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Photocatalysis for the Formation of the C–C Bond

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1. Introduction

Carbon−carbon bond formation is the core of organic synthesis and has been greatly changed in the last decades by the development of transition metal-catalyzed processes.[1,2] Traditional methods often have a poor atom economy and are carried out under rather harsh (e.g., strongly basic) conditions, but the newly developed ones, although having greatly widened the scope of organic synthesis, not always involve a progress with regard to environmental problems. Obviously, using a catalyst rather than a stoichiometric reagent is preferable, but the catalysts used often are labile compounds and require that carefully controlled conditions are used (e.g., with regard to the exclusion of air, moisture, impurities), as well as in many cases cocatalysts or additives.[3−9] Therefore, when all of the reagents are taken into account, not all of the catalytic methods are fully satisfactory in terms of atom economy, and further, the amount of energy required may be relevant.

On the other hand, the increased attention to environmental problems requires that new methods are evaluated also under this respect. In this paper, we intend to review the potential that *photo*catalysis has for the development of 'green' methods for the formation of the C−C bond.

A green method, according to the well-known principles, must reduce or eliminate the use or generation of hazardous substances. In this sense, photochemical reactions are intrinsically advantageous, because activation is obtained by the absorption of a photon, which leaves no residue, whereas most catalytic methods involve the use of toxic/polluting reagents. Such is often the catalyst itself, or some required additive, the residues of which must be eliminated from the end products. Photochemical reactions occur under unparalleled mild conditions and, in many cases, involve deep-seated chemical transformations occurring in high yields and with high selectivity. This allows the researcher to design a shorter synthetic sequence with respect to alternative multistep methods, again in accord with the key postulates of green chemistry.[10−12] Obviously, this does not mean that *any* photochemical reaction can be considered 'green', but certainly suggests that it is reasonable to consider, and assess, photochemical methods in synthesis.

The ideal green method requires that a simple feedstock is transformed in few steps into a highly functionalized compound, and yet, that the use of aggressive reagents and conditions is avoided. A typical issue to be confronted in this frame is activating a C−H bond in an alkane, in particular for the formation of a new carbon−carbon bond.[13−15] Methods that have been used in that instance are cationic addition under strongly acidic conditions, carbene insertion, the use of zeolites, the formation of metal complexes, and the formation of radicals. All of these have a limited scope and occur only under severe conditions, which result in a poor selectivity. Obviously, this is the core business in primary chemistry and has been confronted with large investments for a small number of large-scale processes,

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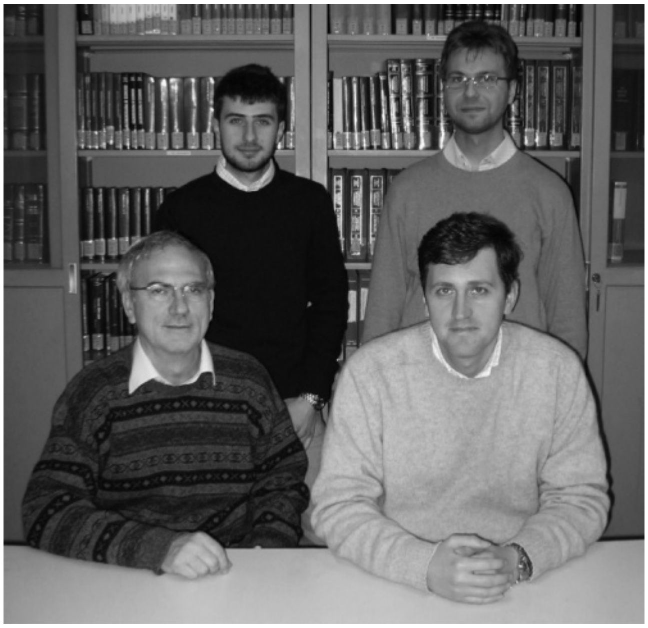


Maurizio Fagnoni (bottom right), born in Piacenza (Italy) in 1968, graduated in Pavia in 1992 with a thesis on the formation of carbon–carbon bonds via photo-SET reactions. He received his Ph.D. degree from the University of Pavia in 1995 (Prof. Albini as the supervisor) and spent part of this period at the University of Muenster (Germany) under the supervision of Prof. Mattay. He spent 2 years at Istituto Ronzoni (Milan, Italy) as research assistant. Since 1998, he is a Research Associate at the University of Pavia, and his current research interests focus on the application of photochemistry in organic synthesis using photoinduced radical alkylations and the chemistry of photogenerated aryl cations.

Daniele Dondi (top right) studied chemistry at the University of Pavia and obtained his B.Sc. in 2000 and Ph.D. in 2003 with a work on synthetic organic photochemistry under the supervision of Angelo Albini and Maurizio Fagnoni. After this period, he spent a year studying the photostability of sunscreens. Currently, he is working on the decatungstate photocatalyzed C–C bond formation in a project sponsored by the INCA consortium.

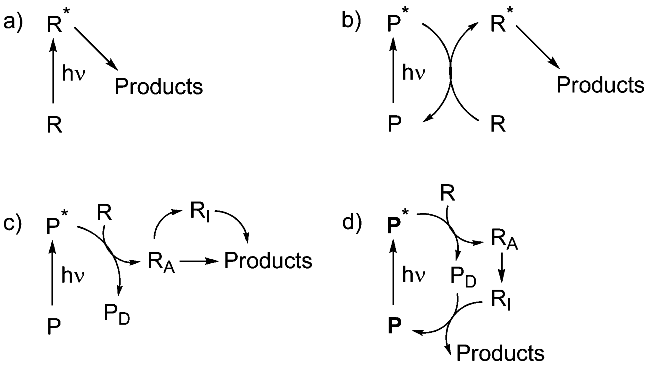
Davide Ravelli (top left), born in 1984, is finishing his undergraduate studies in Pavia, majoring in organic chemistry.

Angelo Albini (bottom left), is currently Professor of Organic Chemistry in Pavia (Italy), where he completed his studies in 1972, followed by postdoctoring at the Max-Plank Institute for Radiation Chemistry in Muelheim, Germany. He has been Visiting Professor at the Universities of Western Ontario, Canada, and Odense (Denmark) and Professor at the University of Torino. He is active in the field of organic photochemistry, organic synthesis via radical and photoinitiated reactions, and applied photochemistry (in particular photoinduced degradation and phototoxicity of drugs and cosmetic products).

for example, for oil reforming, but a similar strategy has been only sparsely used in fine chemistry. Still, activating a simple starting material may be as important as the much more often confronted problem of selectively activating a single group in polyfunctionalized reagents. Indeed, this has remained a ‘Holy Grail’ of chemical research. The very fact that a large amount of energy is involved in the desired processes makes it difficult to avoid harsh conditions and to activate specifically the target molecule (and make it react in the desired way), leaving the other components of the initial mixture (e.g., the solvent) ‘cold’, as well as to remove the activating species (e.g., a strong acid) at the end of the process.

For this case and also more generally, a photochemical method is highly desirable. Irradiation in the UV or visible region is a convenient way for generating electronically excited states and exploiting their high energy and different electronic structure for useful chemical reactions (as shown for compound R in Scheme 1a). As it has been recently stated, “the use of light...as an agent of chemical change can allow very mild reaction conditions”, and, at least as far as solar light is concerned, “is certainly a sustainable raw material”.[16] Indeed, photochemistry has amply demonstrated to be able to effectively contribute to synthesis, as illustrated in several reviews and books.[17,18]

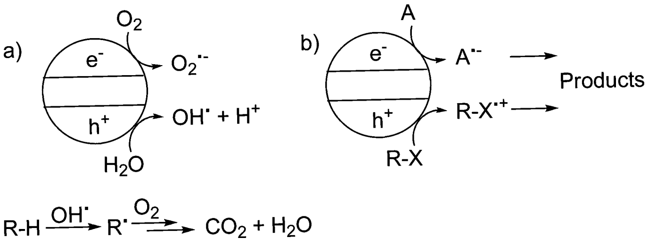
Scheme 1



A concern if the starting material considered is a simple aliphatic derivative is that such compounds do not absorb in the near UV. Their excitation requires the use of high-energy radiation (e.g., $\lambda_{irr} < 220$ nm), for which cheap lamps are presently not available. Furthermore, because of their high energy, the corresponding excited states often undergo various fragmentation processes, scarcely useful in synthesis. However, activation by light does not necessarily implyies that the reagent is directly irradiated. A variation that is often used in photochemistry, for example, when a reaction from the triplet is desired and the reagent considered intersystem crosses inefficiently, is the use of a sensitizer **P** that absorbs light and transfers energy to the reagent (R), so that the (triplet) excited-state of the latter is reached indirectly (*photosensitization*, Scheme 1b).

Apart from energy transfer, there are other ways through which the light-absorbing molecule **P**, which might then generically be indicated as a *photomediator*, activates the reagent R. In particular, some *chemical* reaction may transform inactive R into a highly reactive intermediate R_A that will give the final products, possibly via further intermediates (e.g., R_I, see Scheme 1c; this mode of action has also been included among photosensitizations, but is distinguished because activation is based on a *chemical* reaction, as opposed to energy transfer, a physical phenomenon).[19] Differently from direct irradiation or energy transfer, here the excited-state surface of reagent R is never attained, and, as far as this is concerned, the reaction path involves the *lowest potential energy surface* at any configuration, as it occurs in thermal reactions and contrary to photochemical reactions, where part of the path occurs on an excited surface. However, at least one photon is consumed per every molecule converted in all of the three cases (Scheme 1a−c). In the favorable case, the further condition applies that (one of) the intermediate(s) thus formed (R_I) interact(s) with the deactivated photomediator P_D giving the final product(s) and regenerate(s) **P** in the initial state. Then, **P** is not consumed in the overall process, exactly as it happens with a thermal catalyst (Scheme 1d). It seems, therefore, appropriate to label such a process as *photocatalytic*.[20−25]

Scheme 2



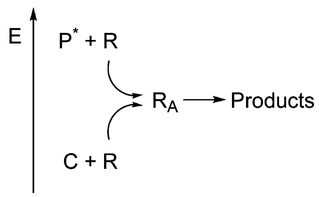
As mentioned, **P** is used in an amount lower than stoichiometric, but light is a stoichiometric reagent.

There are several reasons for reviewing the application of such method to a key synthetic issue such as carbon−carbon bond formation. First, this is indeed a useful way to take advantage of the high energy of the photon and, as it will appear in the following, there are a number of examples showing its potential interest. Second, the reactive intermediates involved (radicals, ions, radical ions) are the same that are generated in thermal reactions (though generally from different precursors) or can be likened with them (as it may be the case for the photocatalytic generation of an ion, which is similar to imparting an ionic character to a group in an organic molecule by forming a metal complex). This has a twofold advantage. From the mechanistic point of view, obtaining the same intermediates under conditions that are much milder than in thermal reactions and more easily amenable to the characterization of the path followed may help in the rationalization also of alternative thermal processes. On the other hand, because the course of the reaction is (at least partially) the same, this allows us to exploit the available knowledge on thermal reactions (much larger than that on photochemical reactions) for making the best synthetic use of the photocatalytic method.

The terms photocatalyst, photomediator, or generically photoinitiator have been previously used and differently defined. As an example, Chanon has offered a lucid discussion of such terms, also with reference to whether part of the light energy is incorporated in the formation of the products from the reagents.[23] We hope to have indicated the usefulness of the present definition of photocatalysis in the introduction above. A major trouble, however, is that the term ‘photocatalysis’, has become popular over the last 30 years as synonymous of the irradiation in the presence of a slurry of semiconductor oxide or sulfide powder or of other inorganic compounds. This definition is generally accepted and refers to processes aimed toward two targets different from synthesis (Scheme 2a). These are the degradation of organic pollutants for recovering contaminated water[24−26] and water splitting for the generation of hydrogen as a fuel.[27,28]

As for the first issue, under these conditions, hydroxyl radicals are typically produced from water and, in most cases, are the active species carrying out the degradation (and hopefully the mineralization) of the organic contaminants. As for the latter one, hydrogen is evolved from water, often as a result of the concomitant oxidation of an organic molecule (a sacrificial donor) and in the presence of a further catalyst. However, even if the term ‘photocatalysis’ is most often use in reference to these applications, the idea that the controlled application of the same or similar methods can lead to ‘green’ synthetic procedures has gradually emerged, and the concept of photocatalysis in this sense has already been presented and reviewed (Scheme 2b).[29−35] Indeed, experience in the application of photocatalysts for the above purposes may be useful for new applications in synthesis. The fortune of the term photocatalysis with reference to the use of semiconductor oxides and sulfides for nonsynthetic methods cannot be disputed, but we see no reason for avoiding its use also in the different context of chemical synthesis, since this underscores the fundamental parallelism with the action of a thermal catalyst (**C**, which also makes it possible to reach an activated intermediate). The difference is that in the former case activation of the catalyst (**P** → **P***) requires that each time a photon is absorbed (as a compensation, the high energy of **P*** may make it able to activate even reagents that are reluctant to thermal catalysis, see Scheme 3). In the following review, it will be evidenced whether yield and selectivity obtained make photochemical alternatives worthy of consideration.

