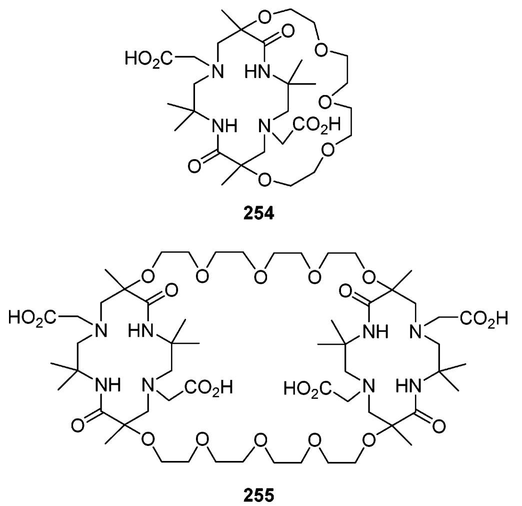
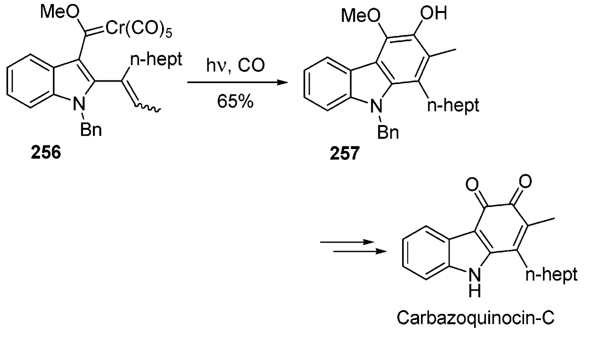


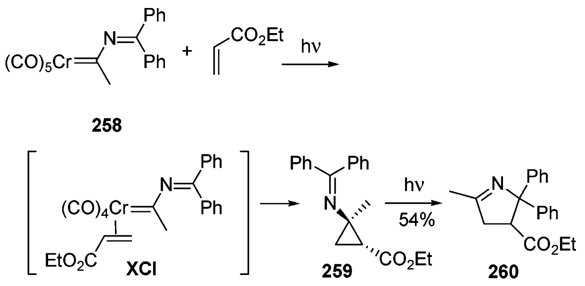
Figure 12.

A large variety of aromatic compounds are accessible by annulation reactions of carbene complexes.[468,472] For example, the carbene **256** was transformed into the carbazole derivative **257** (Scheme 83).[473] Carbazoquinocin-C was obtained after additional steps. These compounds are interesting due to their activity against lipid peroxidation or other cell-protecting activity.

Scheme 83



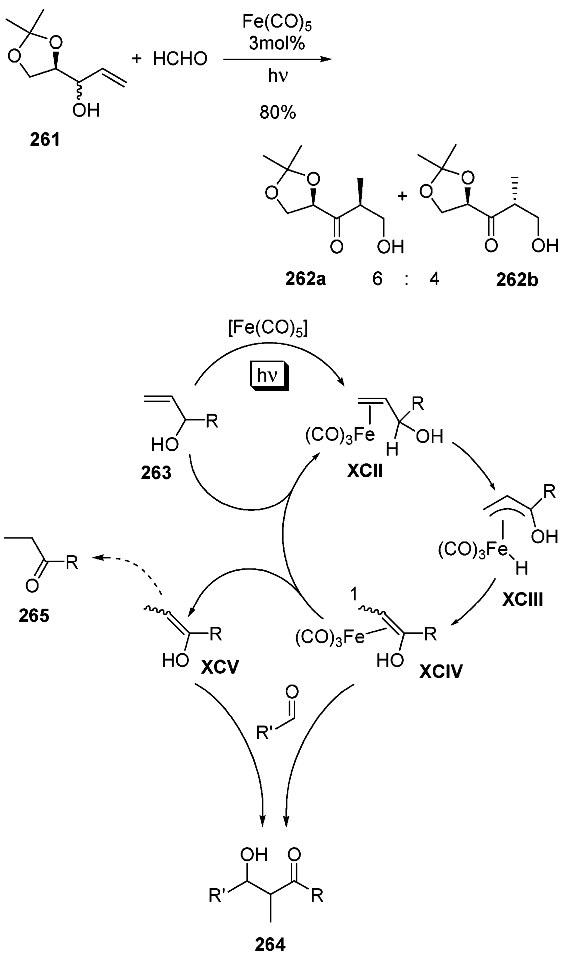
Scheme 84



The imine-derived carbene **258** was transformed into the cyclopropylimine **259** via addition of an acrylic ester (Scheme 84).[198,474] During the first step, a CO ligand is replaced by an acrylic ester (**XCI**) in an elimination/addition sequence. Under these reaction conditions, **259** was transformed into the pyrroline derivative **260** via an aza-analogue vinylcyclopropane rearrangement (compare Scheme 36, eq 25). Applying modified reaction conditions, **259** was isolated. The same reaction of analogue carbene complexes with alkynes led to 2*H*-pyrroles.[475]

Tandem metal-catalyzed reactions can be induced by light. For instance, isomerization of allylic alcohols[476] to ketones or aldehydes is followed by an aldol reaction which is catalyzed by iron pentacarbonyl. For example, the allylic alcohol **261** was transformed into the aldol products **262a**,**b** (Scheme 85).[477] For similar examples, see ref 478, and for other iron catalysts, see ref 479. The reaction products are key intermediates in the synthesis of numerous natural products or compounds possessing biological activity. In a photochemical step, iron pentacarbonyl is partially decarbonylated.[480] The allylic alcohol **263** is then added to yield **XCII**. After transfer of the allylic hydrogen to the metal atom, the π-allyl complex **XCIII** is formed. This hydrogen atom is then retransferred into position 1 of the ligand (**XCIV**). In the presence of an aldehyde, the intermediate **XCIV** or the decomplexed enol **XCV** mainly yields **264** via aldolization. A low percentage of **XCV** tautomerizes to generate ketone **265**. In the absence of the aldehyde, this parallel pathway is the only reaction.[481] This transformation was applied to the synthesis of perfume components.[482] In the mechanism illustrated in Scheme 85, only the starting reaction (the partial decarbonylation of iron pentacarbonyl) is initiated by light absorption. However, it is necessary to continue irradiation during the whole reaction time.[483] This observation may indicate that other reaction steps are also accelerated by light. In a similar photochemical reaction, cyclohexenone derivatives were obtained by CO insertion into a vinylcyclopropane moiety.[484] In this case, iron pentacarbonyl was used in stoichiometric amounts.