Scheme 3



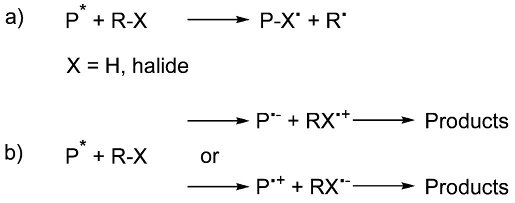
The present classification excludes the photogeneration of a thermally active catalyst. In a typical example, irradiation of a metal complex leads to a coordinatively unsaturated species that has catalytic activity (as may have, for that matter, the ligand set free).[36] This is a convenient and often used method for the preparation of catalysts[37] (also adsorbed on a solid[38−40]), for example, for alkenes and alkynes di- or trimerization, rearrangement,[41] metathesis[42,43] or CO insertion.[44−46] Since the catalyst is active thermally, the process proceeds further in the dark after the initial irradiation, whereas the reactions defined here as photocatalytic require that the irradiation is maintained. This type of process, thus, does not meet the definition proposed above and is not considered here. Notice, however, that this may offer an important access to *photo*catalysts. As an example, a photoactive form of zinc sulfide is obtained from the photolysis of zinc dithiolene.[47] Also not included is the catalysis of the photochemical reaction, viz., favoring or otherwise affecting (e.g., as far as the stereochemistry is concerned) a reaction that occurs via an excited-state of the reagent. The effect may be exerted either by complexing (and thus pre-arranging) the starting ground state, or by interacting with an intermediate or (rarely) an excited state.[48−51]

2. The Photocatalyst

2.1. Modes of Action

Activation by a photocatalyst (**P**) results through one of the following three mechanisms. In the first one, an atom, or a group, is transferred from the reagent R-X to the excited photocatalyst generating a radical $R^\bullet$. This intermediate undergoes some reaction (e.g., coupling, addition), which leads to the desired product (Scheme 4a). In the process, the photocatalyst is regenerated, typically by back atom transfer to a reaction intermediate. The obvious example is hydrogen transfer. The excited state of several classes of organic molecules and inorganic species behaves as an electrophilic radical and abstracts hydrogen from a variety of substrates.[52] Another example is halide transfer, operating in a number of cases with a metal complex as the photocatalyst, and likewise yielding a carbon-centered radical.[53]

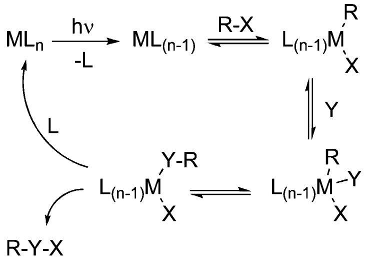
Scheme 4



In the second mode, an electron is transferred, forming the radical cation or anion of the substrate (electron transfer, ET). It is a general property of excited states to be both more easily oxidized and more easily reduced than ground states. Thus, redox processes, a rare occurrence when only ground state organic molecules are involved, are often operating in photoinduced reactions and are a typical mechanism in photocatalysis (Scheme 4b).[54,55] The ensuing reactions of the radical ions, for example, (cyclo)addition reactions, or of further intermediates resulting from them (see below) may give useful reactions, obviously including at some stage of the process a back electron transfer (BET) step regenerating the photocatalyst. In some cases, 'sacrificial' donors or, respectively, acceptors, have been used for regenerating the starting photocatalyst.

Finally, in the third mode, the reaction occurs on a metal center.[56] As an example, a reagent adds onto a metal center that has been activated by a photochemical reaction, and under these conditions, a C−C bond is formed. Then, liberation of the final product regenerates the starting metal catalyst so that the absorption of a further photon is required for initiating a second cycle (this distinguishes photocatalysis from photogeneration of a thermal catalyst, see above and Scheme 5).

Scheme 5



In the following sections, the characteristics of common photocatalysts are briefly reviewed, and the main mechanisms are discussed according to the key intermediate (section 3). Then, a series of significant examples are presented according to the type of process occurring and to the reagent used (section 4). Finally, some comments about the synthetic significance of the method and future developments are offered.

2.2. Classes of Photocatalysts

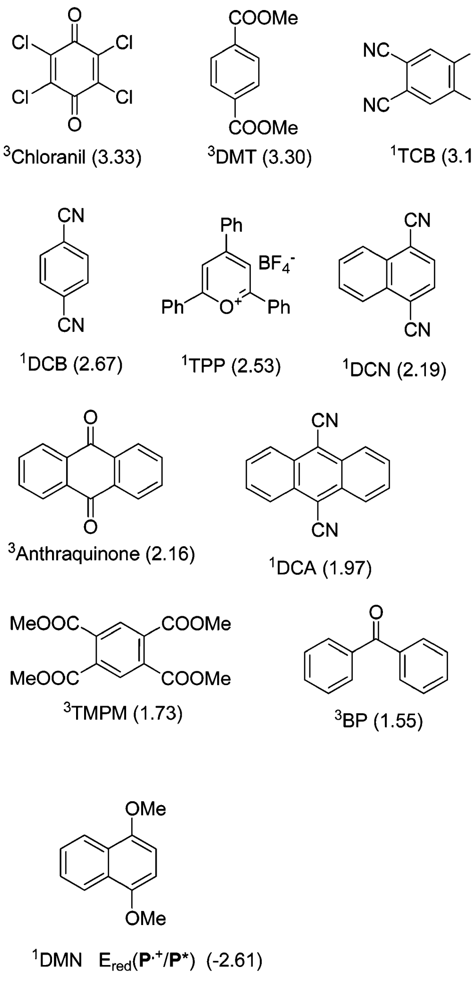
A photocatalyst **P** obviously must undergo neither a thermal reaction nor a monomolecular photochemical reaction. Most importantly, the 'deactivated' state P_D (Scheme 1) form, resulting from the initial photochemical step, must be a persistent species that is sufficiently stable to avoid interfering with the (on the contrary highly reactive) activated substrate R_A and with the other intermediates involved in the process, yet capable of being reconverted into the original form at some stage, so that absorption of a new photon initiates a new cycle. Classes of chemical compounds that have been shown to operate efficiently in this role, with little or no photodecomposition, and to be able to function for many catalytic cycles include the following:

- For the electron-transfer mechanism, aromatic compounds, in particular those bearing strongly electron-withdrawing (to a lesser degree, donating) substituents; quinones; electron-poor heterocycles. Semiconductor oxides and sulfides such as TiO_2, ZnS, and CdS may act via ET, being both strong oxidant and strong reducing agents;[29,57] the redox potential is pH-dependent in water and again different in organic media (Scheme 2b). ET to organic molecules can occur both ways, to the valence band or from the conduction band, and generates both (single electron) oxidized and reduced intermediates, respectively.

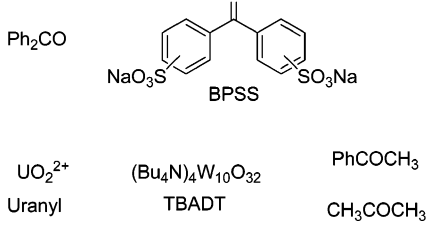
Commonly used photocatalysts are reported in Chart 1. The reduction potential (*vs* SCE) in the relevant excited state,

Chart 1. Examples of Photocatalysts

A. Via Electron Transfer (in parentheses, $E_{red}(\mathbf{P^*/P^{\bullet -}})$ V vs. SCE)[5



B. Via H abstraction



$[E_{red}(\mathbf{P}^*/\mathbf{P}^{\bullet-}) = E_{red}(\mathbf{P}/\mathbf{P}^{\bullet-}) + E_{exc}]$, is reported for those acting via ET activation. The strong oxidizing properties of such derivatives can be appreciated by taking into account that the oxidation potential of amines is around 1.3 V, of stannanes 1.4 V, of alkenes 1.8 V, of benzenes 2.2 V, of silanes and ethers 2.7 V, of alkanes 3.2 V (vs saturated calomelane electrode, SCE). When the difference of the redox potentials is >0.1 V, ET occurs at diffusion controlled rate in a polar solvent. Thus, the range of substrates that can be activated by this method is really large, although BET (e.g., $\mathbf{P}^{\bullet-} + \text{R-X}^{\bullet+} \rightarrow \mathbf{P} + \text{R-X}$) may strongly cut down the efficiency of the catalysis. An example of strongly reducing photocatalyst with the relevant $E_{red}(\mathbf{P}^{\bullet+}/\mathbf{P}^*)$ is also shown.[58]

- For the atom transfer process, largely used hydrogen abstracting photocatalysts are ketones, ranging from acetone, conveniently used as solvent or component of the solvent mixture, to aromatic ketones, provided that they have a $n\pi^*$ triplet. Other ones are various oxygenated inorganic cations (e.g., uranyl) and anions (e.g., polyoxoanions such as decatungstates) and some metal complexes. Practically all of the molecular catalysts listed act via the triplet state and abstract hydrogen, for example, from isopropanol with a rate constant $\geq 1 \times 10^6$ M^{-1} s^{-1}.[60,61] Taking into account the lifetime of the photocatalysts excited states (often ca. 1 μs, but may be lower), this rate is large enough to make the process quite efficient, although reversibility might have a negative effect also in this case. Photoinduced halide abstraction occurs with some metal complexes, for example, by some Pt complexes, while in other cases, an oxidative addition to the metal center occurs (Scheme 5).[62] As mentioned above, semiconductor oxides in water act via $OH^\bullet$ generation and hydrogen abstraction (Scheme 2a).[63]

As it appears from the following sections, photocatalysis has been developed both under homogeneous and under heterogeneous conditions. In principle, changing to heterogeneous leads to the same differences that occur in a thermal-catalyzed process, with the additional key requisite that light must be effectively absorbed by the photoactive material. Apart from semiconductors, which are necessarily heterogeneous, a variety of photocatalysts known for their activity in solution has been 'immobilized' by various techniques. These range from simple adsorption on a material, for example, silica of various porosity or zeolites, to tethering the photocatalyst to a matrix by a covalent bond, to a 'ship-in-the-bottle' synthesis of the catalyst within a porous material, to the incorporation of the photoactive moiety in the chain of a polymer, or its insertion into the chain through a functionalization of a ready-made polymer (e.g., making a ketone-based polymeric photocatalyst by acylation of polystyrene).

3. Photocatalyzed Reactions

3.1. General Scheme

As it appears from the foregoing, activation by photocatalysis[64,65] results in the formation of a radical by atom transfer or a radical ion by electron transfer. These primarily formed active intermediates are not necessarily those involved in the desired carbon−carbon bond forming reaction, however, because some further reaction might take place before. Notice, however, that further reactions involving **P*** need not to be considered. In fact, the photocatalyst is active *only* when in the *excited state*, the steady-state concentration of which is minimal. This makes the interaction with the primary intermediates, themselves short-lived species present in a very low concentration, a negligible occurrence. This characteristic differentiates a photocatalyst from a thermal (ground state) catalyst that is at any rate present in a non-negligible concentration. Different in this respect are also mechanistically related methods. As an example, both ET photocatalysis and electrochemistry involve radical cations, but in the latter case, activation occurs under conditions of high local holes or electrons concentration at the anode or cathode, respectively, making overall two-electron oxidation or reduction processes likely, for example, eq 1.

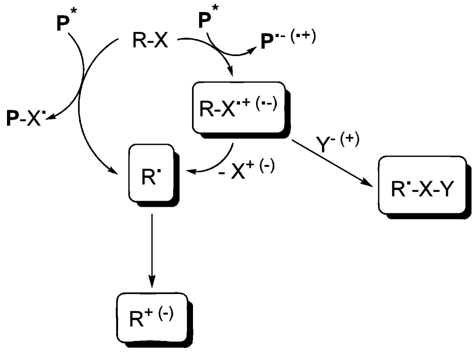
$$\text{R-X} \xrightarrow{-e^-} \text{R-X}^{\bullet+} \xrightarrow{-e^-} \text{R-X}^{++} \qquad (1)$$

Likewise, oxidants (e.g., Mn^{III}) or reductants (e.g., Sm^{II}) that are used in thermal ET induced radicalic reactions are present in a rather high concentration and further redox steps may occur.

Disregarding reactions with **P***, the possibility remains that the first intermediate undergoes either a monomolecular reaction or a reaction with some ground state compound present, so that C−C bond formation involves some later intermediate.

A typical example is the formation of a carbon-centered radical $R^\bullet$ from a radical ion that may occur via different mechanisms. One involves the cleavage of a σ bond,[58] possibly assisted, for example, by a nucleophile in the case of a radical cation $\text{R-X}^{\bullet+}$. Notice that a distonic radical ion is formed when the σ bond involved is part of a cycle, see section 4.4.2. Another one is addition of a nucleophile or an electrophile to radical cations or anions, respectively. On the other hand, if the radical is the first formed intermediate, this may be oxidized to form a carbocation or reduced to form a carbanion (Scheme 6).

Scheme 6

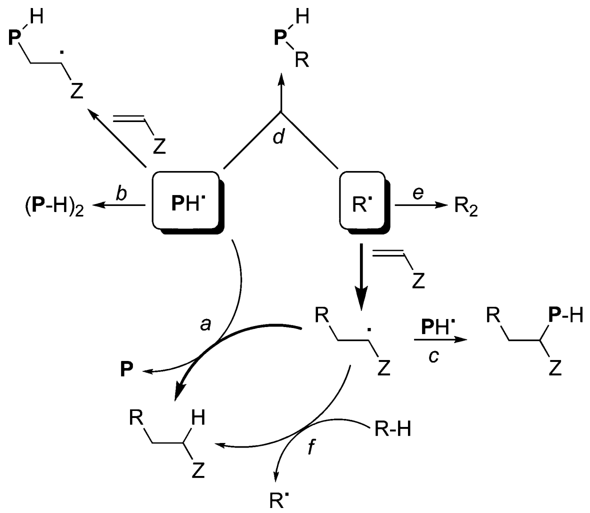


To summarize, the key C−C bond-forming step may involve a radical, a radical ion, or an ion, independently of whether the reacting species is the primarily formed or a subsequent intermediate. Indeed, the chemistry is that expected from such species, with the difference that these are formed under *mild* conditions from *unusual* (nonactivated) precursors.

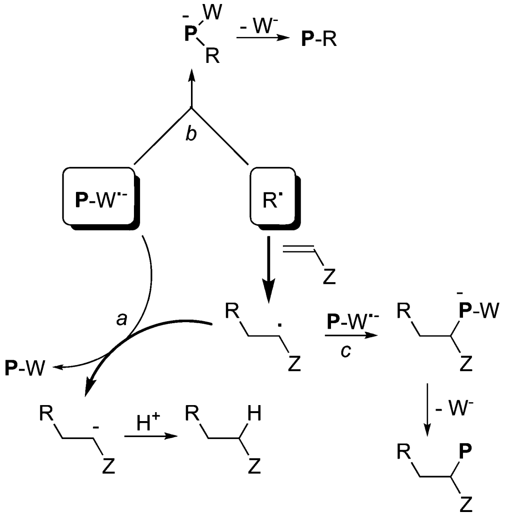
3.2. Radicals

Photocatalysis offers a convenient access to carbon-centered radicals from unconventional precursors. The ensuing chemistry is that expected for such intermediates, such as conjugate addition to electrophilic alkenes by nucleophilic alkyl radicals, both inter- and intramolecularly (in the latter

Scheme 7



Scheme 8



case also onto nonactivated alkenes and with the usual preference for the 5-*exo*-trig cyclization mode).

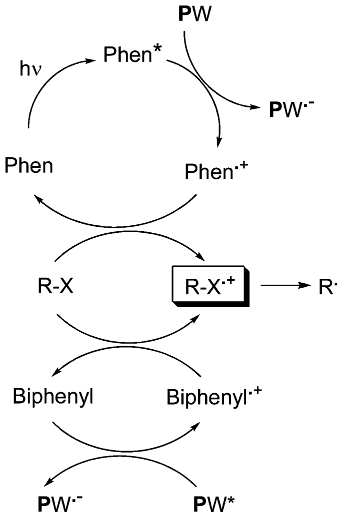
Schemes 7 and 8 demonstrate the course of photocatalyzed alkylation reactions via H-transfer and via ET followed by radical cation fragmentation, respectively. The catalytic cycle is closed when the adduct radical (that is made both more persistent and more easily reduced by the electron-withdrawing substituent Z in α position) undergoes back hydrogen or electron transfer, respectively, regenerating the catalyst (**P**, path *a*; the catalytic mechanism is indicated by bold arrows).

The efficient turnover of the catalyst may be hindered by competing paths. Aromatic ketones are often used in the H transfer mechanism.[66,67] Two radicals are formed (**P**H$^\bullet$ and R$^\bullet$), and when a nonactivated hydrogen has been abstracted, for example, from an alkane, there is no competition by the persistent **P**H$^\bullet$, and only R$^\bullet$ reacts (at least when an electrophilic alkene is used). On the other hand, the same factor makes the ketyl radical (**P**H$^\bullet$ = ArRC$^\bullet$OH) reluctant to back H transfer (path *a*), so that this tends to accumulate and to dimerize to the pinacol [(**P**-H)$_2$ path *b*]. In this case, 1 mol equiv of ketone has to be used, and this has to be considered a reagent rather than a catalyst. Again, because of their persistency, ketyl radicals may add to the adduct radicals (path *c*), thus, introducing side products, or couple with R$^\bullet$ (path *d*). A robust photocatalyst such as the decatungstate anion obviates most of these shortcomings (path *a* is efficient) and indeed functions with a much higher turnover number than ketones.

Alkylation of aromatics has also been reported. In the case that radicals R$^\bullet$ are themselves persistent, dimerization to R$_2$ (path *e*) is an issue, as in some cases is observed with benzyl or α-hydroxyalkyl radicals. Hydrogen abstraction by the stabilized radical adduct (path *f*) is normally unimportant, thus this is not a chain process. An exception is addition to a triple bond forming a vinyl radical.

In a parallel way, the occurrence of the oxidative ET mechanism according to Scheme 8 requires that the radical anion is not protonated.[58,64] In the case of ketones, which often operate through an ET mecanism because of their favorable E$_{red}$(**P***/**P**$^{\bullet-}$), the radical anions are easily protonated forming again ketyl radicals. On the contrary, aromatic nitriles are largely used because the radical anions are very poor nucleophiles, although they are somewhat liable to radical coupling with R$\cdot$, resulting in *ipso*-substitution (path *b*, Scheme 8). Coupling becomes even more competitive when it involves the persistent adduct radicals, thus, introducing a further type of products resulting from Radical Olefin Combination Aromatic Substitution, the ROCAS process (path *c*).[68] The use of secondary donors such as phenanthrene (Phen) or biphenyl together with **P**W (either the acceptor or the donor absorb the light) avoids the formation of **P**W$^{\bullet-}$ and R$^\bullet$ as a pair (Scheme 9). This decreases the likehood of the alkylation of the photocatalyst. A further choice is to use aromatic esters rather than nitriles, because these compounds are comparable oxidants but are not alkylated under these conditions.

Scheme 9



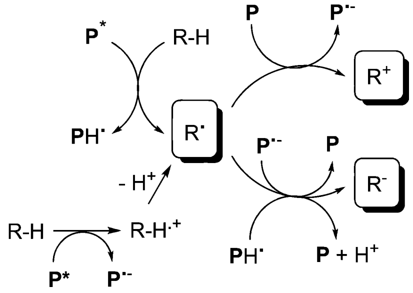
As mentioned above, radical anions of ketones are rather basic. So are the radical anions of other heteroatom containing functionalities, for example, the imine and azo group. This has been applied to obtain hetero coupling via radicals after ET, as exemplified by the semiconductor-photocatalyzed formation of a pair of radical ions (A$^{\bullet-}$ + R-H$^{\bullet+}$, Scheme 2b), followed by proton transfer to give a radical pair (AH$^\bullet$ + R$^\bullet$) and carbon−carbon bond formation to yield H-A-R.

Radicals are obtained also by addition of a nucleophile onto a radical cation (see Scheme 6). In this group of reactions, intramolecular variations are important, perhaps the most typical examples involving the cyclization of 1,6-dienes and polyenes, via radical cation → radical. This scheme has been extended to (biomimetic) cascade polycyclizations (see section 4.3.2.).

3.3. Cations

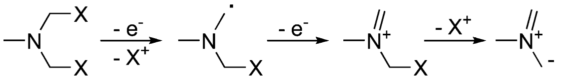
An ascertained photocatalyzed path to carbocations involves oxidation of a carbon-centered radical, in turn generated either via hydrogen abstraction or by ET and fragmentation. The oxidizing agent (see Scheme 10) is either the ground state catalyst[60] (as mentioned above, the tiny steady-state concentration of transients makes their interaction with the excited catalyst insignificant) or a purposely added oxidant.

Scheme 10



This strategy has been mostly applied to easily oxidized radicals, such as α-amino radicals, where a variety of synthesis via iminium ions generated from a (tertiary) amine via overall two electron-transfer process has been reported (see sections 4.1.4. and 4.2.). Notice that if a further electrofugal group is split from the cation, an ylide results (Scheme 11). Thus, photocatalyzed oxidation of an amine is a way for obtaining reactions via different intermediates, including, besides the radical, two even-electrons species, viz., the iminium cation and the ylide (see section 4.4.).

Scheme 11



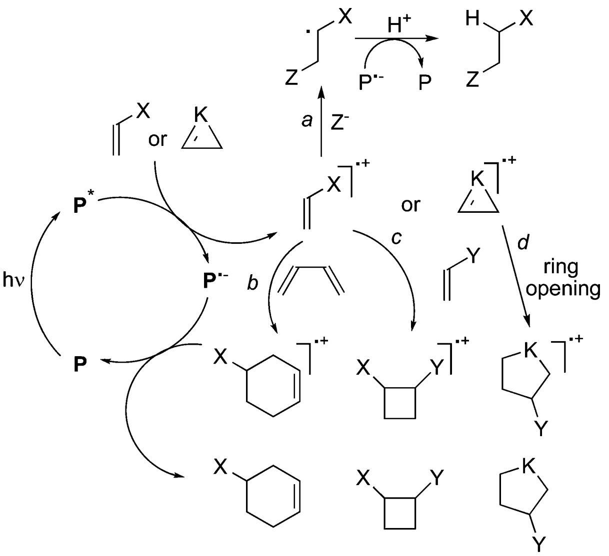
3.4. Anions

A few examples are available of an interesting way of arriving to a carbanion under neutral condition. This is based on the formation of a radical and its reduction by the reduced form of the photocatalyst (see Scheme 10), when this is a persistent species, as in the case of decatungstate or of TiO_2.[69] With acetonitrile as the solvent, trapping of R^- to yield an imine and a methylketone by hydrolysis is the typical result.

3.5. Radical Ions

Radical cations usually react as electrophiles and undergo addition reactions, in typical examples by cyanide (Scheme 12, path *a*) and by alkenes. With alkenes and dienes, a variety of addition and cycloaddition processes (paths *b*−*d*)[70,71] have been developed, as summarized in Scheme 12 (see further section 4.4.).

Scheme 12



Another important class is that of polymerization reactions, which, however, will not be specifically addressed here, since the focus is on molecular synthesis.[72−74] A few reactions that involve the radical anions are known and involve coupling with radicals (see section 4.2.).

4. Syntheses via Photocatalytic C−*C Bond Formation*

4.1. Intermolecular Addition onto Double or Triple C−C Bonds

4.1.1. Of an Alkyl or Phenyl Group

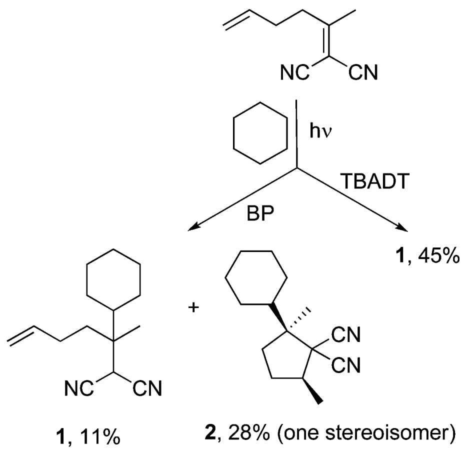
As indicated in section 3.2., photocatalysis allows the generation of alkyl radicals under mild conditions by various mechanisms, including hydrogen abstraction from alkanes, halide abstraction from alkyl halides, and cleavage of the σ R−X bond in various aliphatic derivatives, usually after photooxidative activation. The versatility of alkyl radicals as reactive intermediates, in particular for C−C bond formation via conjugate alkylation, makes this method appealing. The conceptually simplest, and economically most desirable process, is direct activation of a C−H bond in alkanes, in view of the abundance of this feedstock. Photocatalysis is indeed a viable method toward this goal and occurs under mild conditions, although at present not many examples have been reported and not all of these are satisfactory as far as the products' yield/selectivity and the catalyst turnover number are concerned. In addition to C−H activation in alkanes, alkyl radicals have also been obtained by splitting a different group in other precursors,[58] such as carboxylic acids,[75] stannanes,[58,75−79] dioxolanes,[68,75] silanes or silyl ethers,[58,80] and halides.[81,82]

In some cases, the mechanism of the alkylation of an olefin or another compound containing a multiple bond could also be (or was better) envisaged as a coupling between the alkyl radical and the olefin radical anion or between the alkyl radical and a radical derived from the olefin. The end result is the same, but different mechanisms have been invoked, as it will be mentioned when appropriate (see section 4.2.).

The conjugate alkylation using alkanes was initially explored using an aromatic ketone, most often benzophenone (BP), as **P**. Indeed, hydrogen abstraction occurred effectively under these conditions (in an indifferent medium, such as benzene, diethyl carbonate, or *t*-butanol), and the alkyl radical was selectively trapped by an electrophilic alkene. However, back-H transfer to the radical adduct was inefficient, and the persistent diphenylcarbinol radical in part dimerized to pinacol (see section 3.2.). In the event, the BP-catalyzed conjugate alkylation by cycloalkanes of α,β-unsaturated nitriles and ketones was developed and occurred with yields (30−80% at total alkene conversion) that were variable but, at any rate, of some interest in view of the directness of the process and the simplicity of the method.[66,83] For the reasons above, the catalyst was consumed and had to be used in a high amount (50−100% mol equiv with respect to the alkene to be alkylated, see Scheme 7, path *b*). As a consequence, the pinacol formed had to be separated from the desired adduct, which offset one of the merits of the reaction, the simple workup (the formation of byproducts was somewhat diminished by using xanthone rather than BP, however).

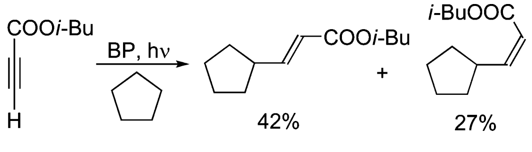
An example of tandem alkylation involving attack onto an unsaturated nitrile followed by cyclization of the first radical adduct onto a pendant alkene (**2** formed in competition with **1**, see Scheme 13) is shown.[83]

Scheme 13



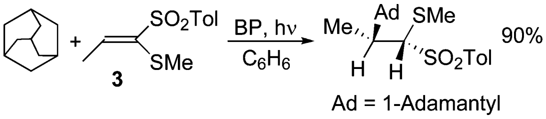
However, a lower than stoichiometric amount of BP (20% mol equiv) was sufficient in the addition to activated triple bonds (esters, nitriles, ketones) in neat cycloalkanes, reasonably because the radical adduct was in this case an energetic vinyl radical that abstracted a hydrogen atom from the alkane, originating a (short) chain reaction (Scheme 14).[84,85] Yields were again variable, but not uninteresting (mostly 30−50%). Among alkanes, the process was most efficient for cyclopentane, while C6 to C8 homologues gave lower yields. As for the alkyne, one electron-withdrawing group (EWG) was necessary for the alkylation to occur (the yields decreased in the series esters > acids > nitriles and ketones), but the presence of two groups could somewhat decrease the total yield. The *E/Z* ratio in the alkenes obtained depended on the occurrence of secondary photoisomerization and, thus, on the choice of the photocatalyst (in the last step functioning as an energy transfer photosensitizer). The reaction could be carried out also with a solid-phase **P**, such as acylated polystyrene or silica gel bearing aminopropyl groups to which carboxylated benzophenone had been covalently bound, thus, making the isolation of the end products easier. Under these conditions, sunlight[86] was effective for promoting the reaction. Although acylated polystyrene was rapidly inactivated, the silica-derived catalyst showed to be more robust and allowed an elevated conversion. The application of these conditions made the method appealing in the 'green chemistry' context.[86]

Scheme 14



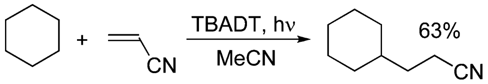
Furthermore, BP photocatalysis was successful in inducing alkylation in some cases where thermal radical alkylation failed (Scheme 15).[76] Thus, a captodative olefin such as the 1-methylthio-1-tosylalkene **3** was not alkylated under thermal radical initiation conditions because the stabilization of the adduct radical prevented the occurring of a chain process. However, the use of light allowed the process to occur, obviously by absorption of a stoichiometric amount of light, as shown by the good yield of the adamantane addition (a regio and stereoselective reaction).