Scheme 85



Several photochemically supported tungsten carbonyl-catalyzed reactions have been recently described. The alkyne derivative **266** has been transformed either into the metal vinylene intermediates **XCVI** or into the metal carbene **XCVII** (Scheme 86, eq 42). These compounds then gave the cyclic enolether **267**, which was further transformed into substructures of altromycin B, a pluramycin antibiotic.[485] The same reaction was performed with the alkyne derivative **268** (Scheme 86, eq 43).[486] In this case, the 2,3,4,5-tetrahydroxepin **269** was isolated. It should be mentioned that cyclization of the dimethyldioxolane derivative **268** possessing a trans configuration is often difficult. Similar reactions have been carried out and applied to the synthesis of natural products.[487] Cyclizations involving a keto function instead of the hydroxyl group can also be carried out under identical reaction conditions.[488] Using the same catalytic system, isocyclizations have been performed with bifunctional alkene alkyne derivatives such as **270** (Table 4).[489] Depending on the silyl

Scheme 86

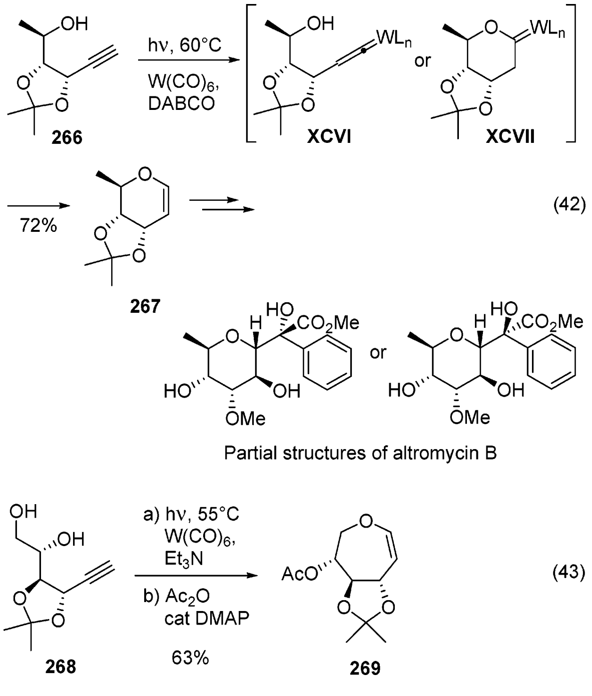
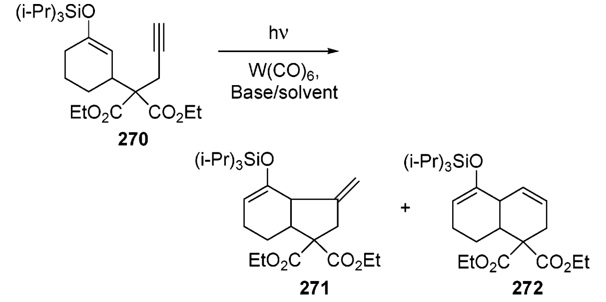


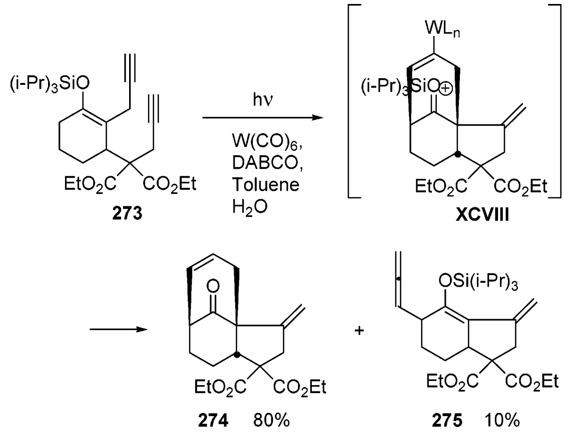
Table 4. Influence of Solvent and Base on the Tungsten Carbonyl-Mediated Cyclization of 270



base	solvent	yield (%)	**271**/**272**
DABCO	THF	92	94/6
Et_3N	toluene	92	17/83

protecting group and the solvent/base system either exo cyclization (**271**) or endo cyclization (**272**) can be selectively carried out. Further examples have been published.[490] Synthesis of corresponding cyclopropane derivatives was recently described.[491] Tandem reactions can be performed under the same conditions. The dialkyne derivative **273** was cyclized to yield the tricyclic compound **274** as the major reaction product (Scheme 87).[489] The minor formation of the allene derivative **275** can be explained by C−C bond cleavage in the intermediate **XCVIII**. Instead of alkene/alkyne systems, alkene/allene[492] and alkene/benzene systems[493] have been cyclized under almost the same reaction conditions. Various nitrogen-containing heterocycles have been obtained with substrates possessing an imine function.[494]

Scheme 87



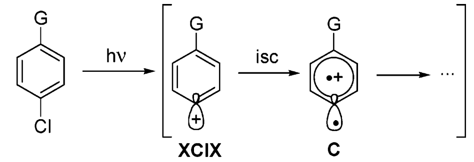
Tricarbonylcycloheptatriene chromium complexes undergo [6 + 4] photocycloadditions.[495] For reviews on these and related reactions, see ref 496.

Titanium or zirconium complexes are frequently used in organic synthesis. Certain characteristic transformations of these organometallic compounds can be carried out in a photochemical way.[497] Photochemical acceleration might also be possible in Wacker-type oxidations.[498]