Scheme 15



An excellent class of photocatalysts for the activation of alkane C−H bond is that of some polyoxoanions, in particular decatungstate and some of its derivatives. The photochemistry of such species has been studied in depth during the last 30 years,[87−89] but synthetic applications have been slower to appear. Tetrabutylammonium decatungstate (TBADT) is soluble in MeCN and has been often used for organic reactions. The initial hydrogen abstraction by the polyoxo anion is fast but reversible; thus, the success of the reaction depends on the presence of a sufficiently high concentration of a good trap. Thus, it was not surprising to find that alkylation was limited to a few percent when using simple alkenes (for the alkylation of a C═X bond, see section 4.2.).[90] However, with electrophilic alkenes, trapping was effective, and the catalytic cycle was closed by back-H transfer to the radical adduct by the reduced catalyst. Thus, when using a catalytic amount of TBADT (2% mol equiv), α,β-unsaturated nitriles,[91] ketones, and esters were alkylated by cycloalkanes in good (60%) yields (Scheme 16).[91]

Scheme 16

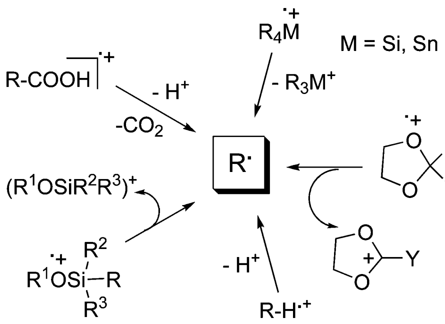


Alkylation of an unsaturated nitrile starting directly from alkanes was obtained also by TiO_2 photocatalysis in the case of adamantane, although the conversion of this hydrocarbon was not extensive.[92]

Photocatalysis on a metal center (Scheme 5) has not been used often for alkylation reactions. As an example, irradiation of $Rh(PMe_3)_2(CO)Cl$ allowed the formation of 1,1-disubstituted alkenes by addition of both aliphatic (selectively at the terminal C−H) and aromatic C−H bonds across the C≡C bond of terminal alkynes. As an example, 2-phenyl-1-octene was obtained from hexane and phenylacetylene.[93]

On the other hand, the ET photocatalyzed generation of alkyl radicals by loss of a good electrofugal group from the initially formed radical cation had a rather large scope (see Schemes 6 and 17).

Scheme 17

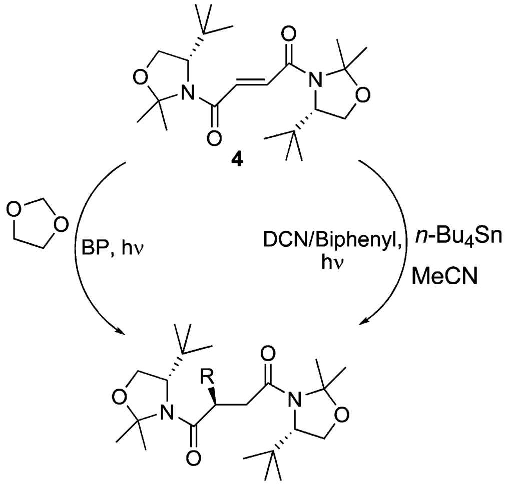


Thus, carboxylic acids such as pivalic and isobutyric acid were used for the alkylation of dimethyl acetylenedicarboxylate in low to moderate yields (22% and 45%, respectively) by using 1,2,4,5-tetracyanobenzene (TCB) as the photocatalyst. The reaction was suggested to involve deprotonation and CO_2 loss from the carboxylic acid radical cation.[75] The corresponding reaction between pivalic acid and dimethyl maleate gave the addition product in a 44% yield.[80] Alkylation of an electron-deficient heterocycle was established in the photolysis of Pt-coated commercial TiO_2 powder suspended in an aqueous solution of an alkylcarboxylic acid and 1-alkylpyridinium perchlorate. Thus, a concomitant reduction of the pyridinium ion to the corresponding radical and oxidation of the carboxylate anion followed by loss of carbon dioxide (to give an alkyl radical) took place. As a result, radical−radical coupling occurred and yielded (after reoxidation) a 4-alkyl-substituted 1-alkylpyridinium salt.[94]

Although less appropriate in the green chemistry context, it should be mentioned that tetraalkylstannanes showed to be effective precursors of alkyl radicals under these conditions, and the results are interesting for assessing the alternative pathways. With asymmetric derivatives, a selective fragmentation giving the most stable radical occurred. Thus, tetrabutylstannane and *t*-butyltrimethylstannane were used for adding a butyl or a *t*-butyl group onto dimethylmaleate (close to 80% isolated yield) or acrylonitrile (40−50%), respectively.[80] Various photocatalysts were used, and the choice was critical for the result. Benzenepolynitriles were effective due to their largely positive reduction potential in the singlet excited state (see Chart 1). However, with these compounds, an important side path, or even the main reaction, involved *ipso* substitution of a cyano by an alkyl group, either by the radical initially produced or by the radical adduct (paths *b* and *c* in Scheme 8). These reactions may have an interest of their own for preparing substituted aromatics but, in the present context, consumed the catalyst. When using TCB, this was not necessarily a stumbling block, since the monoalkylated trinitriles were themselves effective oxidizing agents, so that the photocatalytic process did not terminate. This limitation could be overcome using benzenepolycarboxylic esters, for example, tetramethyl pyromellitate (TMPM), which did not undergo such alkylations, or using cocatalysts such as Phen or biphenyl (see Scheme 9). These were oxidized in the first step so that the radical cation of the substrate was formed in a secondary process, not paired with the catalyst radical anion.[78]

A diastereoselective addition was observed with fumaric acid derivatives bearing chiral oxazolidine auxiliaries, despite the occurrence of *E/Z* alkene isomerization under these conditions. With the 4-*t*-butyl-2,2-dimethyloxazolidine derivative **4** and Bu_4Sn as the radical precursor, the product **5** was obtained in 79% yield and with a de > 98.5%. The selectivity was increased with respect to alternative thermal alkylations, demonstrating the advantage of the mild photochemical method (Scheme 18, right part).[77]

Scheme 18



5, R = *n*-Bu; 79%, > 98.5% d.e.

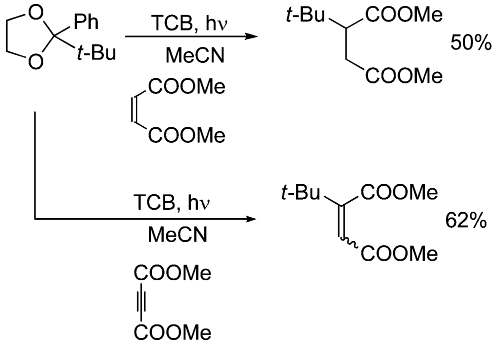
6, R = 2-dioxolanyl; 75%, > 98.5% d.e.

Electrophilic alkynes such as dimethylacetilenedicarboxylate also underwent alkylation with *t*-butyl- and *i*-propyltrimethylstannane (yields near 50%, TMPM as catalyst).[75] Cyclic enones (cyclopentenone and cyclohexenone) and methyl vinyl ketone were likewise alkylated under these conditions. In this case, however, singlet excited-state catalysts such as TCB performed poorly due to competitive light absorption by such substrates. When the catalyst was an ester such as TMPM, active from the triplet, this limitation was overcome, since the unsaturated ketones absorbed light and, after intersystem crossing, transferred energy to the aromatic ester, which was thus able to catalyze the alkylation (see eq 2).[79]

$$^{3}\text{Enone} + \mathbf{P} \rightarrow \text{Enone} + {}^{3}\mathbf{P} \qquad (2)$$

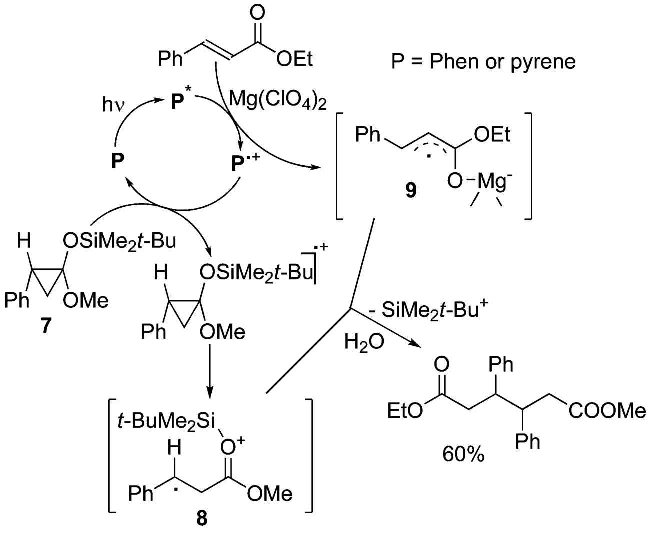
Another class of precursors of alkyl radicals is that of 2,2-dialkyl-1,3-dioxolanes or 2-alkyl-2-phenyl-1,3-dioxolanes (see Scheme 19). The last compounds were easily oxidized, fragmented selectively, and gave good yields of the alkylated alkenes, while minimizing *ipso* substitution of TCB, a process generally competing with the desired alkylation when dialkyldioxolanes were used with this catalyst.[68]

Scheme 19



Further precursors for the generation of alkyl radicals via C−C bond fragmentation are some cyclopropane derivatives. Thus, cyclopropanone silyl acetals[95] (**7** in Scheme 20) were used in this role. Monoelectronic oxidation caused C−C bond cleavage, and loss of the trimethylsilyl cation gave a trappable *β*-alkoxycarbonylethyl radical. Thus, Phen or pyrene (10% mol equiv) photocatalyzed the reaction between cyclopropanone acetals and conjugated esters or ketones. The process required the use of 1 mol equiv of $Mg(ClO_4)_2$, as depicted in Scheme 20.[96]

Scheme 20



The photocatalyst had here a double role, reducing the α,*β*-unsaturated ester and oxidizing the acetal to the open-chain radical cation form **8**. The role of $Mg(ClO_4)_2$ was explained in terms of its stabilization effect on the radical anion (**9**) resulting from the reduction of the ester, which slowed the BET process. The final step was the combination between the two radical ions (or radical−radical anion if the trimethylsilyl cation was lost first) forming an adipate derivative in 60% yield. This reaction was also carried out in an intramolecular way by tethering the cyclopropanone unit to a cyclohexenone ring and using pyrene or DCA as the photocatalyst.[97]

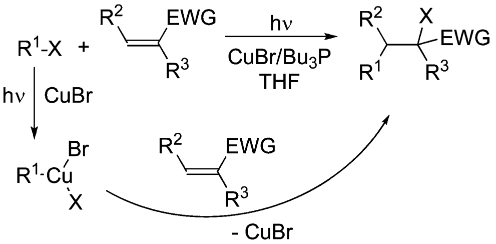
In the same line, irradiation of bicyclic silyloxy cyclopropanes under PET conditions caused endo ring opening of the three-membered ring and loss of the silyl group to give a *β*-carbonylalkyl radical that could be trapped by an electrophilic alkene, for example, by methyl acrylate.[98]

Although carbon-silicon fragmentation in radical cations is well-known, only a single example of olefin conjugate addition by a radical generated by this method was reported,[80a] and involved the addition of a *t*-butyl group onto dimethylmaleate by using n-$C_8H_{17}OSiMe_2t$-Bu as radical precursor and TCB as catalyst. Nucleophilic addition (e.g., ammonia or a primary amine) onto an alkene radical cation and deprotonation is another way to form an alkyl radical, which couples with the radical anion of an aromatic nitrile. This process was recently carried out under photocatalytic conditions.[80b]

As an alternative to the above oxidative activations, alkyl radicals were generated by halide abstraction or monoelectronic reduction of alkyl halides and halide loss.[53] Activation of a C−X bond and trapping by electron-deficient olefins could also involve metal-complexed intermediates (compare Scheme 5).

Copper(I) chloride and bromide in the presence of tributylphosphine were suitable photocatalysts. Mechanistic investigations supported that the organic halide oxidatively added to the Cu^I compound to generate a Cu^{III} intermediate.[81,82] Insertion of the olefin and reductive elimination yielded the alkylated product and regenerated the catalyst (see Scheme 21).

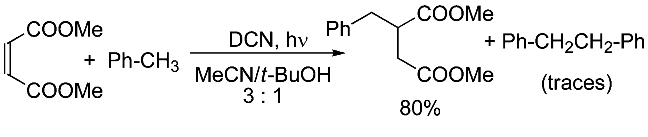
Scheme 21



Primary, secondary, and tertiary alkyl bromides gave good alkylation yields (ranging from 50 to 80%) of α-bromo-*β*-alkyl derivatives from electron-withdrawing-substituted olefins such as acrylonitrile, acrylates, acrolein, enones, and related compounds. This method was compatible with the presence of several functional groups in the alkyl chain. Alkyl chlorides were not reactive, except for dichlorometane and chloroform (see section 4.1.5.). Irradiation of a mixture of cob(II)irinate and $Ru^{II}(bipy)_3$ (or irradiation of a binuclear $Ru^{II}-Co^{II}$ complex) produced a Co^I species that likewise added oxidatively alkyl halides. The radical was intramolecularly trapped by an unsaturated ketone.[99]

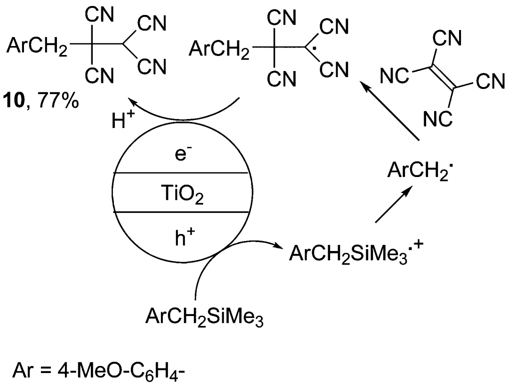
The stabilized allyl and benzyl radicals were easily obtained starting from suitable precursors by photoinduced electron transfer (PET) oxidation followed by loss of an electrofugal group. The toluene radical cation did deprotonate, but when an aromatic nitrile was used as the photocatalyst, in cage reaction between the two aromatic compounds predominated and no alkene benzylation occurred. The ions could be better stabilized using a nucleophilic solvent such as methanol. Under these conditions, both diffusion out of cage and deprotonation of the (free) radical cation were favored. As a result, dimethyl maleate was efficiently benzylated in MeCN/MeOH, although hydroxymethyl radicals formed from the solvent also added competitively.[100] On the contrary, a clean benzylation took place when using *t*-butanol in the place of MeOH (Scheme 22).[100]

Scheme 22



Better results were obtained by shifting (i) to faster-cleaving radical cations and (ii) to heterogeneous rather than homogeneous conditions to avoid pairing. With benzyltrimethylsilanes, the formation of benzyl radical was favored due to the easy elimination of a Me_3Si^+ group from the radical cation. Furthermore, a satisfactory benzylation of conjugated acids, esters, and carbonyls was obtained using TiO_2 as heterogeneous photocatalyst and benzyltrimethylsilanes or, to a lesser extent, phenylacetic acids as precursors of benzyl radicals.[101−103] Under these conditions, maleic and fumaric acids, as well as the corresponding anhydrides and nitriles, were monobenzylated in 40−80% yield. As an example, maleic acid gave 78% of 4-methoxybenzylsuccinic acid, and tetracyanoethylene gave 77% of the corresponding benzylethane **10** from the respective silanes upon titanium dioxide photocatalysis (Scheme 23).[101]

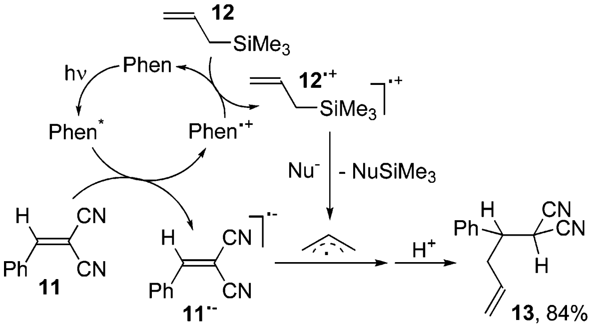
Scheme 23



The generation of benzyl radicals was more efficient when the catalyst was loaded with a small amount of Pt (which facilitates ET)[102] or when an inorganic oxidant (e.g., Ag_2SO_4)[103] was added. The quantum yield of the above benzylations increased, and an otherwise unreactive precursor such as toluene could be used. Under these conditions, a large proportion of the dibenzyl, rather than monobenzyl, derivatives were obtained, reasonably because of the formation of a larger local concentration of benzyl radicals. Obviously in this case, as is generally with heterogeneous catalysis, the adsorption/desorption rates of the reagents and the intermediates were determining the result. The TiO_2 benzylation showed to be well-suited for being effected by using solar light, obviously the best ‘green’ choice. Under these conditions, this photocatalytic reaction was tested on multigram scale and gave satisfactory results.[104]

As for allylation reactions, an example is the alkylation of 1,1-dicyanoalkenes by allylsilanes upon photocatalysis by Phen (ca. 20% mol equiv).[105] The proposed mechanism of this process involved radical−radical anion coupling after two electron-transfer steps, as illustrated in Scheme 24 for the reaction between 1,1-dicyano-2-phenylethene (**11**) and allyltrimethylsilane (**12**).