11. Photochemical Reactions as an Alternative to Metal Catalysis

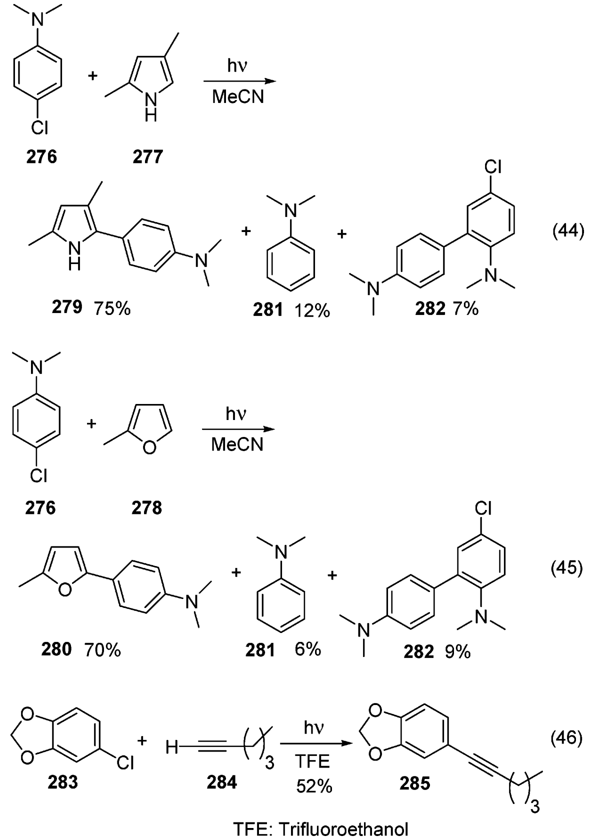
Several organometallic reactions have a photochemical counterpart. In these cases, the activity of the metal catalyst is replaced by photochemical excitation. In this context, the photo-S_N1 reaction has been particularly well studied, most frequently with chlorobenzene derivatives.[499] It has been shown that the reactions start with a heterolytic cleavage of the C−Cl bond. The resulting aryl cations possess singlet (**XCIX**) or triplet (**C**) character (Scheme 88).[499,500] These structures can also be related to carbenes. In a Suzuki analogue reaction, the aminochlorobenzene derivative **276** was added to heterocyclic aromatic compounds such as **277** or **278** (Scheme 89, eqs 44 and 45).[501] The corresponding products **279** and **280** were isolated in good yields. It should be emphasized that this method needs neither metals nor functionalization by a boronic acid group of one of the reaction partners as is the case for the Suzuki reaction. Formation of typical side products **281** and **282** in minor amounts also indicates formation of the intermediates **XCIX** and **C** (Scheme 88). In a Sonogashira analogue reaction 1-hexyne **284** was added to the chlorobenzene derivative **283**, leading to the coupling product **285** in good yields (Scheme 89, eq 46). As in the previous cases, no functionalization of **284** is necessary.[499] Similar reactions have been carried out with a variety of alkenes.[502] A common characteristic of ground-state metal-catalyzed reactions and their photochemical analogues is population of antibonding orbitals of the C−halogen bond at the beginning of the process. In the case of metal catalysis, the electron is provided by the low-valent metal, while in the case of the photochemical reactions, one electron is transferred from the HOMO to the LUMO by photochemical excitation.[499]

Scheme 88



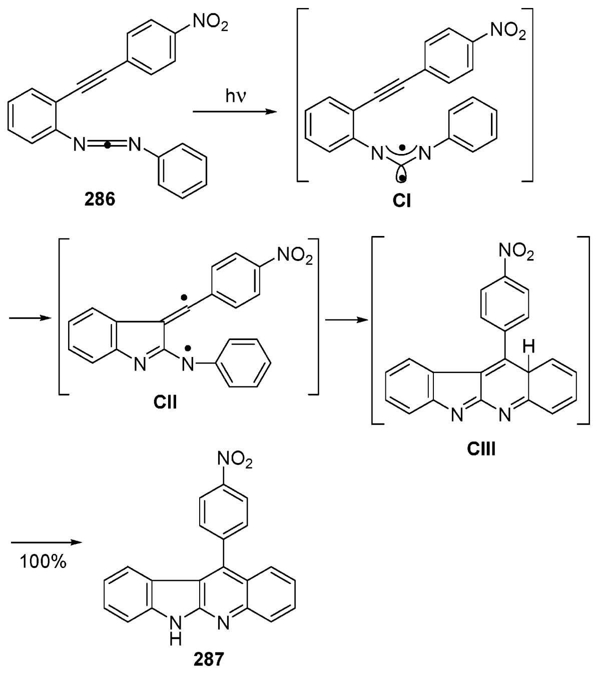
G: electron donating substituent

Scheme 89



TFE: Trifluoroethanol

Scheme 90



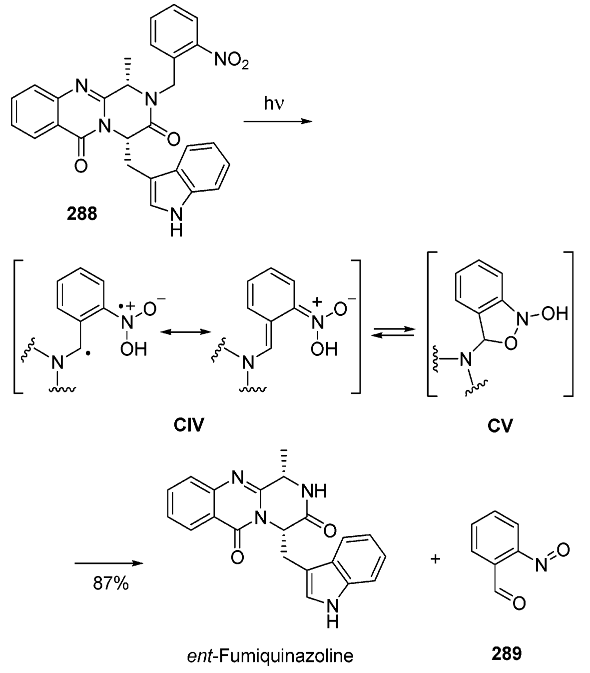
Cyclization reactions of polyunsaturated compounds similar to those described in Schemes 79, 80, 81, and 87 or Tables 3 and 4 can also be performed without the assistance of a metal species. An example in the field of heterocyclic chemistry is shown in Scheme 90. The carbodiimide **286** is transformed into the indoloquinoline derivative **287**.[503] The reaction was performed with a variety of similar derivatives. It is a heteroatom analogue to the Myers−Saito reaction which is carried out with corresponding allene derivatives. The transformation can be performed by direct irradiation or triplet sensitization. It was shown that in both cases the chemical reaction starts at the triplet state (**CI**). In a first cyclization step, the indole ring system **CII** is built. The final product **287** is then obtained in a second cyclization followed by tautomerization via the intermediate **CIII**. Similar photochemical transformations have been described.[504]

12. Protecting Groups

In the synthesis of complex polyfunctional compounds, protecting groups often play a central role and must be meticulously chosen. On one hand, they must resist the transformation conditions of other functional groups, and on the other, they must be removed without damaging the core structure. In most cases, acidic or basic reagents are used for deprotection. Metal and enzyme catalysis have also been used. The major advantage of photochemical protecting groups is that no chemical reagents are needed for deprotection and removal is rapid and clean in most cases.[505] These properties are particularly suitable for applications in the fields of biochemistry and microbiology.[506−509] For example, fast enzyme kinetics can be easily studied in this way.[506,510] Using laser flash photolysis, protecting groups can be removed almost instantaneously from enzymes or ligands. For some recent papers in these fields, see refs 511 and 512. *o*-Nitrobenzyl derivatives are most frequently used for these purposes. In organic synthesis, the interest for photoremovable protecting groups is steadily increasing.[509,513,514]

In a recent example, an *o*-nitrobenzyl protecting group was efficiently eliminated from the substrate **288** in the last step of the synthesis of *ent*-fumiquinazoline (Scheme 91).[515]