Scheme 24



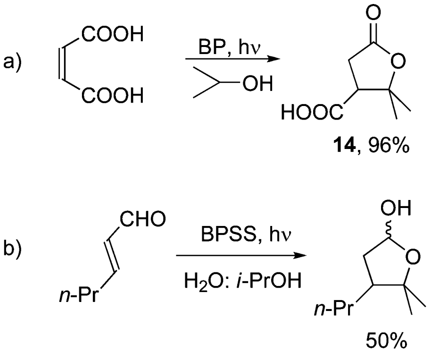
Thus, the reaction was initiated by a PET step between **11** and Phen* yielding the corresponding radical ions pair. Compound **13** was formed by the coupling between $\mathbf{11}^{\bullet -}$ and an allyl radical (formed by desilylation of $\mathbf{12}^{\bullet +}$) and was isolated in 84% yield. The reaction was completely regioselective since allylation occurred at position 2 exclusively.[105] When an alkyl- rather than a phenyl-substituted alkene was used, however, allylation occurred at the position α to the cyano groups. In this case, the success of the reaction required the presence of highly acidic additives.[106−108] The regioselectivity was explained in terms of spin population and anion charge in the radical anion intermediate.[106−108] In every case, Phen was regenerated simultaneously with the oxidation of **12**. Alkylation of 1,1-dicyanoalkenes was achieved by PET reaction with organostannanes such as Bu_4Sn, again through photocatalysis by Phen.[109]

As for phenyl radicals, these were obtained by reductive photocatalysis. Thus, irradiation of $[Pd(PPh_3)_4]$ in the presence of chlorobenzene (and of a sacrificial donor) gave a mixture of chlorobiphenyls (main product, *ortho*) via a two-photon process (the first one induced the oxidative addition on the metal center, the latter caused the detachment of a phenyl radical from the complex; the radical thus formed added to chlorobenzene).[110]

4.1.2. Of an α-Oxysubstituted Alkyl Group

Hydrogen abstraction from the α position of alcohols and ethers by a triplet ketone is an efficient process, and trapping of the resulting nucleophilic radical by an electrophilic alkene offers a convenient method for conjugate addition. The principle was introduced by Schenck, who reported in 1957 the synthesis of terebic acid **14** from maleic acid in isopropanol (96% yield, Scheme 25a).

Scheme 25

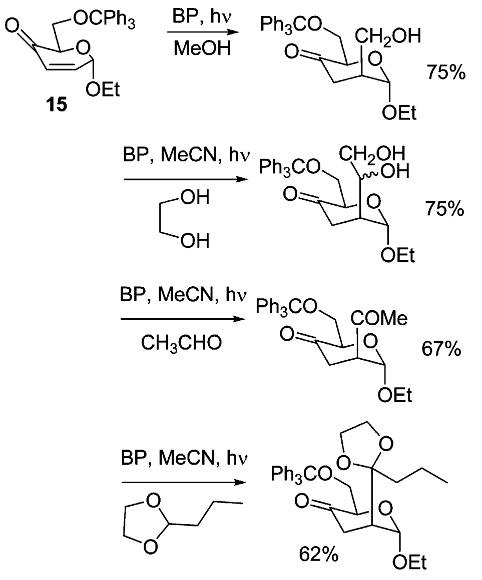


BP could be used as the photocatalyst in 20% molar proportion, but 0.3% mol equiv was sufficient when using anthraquinone.[111] Some diastereoselectivity was achieved in this reaction when using the menthyl ester of maleic acid.[112] However, a different process, viz., the photocatalyzed addition of isopropanol to (5*R*)-5-menthyloxy-2,5-dihydrofuran-2-one (de > 95%), followed by mild oxidation of the resulting 4-(hydroxyalkyl)dihydrofuranone, offered a more convenient access to (−)-terebic acid.[113]

The reaction occurred similarly with unsaturated aldehydes and ketones. As for the former reaction, this was satisfactorily carried out in a 1:1 water−alcohol mixture as the solvent by using a water-soluble **P** such as disodium benzophenondisulfonate (BPSS, in Scheme 25b)[114] and formed γ-lactols, which could be oxidized in situ to the corresponding lactones.

The ketone-photocatalyzed reaction has been employed for preparing highly functionalized branched-chain monosaccharides, which are biologically important compounds, from readily available carbohydrate enones. The products were formed in reasonably good yields (40−80%) and often with a marked stereoselectivity, which depended on the structure (in particular on the substituent in γ). As an example, some OH-protected derivatives of hex-2-enopyranosid-4-ulose (**15**) were alkylated under these conditions with strong selectivity

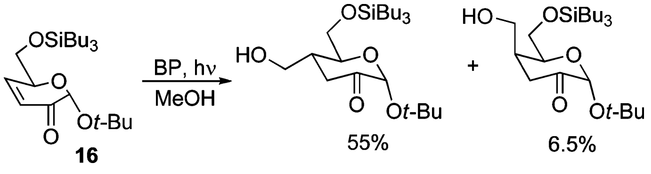
Scheme 26



for axial attack (Scheme 26).[115−119] The reason of such selectivity was investigated by comparison with the related enone lacking the γ axial substituent as well as with the carbocyclic enone likewise lacking that group. This showed that the selectivity was imparted by the steric hindrance by the alkoxy group in γ (position 1 of the sugar) rather than by some effect of the ring-oxygen.[118] These alkylations were carried out using BP (often 15% mol equiv) and the alcohol as the solvent for low molecular weight terms (methanol, ethanol, *i*-propanol). Higher homologues or polyfunctional molecules could be conveniently used in acetonitrile solution, as demonstrated for ethylene and propylene glycols as well as methyl glycollate.[115] Interestingly, the photocatalyzed radical alkylation mostly had a stereochemical course different from that of the copper(I)-mediated carbanion alkylation, and thus offered a useful alternative.[116]

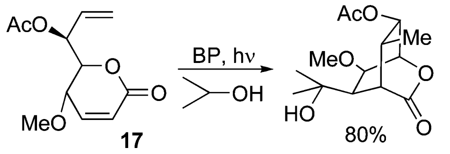
In another example, BP (12−18% mol equiv) photocatalysis caused the addition of alcohols, with predominant equatorial attack onto some hex-3-enopyranosid-2-uloses (**16**, Scheme 27). The thus formed β-hydroxyalkylpyrones were in turn useful synthetic intermediates (e.g., for preparing deoxyaminosugars).[120]

Scheme 27



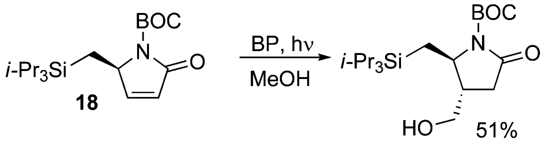
In yet another application, carbohydrate-derived hex-2-enono-δ-lactone **17** bearing a pendant alkene function underwent BP photocatalyzed addition of alcohol-derived radicals, followed by intramolecular attack onto the alkene moiety to give a bicyclic derivative (at least in the *gluco* series, a single isomer, Scheme 28).[121]

Scheme 28



The hydroxyalkylation of some 5-alkylbutenolides in methanol or *i*-propanol has also been carried out successfully giving the 3-alkyl derivatives with exclusive *trans* stereochemistry (by using 1 mol equiv BP, however). The hydroxymethyl derivatives formed in MeOH offered a convenient access to novel nucleosides, and the corresponding *i*-propanol adducts could be converted into derivatives of the *cis* chrysanthemic acid by further elaboration.[122,123] The alkylation occurred effectively also with related dihydropyrrolones **18** (Scheme 29).[124]

Scheme 29



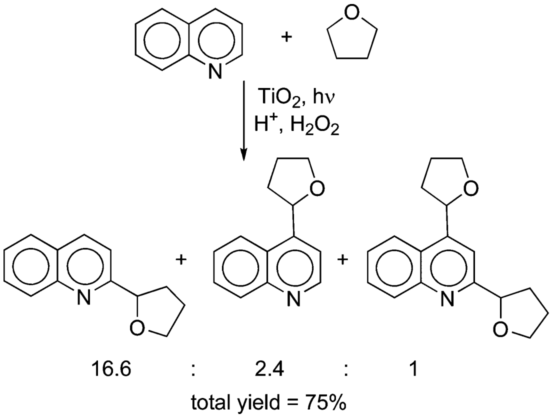
Because of the mild photocatalytic conditions, a good stereoselectivity could be obtained in several cases. Thus, some chiral 3-hydroxy-1-(methylthio)-1-(*p*-tosyl)-1-alkenes gave the corresponding 1-hydroxyalkyl derivatives by BP (1 mol equiv) photocatalysis in methanol and in *i*-propanol with high *syn* selectivity (typically, *syn*/*anti* = 95:5), indicative of a high asymmetric induction in this acyclic system.[125] Likewise, the BP (15% mol equiv) photocatalyzed alkylation has been applied to a pair of 1,3-dioxin-4-ones incorporating (−)-menthone as a chiral auxiliary in position 2. It was found that the radical from *i*-propanol was added from the more exposed a-side with complete selectivity, although in a low yield (again, attack by dialkylcuprate occurred from the opposite face).[126]

Although ketones were the most often used photocatalysts, some inorganic compounds abstracted efficiently hydrogen from alcohols and led to the alkylation of electrophilic alkenes. This was shown to be the case for uranyl chloride.[127,128] A convenient and robust photocatalyst for preparative purposes was again the decatungstate anion. Hydrogen abstraction from alcohols was faster than that from hydrocarbons and, differently from that case, was irreversible. In the absence of the electrophilic alkene, the hydroxyalkyl radicals were oxidized to the corresponding ketones by ground state TBADT, but with a sufficient amount of alkene (0.1 M), trapping was complete. Thus, TBADT (2% mol equiv) was successfully used for the hydroxy (or alkoxy) alkylation of unsaturated esters, nitriles, and ketones, which occurred with good yields (65−75%) and high turnover number.[60] Under these conditions, the reaction was almost insensitive to the presence of oxygen, and the products were isolated by very simple procedures, often a simple distillation. Thus, an appealing synthetic procedure resulted.

Photocatalysis by titanium dioxide has also been used, in particular, for the alkoxylalkylation of heterocycles. This mild functionalization was carried out also by solar irradiation and with quinoline led predominantly to attack to position 2, as shown in Scheme 30 for the irradiation in THF.[129]

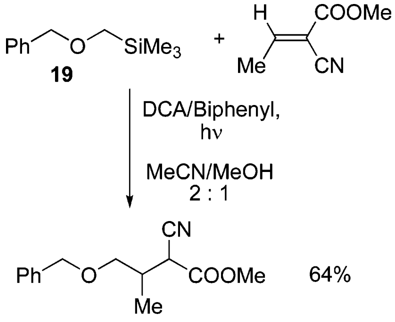
Cleavage of a C−H bond is not the only method of activation. Thus, a different strategy for the generation of hydroxy (and alkoxy) alkyl radicals involved the splitting of a trimethylsilyl cation from α-trimethylsilyl alcohols[130] and ethers[131] via the corresponding radical cations obtained by oxidative photocatalysis. As an example, methoxymethyltrimethylsilane was used successfully in the addition to methyl 2-cyanocrotonate by irradiation in the presence of

Scheme 30



9,10-dicyanoanthracene (DCA). The addition appeared to take place also with unprotected trimethylsilylmethanol, but the product could not be isolated. However, when using protected derivatives such as the benzyl ether **19** in Scheme 31 the reaction was successful. A similar functionalization was obtained when using unsaturated esters and imides as traps.