Scheme 91



Numerous mechanistic studies have been performed on the removal of this protecting group.[516] After photochemical excitation, hydrogen transfer occurs from the benzyl position to the nitro function, yielding intermediate **CIV**. This species is in equilibrium with the bicyclic intermediate **CV**. *o*-Nitrosobenzaldehyde **289** is then eliminated from **CV**. This protecting group was also used in the synthesis of (−)-diazonamide A[517] (compare Scheme 67 and see ref 361). This protecting group has been used in the sol−gel production of silica modified by a free carboxylic acid function.[518] Other research efforts concern structural modification in order to make this protecting group hydrosoluble. In this way the absorption wavelength is also modified and the quantum yield of the deprotection is increased. Structural variation also enables protection of a larger variety of functional groups.[508,519,520] In solid-phase synthesis, a system of an NO_2 protecting group and photoremovable spacer or linker has been developed.[512,514] See also ref 521. Several studies have focused on the 2-(2-nitrophenylpropan-1-yl) derivatives **290** (Figure 13).[522] These protecting groups have been applied to microarray chips using oligonucleotides and cyclopeptides.[523] The protecting group **291** carrying a fluorophore has been synthesized.[524] During the synthesis of oligonucleotides,

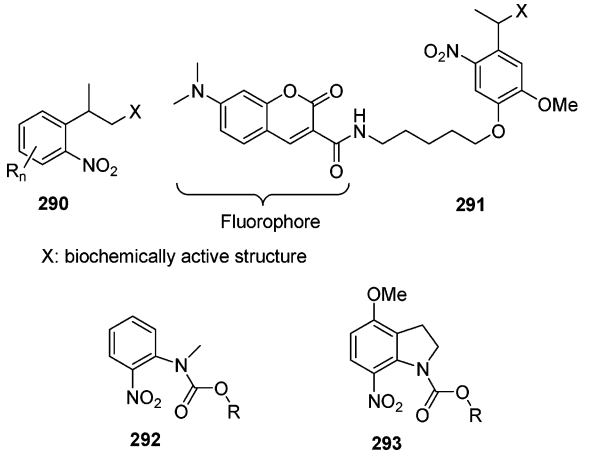
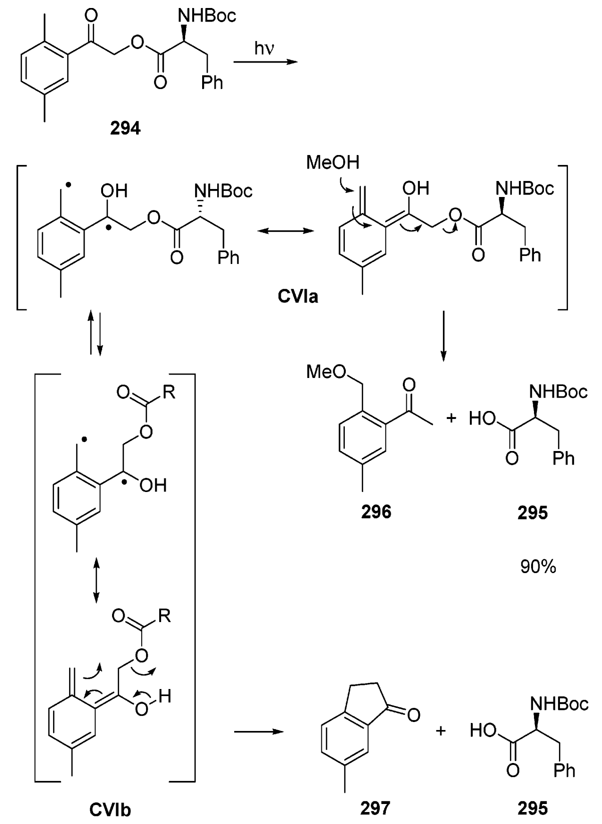


Figure 13.

Scheme 92

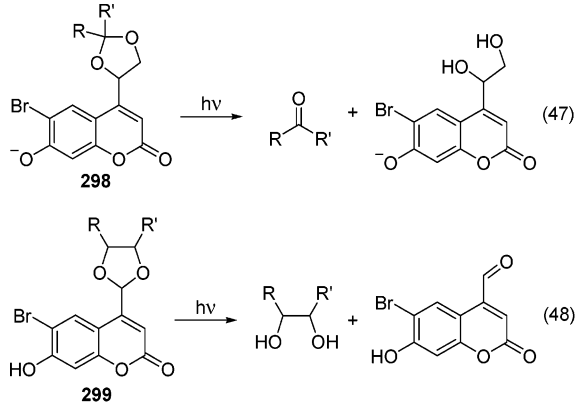


this group facilitates visualization and quantification of the deprotection using fluorescence detection. The presence of a fluorophore has little or no effect on cleavage efficiency. Oxobenzo[*f*]benzopyrans have been studied in the same context. These compounds possess a fluorophore and a protecting group in one entity.[525] Carbamate derivatives of *o*-nitroaniline (e.g., **292**[526]) or indole (**293**)[527] have also been developed as protecting groups.

A phenacyl moiety is also a photoactive protecting group. For example, deprotection of the phenylalanine derivative **294** is easily achieved (Scheme 92).[528] Excitation and hydrogen transfer yields the intermediate **CVI**. The conformer **CVIa** preferentially reacts with a solvent molecule (methanol) in order to liberate the amino acid **295** and ketone **296**. In contrast, the conformer **CVIb**, preferentially formed in apolar solvents, leads to the amino acid **295** and methylindanone **297**. For further mechanistic details, see ref 529. Other derivatives of this photoremovable group have also been studied.[530] Depending on the substitution pattern, the deprotection mechanism may change. This principle of photolabile groups has also been performed with coumarin analogues such as **298** (Scheme 93, eq 47).[531] This chromophore can be used for protection of ketones and aldehydes.[532] See also ref 520. Likewise 1,2-diols (**299**), have also been protected (Scheme 93, eq 48).[533] Hydroxymethylquinoline derivatives can also be used as photoremovable protecting groups.[534] About 10 years ago, the *p*-hydroxyphenacyl group was used to protect phosphates such as adenosin triphosphate.[535] The deprotection occurs via a very efficient photo-Favorskii reaction.

Silicon-containing protecting groups are well established in organic synthesis. Photochemically removable silyl groups have been developed based on the photo-Brook rearrangement (compare Scheme 33).[184] Presently, new approaches using photoinduced electron transfer are being investigated.[536]

Scheme 93



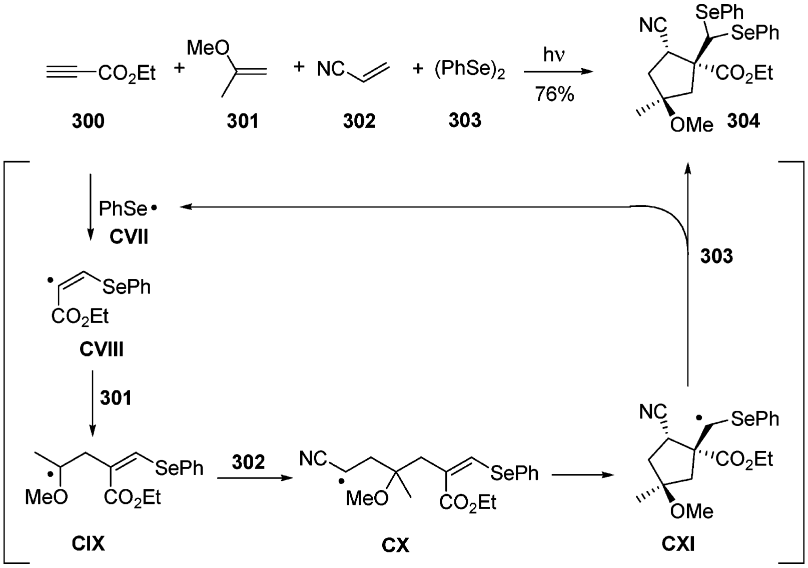
13. Auxiliary Reactions for Radical Chemistry

Numerous radical and radical tandem reactions or radical polymerizations are started with a photochemical step.[537,538] In the context of combinatorial chemistry, multicomponent reactions have become particularly interesting because in a one step reaction a large number of compounds of a product family possessing different substituents can be obtained.[539] The multicomponent radical reaction[540] of **300**, **301**, and **302** is started by the photochemical fragmentation of diphenyldiselenide **303** (Scheme 94).[541] The fragment **CVII** adds easily to the alkyne **300**, a compound of low steric hindrance. The electrophilic radical **CVIII** then reacts with the electron-rich alkene, yielding the intermediate **CIX**, which is also an electron-rich radical. Addition to the electron-poor alkene, acrylonitrile, leads to the radical **CX**, which cyclizes in an exo-trig way. Finally, in a reaction with diphenyldiselenide **303**, the cyclic radical intermediate **CXI** is saturated. This reaction generates a phenylselenide radical **CVII** and completes the radical chain process to afford the final product **304**. The alternating polarities in the sequence of radical additions[264] are essential for the efficiency of the overall reaction. For similar reactions induced by photofragmentation of diphenylselenide, see ref 542. Other selenium derivatives also undergo photofragmentation. Photochemical activation is frequently more efficient than the corresponding thermal activation.[543]

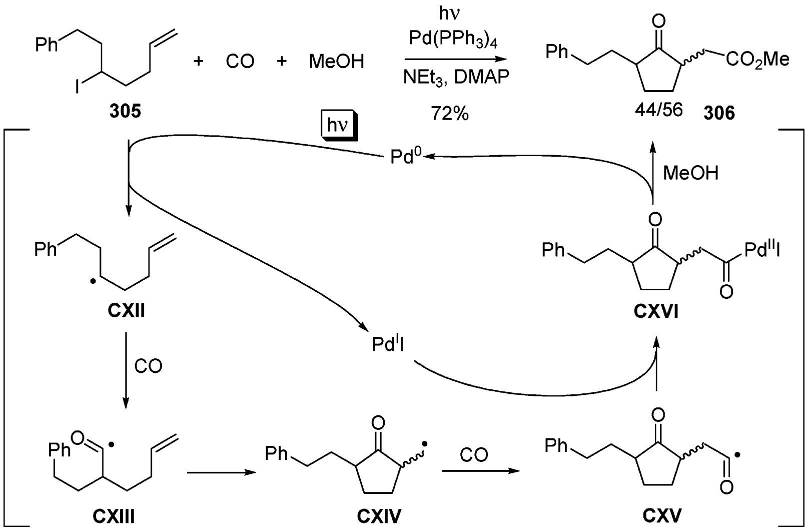
Addition of CO to carbon-centered radicals is a highly potential transformation in organic synthesis.[544] Some of these reactions are accelerated under photochemical conditions. Recently, the radical cyclizing carbonylation of alkyl halides using palladium catalysis was significantly improved by UV irradiation. In a photoinduced and palladium-catalyzed reaction, the alkyl iodide **305** was transformed into the secondary radical **CXII** (Scheme 95).[545] In this step, the authors assumed formation of a Pd^I−iodide species. The acyl radical **CXIII** formed by addition of carbon monoxide then cyclized in an exo-trig process (**CXIV**). Addition of a second CO molecule leads to the acyl radical **CXV**. This radical reacted with the Pd^I species, leading to **CXVI**. The final product **306** was obtained after addition of methanol and elimination of a Pd^0 species. Further examples have been published.[546] It should be noted that the palladium-catalyzed transformation of alkyl halides involving a halogen−carbon sp^3 bond (oxidative addition) is extremely rare.

Addition of xanthates to double bonds can be induced by a photochemical reaction. Under light irradiation, the xanthate **307** was cleaved and the cyclopropylacyl radical **CXVII** was

Scheme 94

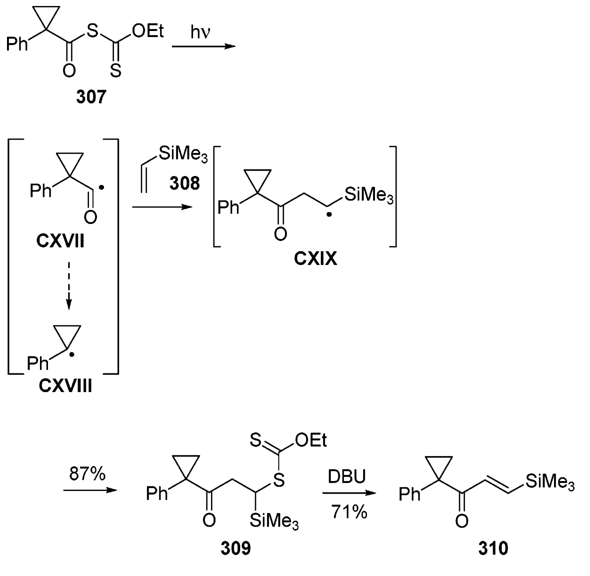


Scheme 95



generated (Scheme 96).[547] In the absence of a carbon monoxide atmosphere, these radicals tend to eliminate CO, leading to **CXVIII** (see, for example, refs 544 and 546). In the present case, this elimination was slow. Therefore, the radical intermediate **CXVII** added to alkenes such as **308** to yield **309** after transfer of a xanthate function to **CXIX**. For further examples of xanthate radical additions to alkenes, see refs 268 and 548. In basic medium, **309** was transformed into the *β*-silylated α,*β*-unsaturated ketone **310**. Such compounds are interesting intermediates, and their synthesis is not trivial.[549] The well-known Barton esters (*N*-hydroxypyridinethione esters) have also been activated by light.[550] In the context of radical reactions, these derivatives can be related to the family of xanthates such as **307**.