Scheme 31

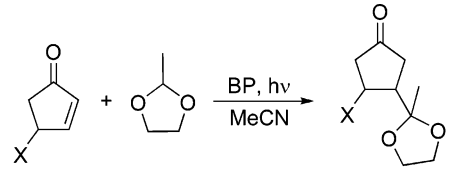


On the other hand, an α-oxyalkyl radical could be generated also by addition of an (oxyphilic) radical to the oxygen atom in a C═O double bond. An example of such a process in photocatalysis was reported in the photocatalyzed cleavage (by using a N^{21}, N^{22}-bridged porphyrin as catalyst) of methyl trimethylsilyl ketene acetals in MeCN. This produced trimethylsilyl radicals that added to aldehydes or ketones. Coupling of the resulting α-silyloxyalkyl radicals with those resulting from the acetal led to a photoinduced Mukayama reaction (aldehyde or ketone and a silylenol ether giving the silylated β-hydroxycarbonyl). The process showed an induction period before the formation of the products, but did not proceed in the dark and thus was considered a photocatalytic reaction.[132]

4.1.3. Of an α,α-Dioxysubstituted Alkyl Group

Acetals are easily activated by photocatalysis, both via hydrogen abstraction and via electron transfer. In the former case, the α,α-dioxyalkyl radicals formed added to electrophilic alkenes. This is a favorite method for the introduction of a masked formyl or acyl group. Thus, BP or anthraquinone photocatalysis was employed for the synthesis of monoprotected 1,4-dialdehydes,[114] 4-ketoaldehydes,[133] and 1,4-diketones[134] from unsaturated aldehydes or ketones and 1,3-dioxolane or 2-alkyl-1,3-dioxolanes. As an example, cyclopentenone was alkylated by various alkyldioxolanes to give monoprotected 1,4-diketones (**20**) in >70% yield (Scheme 32). Noteworthy, the reaction could *not* be carried out by using thermal initiators such as AIBN or dibenzoylperoxide, since a relatively high temperature was required, and under those conditions, rearrangement (ring opening) of the dioxolanyl radicals made trapping by the alkenes ineffective. 4-Hydroxycyclopentenone was likewise alkylated, and the resulting mixture (**21**, main isomer, *trans*) could be directly converted into protected 4-acylcyclopent-2-enones, useful synthetic intermediates (Scheme 32).[134]

Scheme 32

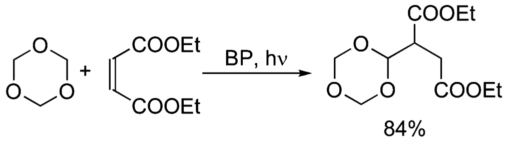


20, X = H (78%)
(±)-**21**, X = OH (75%, *trans/cis* 11/1)

The BP photocatalyzed addition of the dioxolanyl radical has been recently applied to some sugar-related C3-ketoxime ethers bearing a terminal δ-yne function. The reaction led to tandem addition onto the pendant alkyne followed by intramolecular attack onto an oxime function forming a new five- and/or six-membered carbocyclic ring.[135]

As with other nucleophilic radicals, an effective alkylation required that an electrophilic trap be used. As an example, the alkylation yield when using 1,3-dioxolane as the precursor was 90% with dimethyl maleate as the trap, but it did not overcome 50% with a nonactivated trap such as a terminal olefin. When using trioxane, the yields were 84% and 25% with the two traps, respectively (Scheme 33).[136,137]

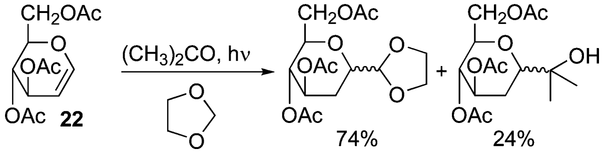
Scheme 33



As for selectivity, when using a chiral 4-*t*-butyl-2,2-dimethyloxazolidine fumaric acid derivative **4** as a trap, a diastereoselective addition of the 2-dioxolanyl radical (from dioxolane) was obtained (75% isolated yield of product **6**, de > 98.5%, Scheme 18 left part).[77] The reaction was also applied to sugar-derived enones, where it proceeded with comparable yields and stereoselectivity to those in the above case of α-oxy radicals (Scheme 26).[115,138]

Electron-poor alkynes (e.g., methyl propiolate) were likewise effective substrates for the BP (40% mol equiv) photocatalyzed addition of (2-alkyl-)1,3-dioxolanes.[139a] Indeed, by the use of acetone photocatalysis, alkylation was obtained also with nonelectrophilic sugar-derived alkenes such as enoses. Under these conditions, however, the acetone-derived radical competed in the addition, and stereoisomeric mixtures of the two different adducts were obtained, as shown in Scheme 34 for the case of the triacetylglucal **22**.[139b]

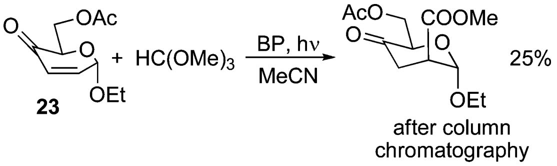
Scheme 34



Despite these limitations, the reaction was considered a useful way for the *C*-alkylation of sugars.

Again in this family of intermediates, the α,α,α-trimethoxymethyl radical was generated by BP photocatalysis from trimethyl orthoformate and was found to add to a hex-2-enopyranosid-4-ulose **23** (Scheme 35). The isolated product after chromatography was the corresponding methyl ester, apparently arising from the hydrolysis of the orthoester function during workup.[138]

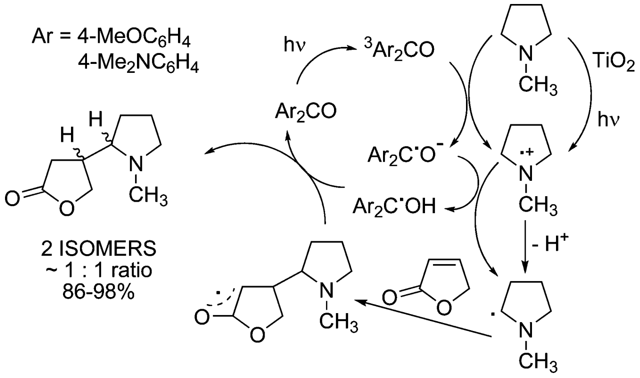
Scheme 35



4.1.4. Of an α-Aminosubstituted Alkyl Group

Nucleophilic α-amino radicals are attractive intermediates for the synthesis of nitrogen-containing derivatives, in particular of products of biological interest such as alkaloids.[140] These radicals are generated by deprotonation of the radical cations of amines, which are easily formed by PET due to the low oxidation potential of these compounds.[141] As an example, with amines, aromatic ketones were active as photocatalysts via an ET mechanism (compare Scheme 36), not hydrogen transfer as with alcohols. The first process occurred at a much faster rate than the latter one, but this did not necessarily mean that it was efficient. In fact, possible causes of inefficiency were both BET that competed with α-deprotonation from the radical cation and radical termination paths not leading to the closure of the catalytic cycle. Indeed, BP and acetophenone were initially tested as photocatalysts, but they had to be used in stoichiometric or larger amounts because of the considerable degradation during the reaction.[142,143] Moreover, the yields of the addition products from alkenes were quite low ($<$40%). Recently, Hoffmann and co-workers discovered that electron-donating substituents on the aromatic ring of phenyl ketones largely suppressed undesirable coupling reactions of ketyl radicals and allowed an important increase in the adducts yield.[144] Accordingly, the photocatalyzed radical addition of tertiary amines (e.g., *N*-alkylpyrrolidines) to electrophilic alkenes by using 4,4′-dimethoxybenzophenone or Michler's ketone (MK, both 10% mol equiv) was successful, as shown in Scheme 36.

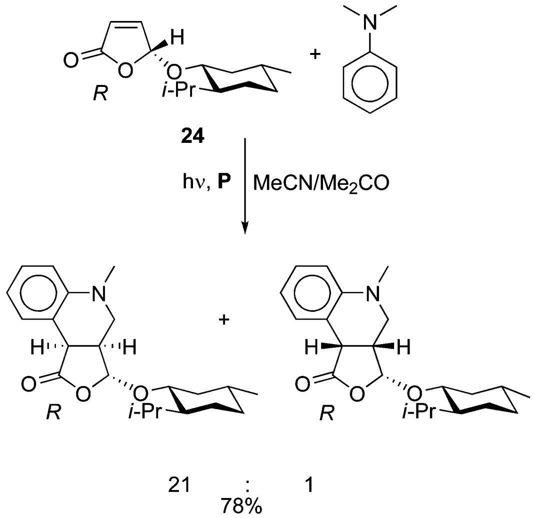
Scheme 36



The reaction also applied to *N*-protected (e.g., by a *t*-butyldimethylsilyl group) pyrrolidines that gave high yields of alkylated products.[144]

When a chiral enone such as (5*R*)-5-menthyloxy-2,5-dihydrofuran-2-one **24** was used, a complete facial stereoselectivity was observed in the radical addition step.[144−146] Accordingly, the MK catalyzed reaction was exploited as a key step for the enantioselective synthesis of some necine bases, namely, (+)-laburnine and (−)-isoretronecanol.[145,146] Among tertiary amines, *N*,*N*-dialkylanilines were conveniently used in the synthesis of 1,2,3,4-tetrahydroquinoline derivatives. The ring-building strategy was based on the stereoselective radical-tandem reaction of aniline derivatives with **24**, where the initial radical attack onto the enone was followed by intramolecular attack of the adduct radical onto the aromatic ring.[147−149] Under these conditions, a side product was the dihydro derivative of furanone, which was completely suppressed, however, when carrying out the reaction in the presence of acetone (ca. 6% vol). The reaction showed a high degree of stereoselectivity, as shown in Scheme 37. Recently, the (5*S*) isomer of furanone **24** was synthesized and proven to give the adducts with the opposite stereoselectivity.[150]

Scheme 37



α-Amino radicals could be photochemically generated also under heterogeneous rather than homogeneous conditions by using TiO_2 (2% mol equiv) or ZnS as the photocatalyst (Scheme 36).[151−153] In this case, a large excess of amine (preferably used as the solvent) was required to obtain a high product yield. This was explained by the occurring of the electron-transfer process only at the semiconductor surface. Thus, only molecules adsorbed at the surface were involved, and since the mobility of radical cations was limited, their deprotonation had to compete with the favored BET process and was improved only when using a large amount of amine acting as a base.[151−153] Since the excess amine could be recovered by distillation and reused and the inexpensive photocatalyst could be easily removed by filtration, the process was still considered environmentally friendly.[152] Noteworthy, when *N*-methylpiperidine was used in the place of the analogue pyrrolidine, deprotonation from the methyl group, followed by oxidation and loss of the substituent to yield piperidine, became competitive with deprotonation from a ring methylene.[151]

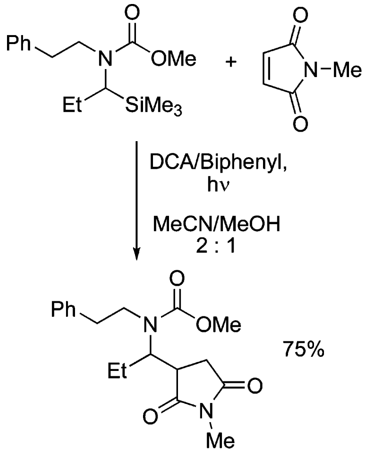
The above method could not be extended to acyclic amines, which gave no alkylation under these conditions.

Nevertheless, the addition of some thiocarbonyl or xanthate derivatives (e.g., *S*-methyl-*N*,*N*-diethyldithiocarbamate, 5 mol equiv) allowed the reaction to occur and affected both the regio- and the stereoselectivity of the process.[154] This behavior was explained by the reversible radical trapping of the amino radical by the thiocarbonyl species, which stabilized these radicals and allowed their addition to alkenes.

Anthraquinone (or its 2-sodium sulfonate derivative) was likewise used as the photocatalyst in the reaction of tertiary, secondary, and primary amines with electron-poor olefins.[155−158] When triethylamine was used, the addition of α-amino radicals onto methacrylates was followed by a 1,5-hydrogen abstraction reaction allowing a further radical addition step. Thus, multiple-olefin addition products were isolated at the end of the reaction.[155] Furthermore, when the amine used had a free N−H bond, a lactam was obtained by intramolecular reaction of the first formed *δ*-amino esters.[156,157] In the last case, however, the strongly competitive (thermal) aza-Michael addition of the starting amine onto the α,*β*-unsaturated esters used was a serious drawback. This could be mitigated, however, by carrying out the irradiation at a lower temperature and, thus, slowing the thermal path. On the contrary, lactams could be easily obtained using *N*-allylamines as the substrates.[158]

An alternative to increase the efficiency of the PET-produced radical cation cleavage was to insert a better electrofugal group. This principle was applied using a α-silyl carbamate.[159,160] The DCA/biphenyl couple was the most efficient photocatalyst for this reaction, although pyrilium salts could be used with some success. As expected, the radicals formed added efficiently to electron-poor alkenes, whereas electron-rich olefins (e.g., cyclohexene) were unreactive (Scheme 38).[159]

Scheme 38

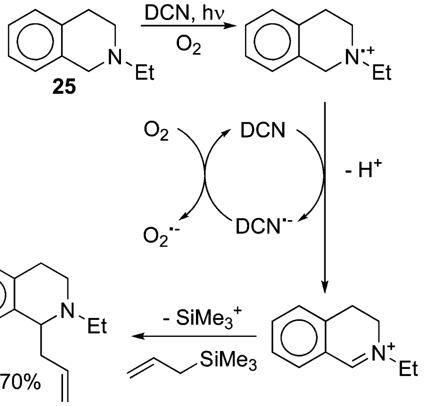


The intramolecular version of this alkylation was applied in peptide chemistry when *N*-trimethylsilylmethyl amino acid derivatives were employed in the place of carbamates.[160] Accordingly, cyclization took place forming a proline ring, and this caused a structural change in the α-helix secondary structure with respect to the starting peptide.[160]

N,*N*-Dimethylformamide (or acetamide) functioned as an α-*N*-disubstituted radical source under heterogeneous photocatalytic (TiO_2, solar light used) conditions for the functionalization of heteroaromatics (e.g., quinoline) in the presence of H_2O_2 and H_2SO_4 (for rearomatizing the adducts).[161] Small amounts of acylated heterocycles were also obtained (see next section).