Scheme 96

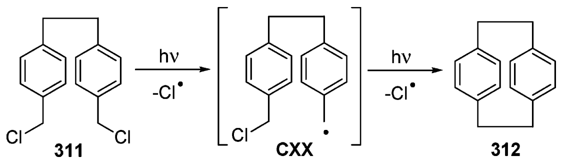


14. Multiphoton Reactions

In physical organic chemistry, many investigations concerning detection and characterization of intermediates possessing short lifetimes are carried out with lasers. In organic synthesis, lasers are rarely used for chemical transformations because in most cases only low quantities of a substrate can be transformed. However, these methods enable bi- or multiphoton reactions.[551−553] In general, two types of transformations can be distinguished. (1) In the first photochemical step, an intermediate of short lifetime is formed. Due to high irradiation intensity, significant quantities of this intermediate can absorb a second photon, which starts the desired photochemical reaction. (2) Repeated photon absorption leads to a population of higher excitation states, which enables characteristic reactions from these species.

Recently, an application of this technique to the synthesis of cyclophanes was described. In a first photochemical step, the dichlorinated derivative **311** was partially dehalogenated (**CXX**) (Scheme 97).[554] [2.2]Paracyclophane **312** was obtained by absorption of a second photon. Applying conventional reaction conditions using high-pressure mercury vapor lamps lead to the complex and unselective transformation of compound **311**.

Scheme 97



Large-scale transformations may be performed with a particular experimental setup (Figure 14).[551] This apparatus enables continuous high-intensity laser photolysis. The reaction mixture is continuously pumped through a glass capillary so that a liquid jet is generated. Irradiation with lasers is carried out just below the outlet of the capillary. Using two or three lasers of different wavelength, the substrate and intermediates can be selectively excited in an optimized setup.[555] Matching the timing of intermediate generation and laser irradiation can be performed by controlling the flow rate (also see ref 552).

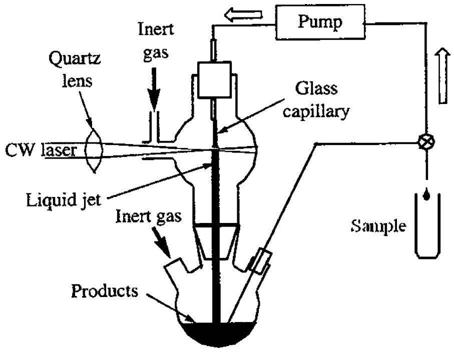


Figure 14.

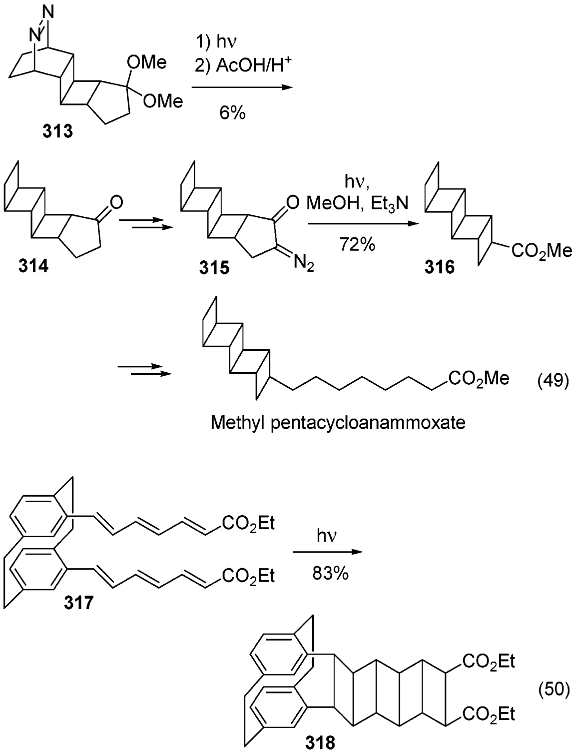
Multiphoton reactions which are discussed here should not be confused with multiphoton absorption. In the latter case, for example, a low energetic excited state (S_1, T_1,...) is generated by absorption of two or more photons possessing energies below the excitation energies of the corresponding molecule.[556] These processes are now frequently applied in the fields of biochemistry and cell biology.[557]

15. Exotic Molecules

Molecules possessing high symmetry, constraints, or unusual bond parameters are particularly attractive and challenging targets for organic chemists. Such synthetic projects require high levels of conception, handling, and methodology. Moreover, this kind of synthesis significantly contributes to a better understanding of fundamental phenomena of chemical reactivity and the chemical bond. Some examples of such molecules have already been discussed in previous sections. Hydrocarbons have been frequently chosen as targets since these compounds constitute the basis of organic chemistry.[558,559] Sometimes a certain motif is also encountered as a partial structure in natural products. As already pointed out, photochemical reactions differ significantly from ground-state reactions since they occur on different potential-energy hypersurfaces.[2] Use of photochemistry is therefore particularly appropriate for synthesis of such unusual compounds.

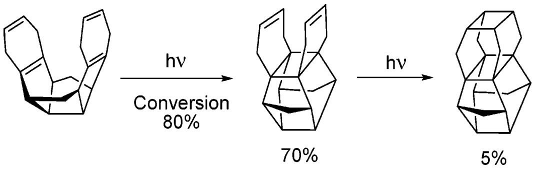
In many cases, more than one photochemical step can be involved in these syntheses. For example, extrusion reactions enable the construction of small rings possessing high strain energies. The diazo compound **313** was transformed into **314**, a ladderane derivative,[559,560] via photochemical extrusion of nitrogen (Scheme 98, eq 49).[561] In a second photochemical step, a photo-Wolf rearrangement,[562] the α-diazoketone **315** was transformed into the ester **316**. Chain elongation of **316** yielded methyl pentacycloammoxate. The corresponding acid was then obtained by saponification. A similar enantioselective synthesis was recently carried out.[563] This C_{20} fatty acid was isolated from the bacteria *Candidatus brocadia* anammoxidans.[564] These anaerobic bacteria are capable of transforming nitrate and ammonium to nitrogen. A multiple [2 + 2] photocycloaddition with two polyenes may also be envisaged as the key step if the two molecules are well oriented in a supramolecular crystalline structure.[565,206] [2 + 2] Photocycloaddition of comparable molecules has been investigated in polymer chemistry for either polymerization or cross linking.[566] As previously discussed, the orientation in a crystal is frequently used to control reactivity as well as stereoselectivity.[203,207] Multiple [2 + 2] photocycloadditions performed with polyene chains attached and oriented in a cyclophane system can also lead to ladderanes as shown for the transformation of **317** into **318** (Scheme 98, eq 50).[567] This reaction was performed in solution. The same kind of structure was obtained by two consecutive [2 + 2] photocycloadditions.[568]

Scheme 98



Photocycloadditions have also been applied to the synthesis of cage hydrocarbons[569] and molecules possessing high strain.[570] In a [2 + 2] photocycloaddition, the hexacyclic compound **319** was transformed into the heptacyclic compound **320** (Scheme 99).[571] During the reaction, part of **320** reacted in a second [2 + 2] photocycloaddition leading to **321**. Azaanalogue [2 + 2] photocycloadditions afford similar products.[572] Prismanes represent an interesting family of target molecules (Figure 15). [559,573] For recent work on the synthesis of hexaprismane starting from cyclophane structures, see ref 574. The same strategy was successfully applied to the synthesis of an octahedrane derivative.[575] The final product was obtained by intramolecular dimerization of two benzene moieties.