A further group of reactions resulted from the fact that α-aminoradicals had a low oxidation potential, and further oxidation of such intermediates, in general by the ground state photocatalyst, occurred efficiently (see Scheme 11). In such a case, reactions via iminium cations, formed via an overall two-electron process, occurred in the place of the previously considered radical processes. The scope of the reaction was obviously different from that via radicals.[162−164] As an example, the nonsilylated amine **25** was smoothly oxidized upon DCN photocatalysis in MeCN−water 4:1. The reaction took place through two subsequent ET steps (involving excited and ground state DCN, respectively) with a deprotonation step (assisted by water present in the medium) interposed. The iminium cation reacted with allyltrimethylsilane and afforded the allylated derivative **26** in 70% yield (Scheme 39).[163]

Scheme 39



The rapid regeneration of the photocatalyst by reaction of the corresponding radical anion with oxygen allowed its use in a catalytic amount. This is an example of the use of a sacrificial oxidant, as demonstrated by the nonoccurrence of the reaction when the solution was in equilibrium with an inert gas. Furthermore, purposely adding an oxidant such as methyl viologen accelerated the reaction.[162−164]

4.1.5. Of Other Groups

Halogenated and electron-withdrawing substituted *C*-centered radicals as well as acyl radicals are considered in this section. As mentioned in section 4.1.1., alkyl radicals were obtained by reductive activation of the C−X bond in halides. With polyhalides, the process was easier and led to halosubstituted radicals. As an example, both TiO_2 and CdS activated carbon tetrachloride. In the presence of alkenes (or alkynes), addition of CCl_3 and Cl (or H) across the double (or triple) bond occurred. Preparatively interesting yields were obtained in polar solvents or when TiO_2 was doped by Ag or Fe_3O_4 (Scheme 40).[165] Furthermore, the addition of a (di)chloromethyl group and a chlorine atom across a double

Scheme 40

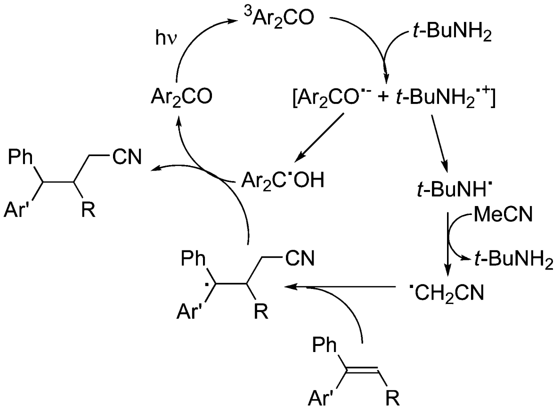
$$CCl_4 + CH_2{=}CH(CH_2)_3CH_3 \xrightarrow[\text{DMF}]{h\nu}$$

	A) TiO_2/Ag	B) TiO_2/Fe_3O_4
$CCl_3CH_2CHCl(CH_2)_3CH_3$ +	48%	60%
$CCl_3(CH_2)_5CH_3$	22%	20%

bond was obtained from di- and trichloromethane by using Cu^I complexes as photocatalysts (see again Scheme 21).

Dichloro and trichloromethane were activated also via the auxiliary radical method (see Scheme 41 for a related example) using BP in the presence of t-$BuNH_2$ as demonstrated in the chloromethylation of 1,1-diphenylethylene.[166a]

Scheme 41



Because of their electrophilic character, triplet ketones were inefficient in hydrogen abstraction from an electron-withdrawing-substituted carbon. TBADT was more active in this respect; for example, it formed some succinonitrile (by dimerization of $^\bullet CH_2CN$) when irradiated in MeCN.[60] The activation, however, was still too inefficient for making alkylation via radicals of this type a viable synthetic path.

On the other hand, ET photocatalysis via fragmentation of a radical cation of the type EWG-$CH_2X^{\bullet+}$ should be effective also for the generation of electron-withdrawing-substituted radicals, provided that a strong oxidant was used and a good electrofugal group X^+ was present in the precursor. A different approach involving O−Si rather than the C−Si bond cleavage was reported to occur after oxidative activation (in the presence of pyrene and β-phenyl-α,β-unsaturated nitriles) of ketene silyl acetals [($>C{=}C(OMe)(OSiMe_3)$)]. The corresponding radical cation underwent loss of the silyl cation to form α-alkoxycarbonyl radicals [$>C^\bullet CO_2Me$], and these in turn added to the alkenes.[166b]

A different strategy for bypassing the limitation of the catalyst and obtaining this type of radicals was based on the generation of an auxiliary radical possessing the required reactivity. Aminyl radicals showed to be well-suited. Thus, BP (25−50% mol equiv) abstracted a N−H hydrogen from t-butylamine via electron/proton transfer (no C−H abstraction possible, compare section 4.1.4.). The resulting t-$BuNH^\bullet$ radical reacted with acetonitrile forming the desired cyanomethyl radical. The last species added to nucleophilic alkenes, typically arylated derivatives, and back-H transfer from the reduced BP to the radical adduct closed the catalytic cycle (Scheme 41). Hydrogen abstraction from ketones, esters and, sulfoxides was similarly obtained and exploited for alkylation reactions.[166a,167]

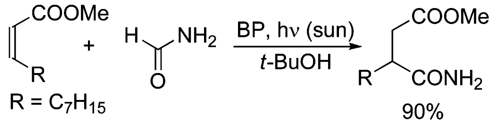
Another case of the use of an auxiliary radical involved the generation of a silyl radical by photocatalytic reductive activation (by 1,4-dimethoxynaphthalene, DMN) of a selenylsilane. The strong affinity for halogens made this radical abstract a bromine atom from a α-bromo ester. The resulting C-radical added to a terminal olefin, and the adduct, in turn, reacted with the selenyl anion, finally giving a γ-selenyl ester.[168,169]

Acyl radicals were obtained by BP photocatalyzed H abstraction from aldehydes, as once again demonstrated by the addition to a sugar-derived enone, where the acetyl derivative was obtained by using acetaldehyde as the precursor (see Scheme 26).[115]

The acylation of quinones to acylhydroquinones was carried out photochemically in a 'green' way by using aldehydes (and solar light). Although no photocatalyst was used with aliphatic aldehydes, with the aromatic analogues, a catalytic amount of BP was required.[170,171] This reaction, where the reagents were 100% incorporated into the product in a single step, had no comparable thermal alternative. The auxiliary radical method was also applied in the acylation of some 2-alkylamino-1,4-naphthoquinones by aldehydes, which was obtained by using the BP (2 mol equiv)/t-$BuNH_2$ system.[172]

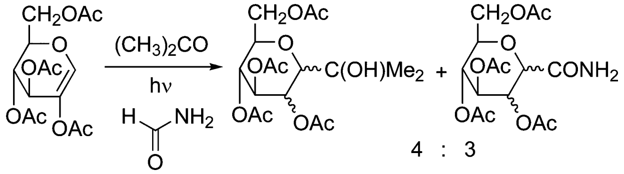
One oxidation level above, BP photocatalyzed hydrogen abstraction from formamide was shown to be a viable method for the preparation of amides from nonterminal alkenes (1:1 regioisomeric mixtures were obtained from asymmetric alkenes)[173,174] as well as from α,β-unsaturated esters (where the addition was regioselective, Scheme 42).[173,175]

Scheme 42



This synthesis of amides was applied to some glucals, which were irradiated in a mixture of acetone (functioning as the photocatalyst) and formamide. In this case, however, both the ketone-derived radical and the carbamoyl radical added competitively giving a mixture of the respective stereoisomers (see Scheme 43), which however could be converted into useful C-glycosyl derivatives.[176]

Scheme 43



Titanium dioxide was found effective for the acylation of quinoline and quinoxaline in formamide.[161]

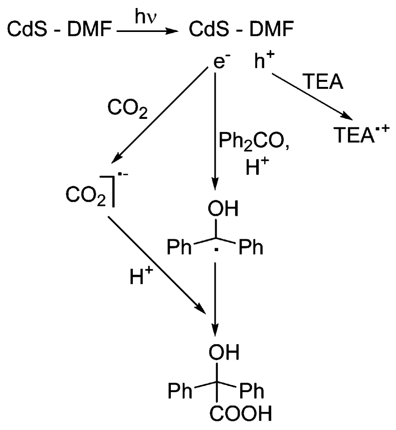
4.2. Intermolecular Addition onto C=X Bonds

Various reactions have been reported that involve the alkylation of CO, CO_2, imines, organic nitriles and, cyanide ion.

Alkyl radicals generated from alkanes by photocatalysis were carbonylated when CO under pressure (20−80 atm) was present. When acetophenone or BP were used, these were consumed in the process, but 2-trifluoromethylbenzophenone behaved catalytically and gave a good yield of the aldehydes. As expected, abstraction from methylenes rather than terminal methyl groups was preferred with linear alkanes. Adding CCl_4 diverted the reaction toward the formation of both alkyl and acyl chlorides.[177,178] Notice further that when alkyl radicals were generated by a different photocatalytic method, viz., by using TBADT, aldehydes were likewise formed. However, under these conditions (1 atm CO), the products in part decomposed and did not accumulate beyond a few percent.[179] The carbonylation could be carried out under atmospheric pressure also by using some metal complexes such as $Rh(PMe_3)_2(CO)Cl$. In this case, the reaction was slower and gave linear aldehydes exclusively.[180,181] It was proposed that under these conditions the process involved metal-coordinated intermediates (compare Scheme 5), rather than free radicals, and might involve the absorption of two photons.[182] The carbonylation of benzene was likewise obtained by photocatalysis with $Rh(PR_3)(CO)Cl$ ($R = Me$, Ph). As in the case of alkanes, the reaction (that was extended to thiophene[183] as well as to other Rh^I and Ir^I catalysts)[184,185] appeared to require two photons (the first one for the addition of benzene onto the metal center, the latter one for C−C bond formation with CO).[186] Interestingly, substituted benzenes gave *meta* aldehydes as the main products.[181]

Photofixation of carbon dioxide was also investigated in the frame of artificial photosynthesis. Yanagida and coworkers found that visible light-absorbing compounds such as poly(*p*-phenylene) and, even better, CdS−DMF were efficient photocatalysts for this reaction.[187−189] Initially, CO_2 was introduced into a DMF solution containing CdS−DMF and pre-irradiated for 1 h. Then triethylamine (TEA, as a sacrificial donor) and aromatic ketones or benzyl halides were added as photofixation substrates. Photolysis took place in a sealed tube. The mechanism is shown in Scheme 44.

Scheme 44

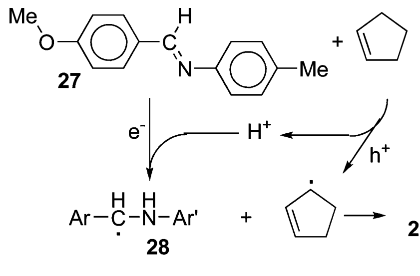


The catalyst was able to reduce both carbon dioxide and the organic additive. A benzylic acid was finally formed in a modest yield by radical−radical anion coupling along with a roughly equimolar amount of benzopinacol.

The alkylation of imines has also been reported. The reaction has been rationalized as cross radical−radical coupling, rather than radical−radical anion, an alternative mechanism that has been reported in several cases. This is a useful reaction that gives amines **29** by using a Schiff base **27** and cyclopentene as the reagents (Scheme 45).[190−192]

Thus, irradiation of CdS caused concomitant hole oxidation of the alkene and monoelectronic reduction of the imine. A radical pair was then formed after proton exchange between the two radical ions. Aniline **29** was isolated in a high yield (80%).[190] However, dimerization of radicals **28** took place to a significant extent when the substituents on the aromatic rings of the imine were changed. Thus, unsaturated *N*-phenyl-α-amino esters were prepared from the corresponding phenyl(phenylimino)acetate and cyclic alkenes in a modest yield (<50%) by using silica-supported cadmium sulfide powder ($CdS-30SiO_2$) as the photocatalyst and a tungsten halogen lamp ($\lambda_{irr} \geq 350$ nm) as the light source.[192] *N*-Phenylbenzophenoneimines were likewise alkylated yielding homoallyl amines.[193] The same approach was exploited for the formation of a C−N bond in the synthesis of allylhydrazine derivatives by photocatalyzed reaction between enol ethers (or olefins) and 1,2-diaryl- and 1-aryl-2-alkyl-1,2-diazenes.[194−196]

Scheme 45



Ar = 4-MeO-C_6H_4; Ar' = 4-Me-C_6H_4

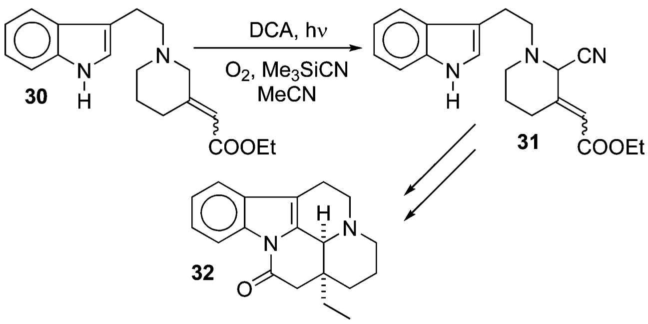
All of the reactions described above involving X═N (X = C, N) multiple bonds gave (mainly) a *single* product by cross-coupling between two intermediates arising from the oxidative and reductive paths of the semiconductor photocatalysis. These were classified as type B reactions by Kisch and differentiated from the more common type A reactions, where both an oxidized and a reduced products were obtained.[29,31]

Aldimines were produced by irradiation of an iron isonitrile complex, but the turnover number was quite low.[197] In contrast, methyl cyanoformate was shown to be an efficient trap of alkyl radicals produced by decatungstate photocatalysis. Iminyl radicals $R-C(=N•)CO_2Me$ were formed in this case and gave α-iminoesters in good yields as the end products. Noteworthy, when the reaction was carried out at 90 °C rather than at 22 °C, the radicals decomposed ($\rightarrow RCN + CO_2 + Me•$), and nitriles were obtained in about the same yield.[198]

A different way for adding an alkyl group to a heteroatom-containing multiple bond involved carbanions as the key intermediates. These could be formed by reduction of the primarily produced radicals, either when the photocatalyst used was able to act as reducing (as well as oxidizing) agent, such as TiO_2, or when the reduced photocatalyst was so persistent that it accumulated at a sufficient extent as to reduce the short-lived alkyl radical, as it was the case for decatungstates. When the reaction was carried out in MeCN, the formation of carbanions was revealed by the formation of alkyl methyl ketones. As a matter of fact, small amounts of cyclohexyl and, respectively, 1-adamantyl methyl ketone were obtained from cyclohexane[91] and adamantane upon TBADT and, respectively, TiO_2 photocatalysis.[92] When using a hexacyclic hydrocarbon as the substrate, sodium decatungstate photocatalysis gave an interesting (>60%) yield of the methyl ketone.[69]

A group of cyanation reactions will be mentioned here. The synthesis of a class of versatile intermediates such as α-cyanoamines[199−208] was developed by exploiting photogenerated iminium ions (see Scheme 11) in cyanation reactions in the presence of cyanide ions or of trimethylsilylcyanide (TMSCN). These compounds were in turn intermediates for the synthesis of indole alkaloids. A typical example is shown in Scheme 46 where cyanoamine **31** was