Scheme 99



319 **320** **321**

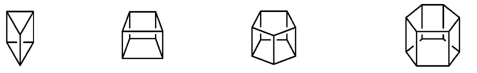
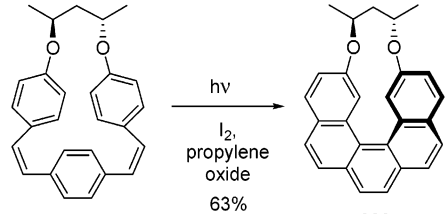


Figure 15.

Photochemical reactions also play an important role in the synthesis of helicenes. Beyond inherent chirality, these compounds are interesting due to their extraordinary optical and electronic properties.[558,576] Among photochemical reactions, pericyclization has frequently been used as a key step. In such a reaction, the bisstilbene derivative **322** underwent cyclization, leading stereoselectively to the optically active helicene **323** (Scheme 100).[577] The oxidation conditions (presence of iodine and propylene oxide) are necessary to establish aromaticity in the final product after cyclization. Based on the fact that [5]helicen slowly racemizes at room temperature, formation of a mixture of diastereomers of **323** could be expected. However, only one isomer was obtained. NMR studies have shown that the bis-ether tether locks the configuration of the helix in the temperature range from −40 to +80 °C. For another recent example, see ref 578. Heterocycles, in particular thiophene-containing helicenes, have been synthesized in the same way.[579] Azahelicenes containing pyridine moieties have also been prepared.[580] The photochemical supported intramolecular cyclization of three alkynes which leads to benzene rings has been used for the synthesis of helicenes. In this way compounds **324** and **325** have been obtained from cyclization of the corresponding polyalkyne precursors (Figure 16, X-ray structures).[581] These two helicenes are built up of benzocyclobutene moieties. Compounds **324** and **325** contain seven and eight benzene rings, respectively. Crystals of **325** contain solvent molecules. Photochemical and corresponding ground-state cyclizations of triynes have been applied to the synthesis of helicenes.[582]

Scheme 100



322 **323**

Aromaticity is one of the most important organic functions. A specific arrangement of double bonds in a conjugated polyene system is necessary to establish aromatic stability.[583] Such polyenes are cyclic and planar. Generally, all p orbitals of an aromatic π system are parallel, in a belt-like arrangement as shown for benzene (**326**) (Figure 17). These systems contain $(4n + 2)$ π electrons, (n = natural number) and are also called Hückel aromatic. The basic theory of aromaticity also predicts uncommon arrangements such as the Möbius strip, which should be able to create aromatic character.[584,585] When a belt-like strip is cut and the ends are assembled in the opposite sense, a Möbius strip with one twist is obtained. p Orbitals building up a polyene system can be oriented in the same way (**327**). Such structures possess a C_2 axis as an inherent symmetry element. These systems are aromatic when they contain $4n$ π electrons. Such arrangements can stabilize transition states, for example, in cis/trans isomerizations in polyene systems as shown for a [12] annulene.[586] Recently, the first stable Möbius-type aromatic compound has been synthesized. A [2 + 2] photocycloaddition between tetradehydrodianthracene **328** and tricyclooctadiene **329** leads to the latterane derivative **330** (Scheme 101).[587] Compound **331** was formed in two consecutive cycloreversion reactions. Photochemical ring opening yielded five isomers of the [16] annulene **332**. Two of them possess a Möbius belt structure and one a Hückel structure. X-ray structure analysis was successfully carried out with compounds **332a** and **332b**. For a controversial discussion of these results, see refs 585 and 588.

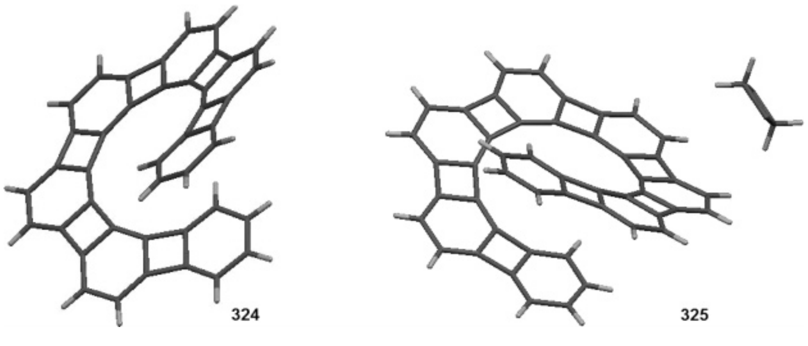


Figure 16.

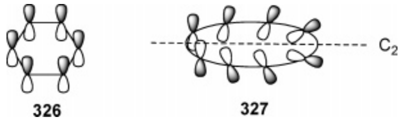
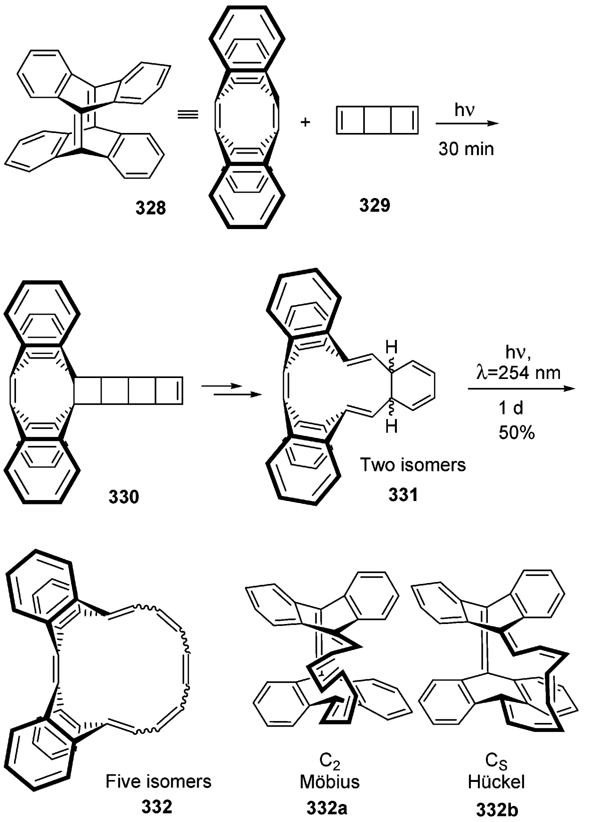
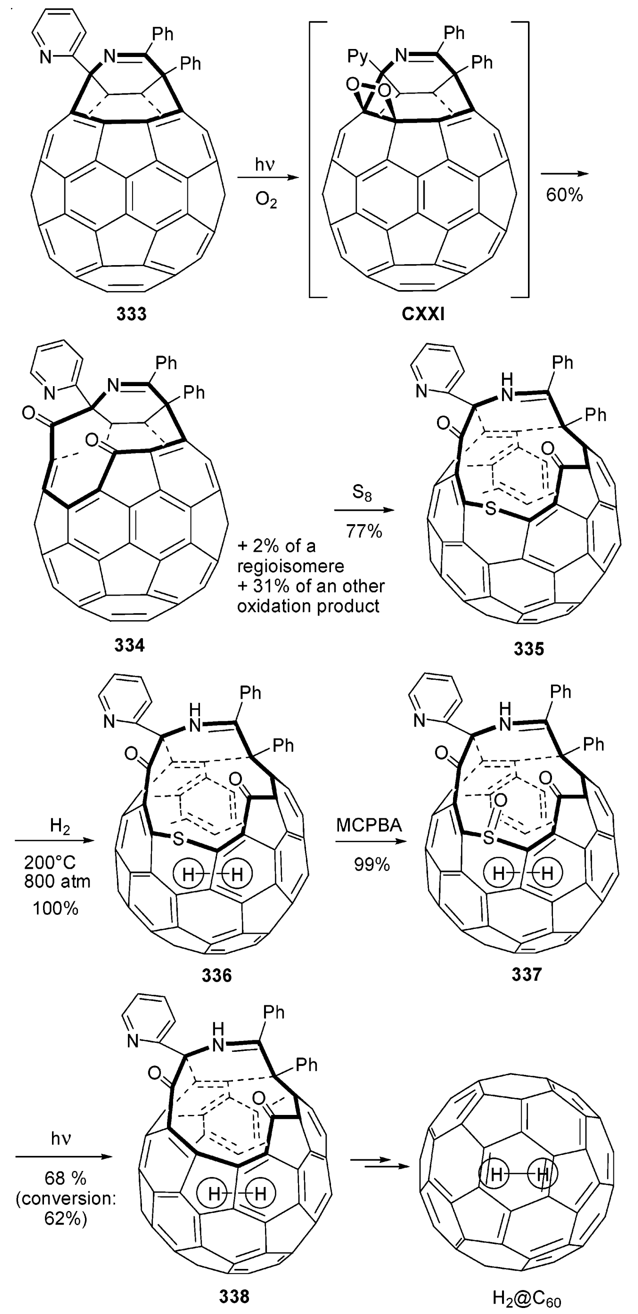


Figure 17.

Scheme 101



Scheme 102



Two photochemical steps were used for the encapsulation of one molecule of hydrogen in the fullerene C_{60} by organic synthesis. The first challenge was to generate an orifice which was sufficiently large to enable the hydrogen molecule to enter under high hydrogen pressure and sufficiently small to prevent its escape (favored by entropy) under different reaction and storage conditions. During the multistep transformation of C_{60}, a photo-oxygenation of the derivative **333** into **334** was performed using visible light (Scheme 102).[589] The dioxetane intermediate **CXXI** was formed by addition of singlet oxygen (compare to Scheme 70). No additional sensitizer was needed since the oxidation was sensitized by either the substrate or the product. The orifice was enlarged by cleavage of a C−C bond in **334** and fixation of a sulfur bridge (**335**).[590] Incorporation of one molecule of hydrogen was quantitative (**336**).[591] At this stage, an X-ray structure analysis was performed.[592] See also ref 593. It should be noted that yields of earlier attempts of hydrogen encapsulation with other derivatives ranged only between 1.5% and 5%. The first steps of closing the container now had to occur under mild reaction conditions in order to prevent the hydrogen from escaping. First, mild oxidation of the sulfide was carried out using *m*-chloroperbenzoic acid (MCPBA). Photochemical elimination of the sulfoxide bridge in **337** was easily performed at room temperature.[594] The orifice in **338** was now sufficiently narrow, and further closing transformations could be carried out at temperatures of 80 and 320 °C in order to obtain $H_2@C_{60}$. The same fullerene derivatives have been used for inclusion of ^3He.[595] The yield for this encapsulation was only 0.1%. For other references on this inclusion strategy of atoms or small molecules in C_{60}, see ref 596.

16. Conclusions

This short review on recent applications of photochemical reactions to organic synthesis shows a highly dynamic research field. Almost all domains of organic synthesis are concerned. Photochemistry frequently provides solutions to problems which are difficult to solve with ground-state reactions. This fact results from significant differences between these two reactions modes. Photochemical excitation considerably modifies the electron configuration and consequently the chemical nature of a molecule. The traditionally strong interaction existing between different disciplines of photochemistry, on one hand, and with physical chemistry or physics, on the other, enables a high level of characterization and understanding of the reactions. These circumstances also facilitate their optimization and application in various fields. Organic photochemistry also establishes interdisciplinary links between organic chemistry and biology and other research domains such as material science, supramolecular chemistry, or nanoscience. In this context, research activities will certainly increase in the near future in both directions, in basic and applied research. The fact that many organic photochemical reactions do not need polluting or toxic reagents offers perspectives in the context of sustainable processes and green chemistry. Using solar light, especially in climatically favored and economically disfavored regions, opens perspectives of sustainable development.

17. Acknowledgments

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18. Note Added in Proof

Since submission of this review, several significant publications have appeared. They are related to the following research areas: Photochemical reactions in the context of green chemistry,[597] [2 + 2] photocycloadditions of α,β-unsaturated carbonyl compounds,[598] photocycloaddition of aromatic compounds,[599] photochemistry of pyridinium salts,[600] photochemical electron-transfer reactions applied to the synthesis of natural products,[601] synthesis of pyridines using the transition-metal-catalyzed [2 + 2 + 2] cycloaddition,[602] metal-free photochemically induced aryl−aryl coupling,[603] photo-oxygenations and solar photochemistry,[604] and microreactor technology.[605]

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