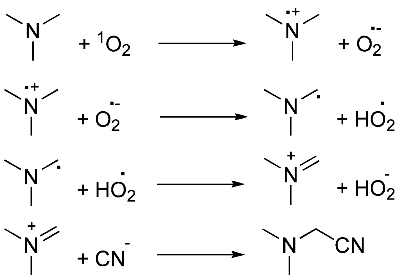
Scheme 46



formed upon DCA-catalyzed photolysis of amine **30** and was converted into (±)-eburnamonine **32** in two steps from **31**.[199]

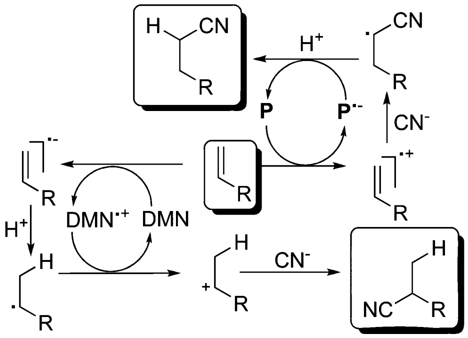
Both 6-cyano-1,2,3,6-tetrahydropyridines[200,201] and indoloquinolizidine alkaloids[202] were obtained analogously. Visible light could be conveniently adopted when using photocatalysts such as *N*,*N*′-dimethyl-2,7-diazapyrenium bis(tetrafluoroborate) [$DAP^{2+}(BF_4^-)_2$] or the dyes methylene blue and eosin.[203−207] Interestingly, the reaction took place both in the presence and in the absence of oxygen. In the former case, singlet oxygen was envisaged as the first intermediate involved in the electron-transfer steps (Scheme 47), as supported by the occurrence of the reaction also when $^1O_2$ was thermally generated from 1,4-dimethylnaphthalene endoperoxide.[208,209]

Scheme 47



Photochemical addition of cyanide ion onto a double bond could be accomplished both by monoelectronic oxidation and by monoelectronic reduction of the olefin.[210,211] Noteworthy, a different regioselectivity was observed according to the mechanism involved. Thus, 1-cyanonaphthalene (**P** in Scheme 48) induced oxidation of a phenylated olefin, for example, 2-phenylnorbornene, and gave the anti-Markovnikov-cyanated product,[210] whereas the DMN-induced reduction of 1,1-diphenylethylene afforded the Markovnikoff adduct.[211] As shown in Scheme 48, this was due to the opposite order of addition of H and the CN group: in the first case, the first step was addition of cyanide to the radical cation; in the latter one, protonation of the radical anion occurred first.

Scheme 48

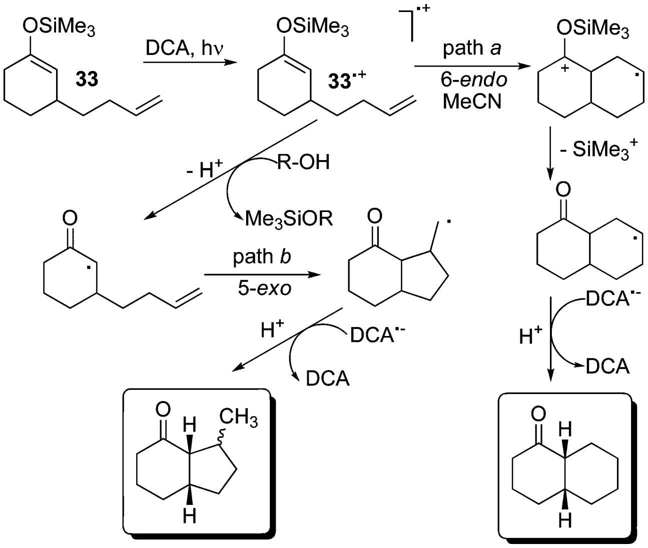


4.3. Intramolecular Addition onto C=C Bonds

4.3.1. Via Silyl Enol Ethers

Photocatalysis via ET (generally oxidative) mechanism was exploited for a varied series of cyclization reactions. Silyl enol ethers were typical substrates for such reactions. Thus, oxidative cyclization in MeCN of a *ω*-pentenylsilylated ether was obtained by a PET process (λ_{irr} = 410 nm) in the presence of DCA as the photocatalyst. The radical cation of silyl ether **33** formed in the initial step underwent intramolecular addition onto the side-chain double bond. A cyclic ketone was finally obtained after trimethylsilyl cation loss, BET and protonation,[212,213] with exclusive formation of a 6-membered ring via the 6-*endo*-trig cyclization path (see Scheme 49, path *a*). DCN could also be adopted as the photocatalyst, but a higher amount (up to 1 mol equiv) had to be used, and a shorter wavelength was required (λ_{irr} = 350 nm). This had the disantavage of making ensuing photoinduced reactions of the primary products significant, in this case, mainly the Norrish Type II cleavage of the ketones formed.

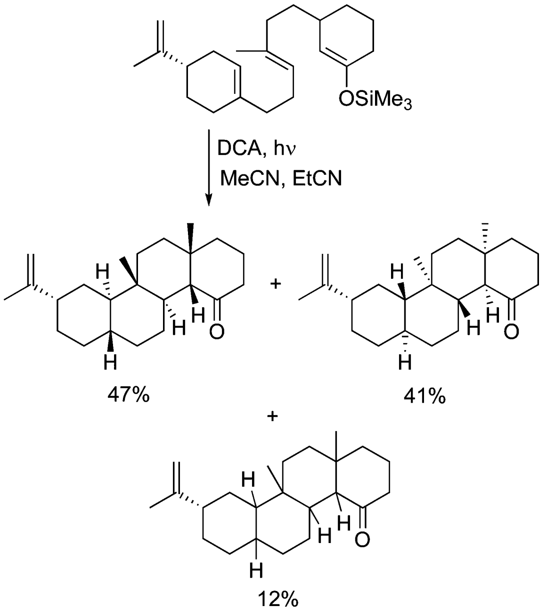
Scheme 49



The mode of cyclization could be tuned by the addition of alcohols that acted as nucleophiles and assisted the dissociation of the Si−O bond of the silylated radical cation. In this case, an α-keto radical could be envisaged as the intermediate and cyclized via a 5-*exo*-trig mode according to Baldwin's rule (Scheme 49, path *b*[214,215]). Interestingly, when the reaction was carried out in neat MeCN but under a high pressure (1500 bar), the 5-*exo*-trig regioselectivity became by far the main path. This change could be ascribed to the increased nucleophilicity of MeCN at this pressure.[216,217] In contrast, the presence of substituents on the attacking double bond could affect both the regiochemistry of the cyclization step and the overall yield. Thus, when using highly substituted double bonds and cyclic enol ethers, polymerization (assumed as the major side reaction) was hampered. Interestingly, a *cis* ring juncture was always obtained, a fact that was presumably due to a preferred reaction from the chair conformer that had the substituents pseudoaxially arranged.

When cocatalysis was applied by using the DCA/Phen system, the irradiation time was decreased down to ca. 40% of the initial value.[216,217] Furthermore, the smaller was the steric hindrance by the silyl group; the larger was the competitive formation of the open chain rather than the cyclized ketone. The stereoselectivity observed in these reactions was recently supported by DFT calculations.[218] When the silyl enol ether moiety was embedded in a carbocyclic ring with a stereogenic center adjacent to the double bond, the latter controlled the stereochemical outcome of the reaction as illustrated in Scheme 50.

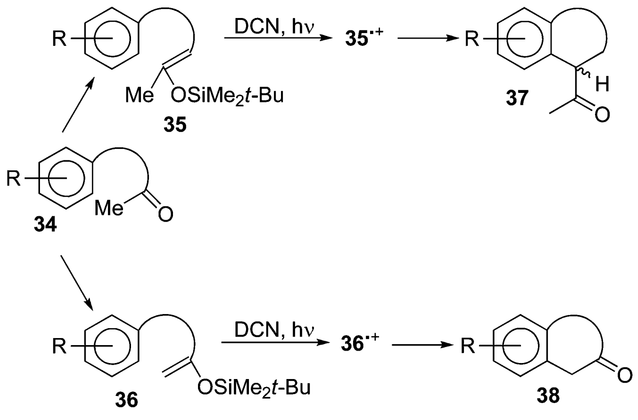
Scheme 50



In this case PET cyclization represented a new strategy for the stereoselective synthesis of a (quasisteroidal) polycyclic carbon framework through a cascade cyclization.[219]

Silyl enol ethers also found application in the intramolecular alkylation of aromatic compounds. Thus, methyl ketones **34** were converted into ethers **35** and **36**. DCN-catalyzed PET oxidation of the last compounds yielded carboannelated products, viz., methyl ketones **37** and cyclic ketones **38**, respectively (Scheme 51).[220,221]

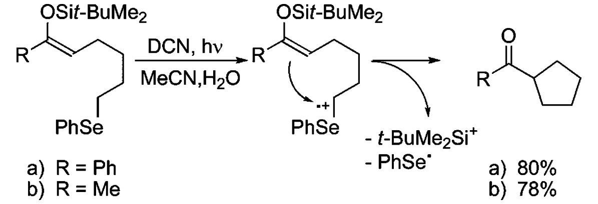
Scheme 51



A synthesis of phenanthridone alkaloids (e.g., 2,7-dideoxypancratistatin) was based on the above PET carbocyclization path, and again exploited enol silyl ethers as easily oxidized starting materials.[222]

In the intramolecular reaction of enol silyl ethers bearing an alkyl chain containing a phenylselenyl group (see Scheme 52), the mechanism was slightly different. In this case, the organoselenium moiety was thought to be oxidized preferentially. At any rate, the subsequent cyclization led to cyclopentyl ketones in high yields.[223] Interestingly, the intermolecular version of the reaction likewise gave satisfactory yields (60−70%).[223]

Scheme 52



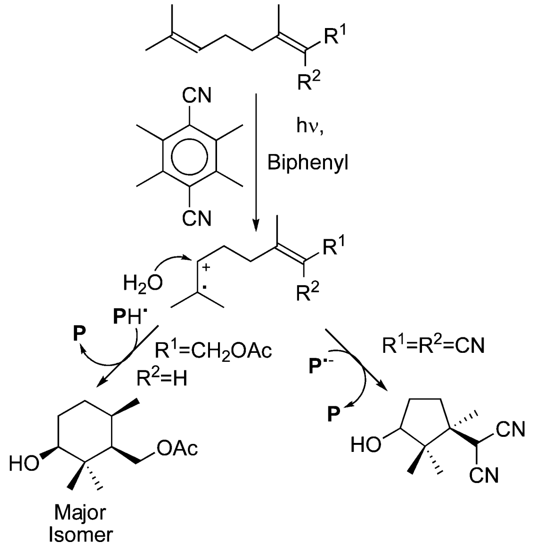
As mentioned in section 4.1.1., PET-induced cleavage of a cyclopropane ring was another path for generating alkyl radicals via C−C bond fragmentation. This principle was applied to bicyclic silyloxycyclopropanes that underwent cleavage of the endo C−C bond and desilylation to give monocyclic *β*-keto radicals. When a double bond was present in the ring or in a pendant chain, interesting cyclization reactions took place.[224,225]

4.3.2. Via Olefins

The application of polyene cyclizations via PET in order to mimic in vivo cyclizations that form polycyclic terpenoids was extensively investigated by Demuth and co-workers. To ensure the correct folding of the polyalkene prior to cyclization and/or to suppress BET by the enhanced separation of the radical ions, a microheterogeneous medium (generated by using a surfactant anion such as sodium dodecyl sulfate, SDS) was initially identified as the only effective condition.[226,227] However, when a sterically hindered electron acceptor such as 1,4-dicyano-2,3,5,6-tetramethylbenzene (DCTMB) was used in combination with a secondary donor (biphenyl), cascade cyclizations could be performed also in homogeneous media (MeCN−water or MeCN−MeOH mixtures as the solvent). The cyclization was reasonably initiated by single electron transfer from the *ω*-alkene moiety of the polyalkene to the excited catalyst. The radical cation thus obtained was trapped by *anti-Markovnikov* addition of water, and the resulting *β*-hydroxy radical initiated the cyclization cascade. The cyclization step itself had therefore to be regarded as involving radicals, rather than the radical cations[228,229] usually invoked in the analogous enzymatic processes. Interestingly, the substituents present at the end of the polyalkene chain could direct the last step of the cyclization either toward the *6-endo*-trig or the *5-exo*-trig mode (Scheme 53).

Indeed, cyclization onto an allylic acetate moiety led to a 6-membered ring, whereas cyclization onto α,*β*-unsaturated nitriles gave a five-membered cycle. Thus, it was the stability of the radical adduct formed that determined the mode of termination. As a matter of fact, in the second case, reduction by the photocatalyst radical anion $\mathbf{P}^{\bullet-}$ followed by protonation terminated the reaction, as confirmed by experiments carried out in the presence of D_2O, where deuterium was incorporated in the end product. Different was the case of polyalkene acetates, where hydrogen atom transfer (from $\mathbf{PH}^{\bullet}$, the conjugate acid of $\mathbf{P}^{\bullet-}$) rather than reduction from $\mathbf{P}^{\bullet-}$ was envisaged[230] (Scheme 53).

Scheme 53



In the event, a biomimetic synthesis of a steroid was accomplished in MeCN−H_2O 10:1 mixed solvent at −25 °C starting from all-*trans* geranylgeranyl acetate.[230−233] To induce chirality in such PET-triggered cyclizations, a chiral auxiliary was linked to the starting polyunsaturated compound via a ketal function (see **39** in Scheme 54). The degree of asymmetric induction associated with this cyclization was quite remarkable (eight stereogenic centers were generated in the reaction and only 2 out of 256 possible isomers were formed, viz., **40** and **41**), despite the fact that the chiral moiety was remote from the initiation site (Scheme 54).

This strategy was successfully applied in the formal synthesis of the antitumoral (±)-stypoldione[234,235] and of oxygenated tetracyclic diterpenes such as (±)-3-hydroxyspongian-16-one.[236] Cyclization reactions could be carried out also in a less polar solvent such as dichloromethane or in CH_2Cl_2/MeOH mixtures, but not with DCTMB as the photocatalyst, since BET inhibited the process in this case. However, a charged photocatalyst such as *N*-methylquinolinium hexafluorophosphate ($NMQ^+PF_6^-$) was effective.[237] Indeed, in this case, the electron-transfer step led to the reduction of the NMQ^+ cation to the corresponding neutral radical. Since, differently from when the acceptor radical anion was formed, there was no Coulombic attraction between this species and the radical cation of the polyalkene, the overall process was less dependent on the solvent polarity.

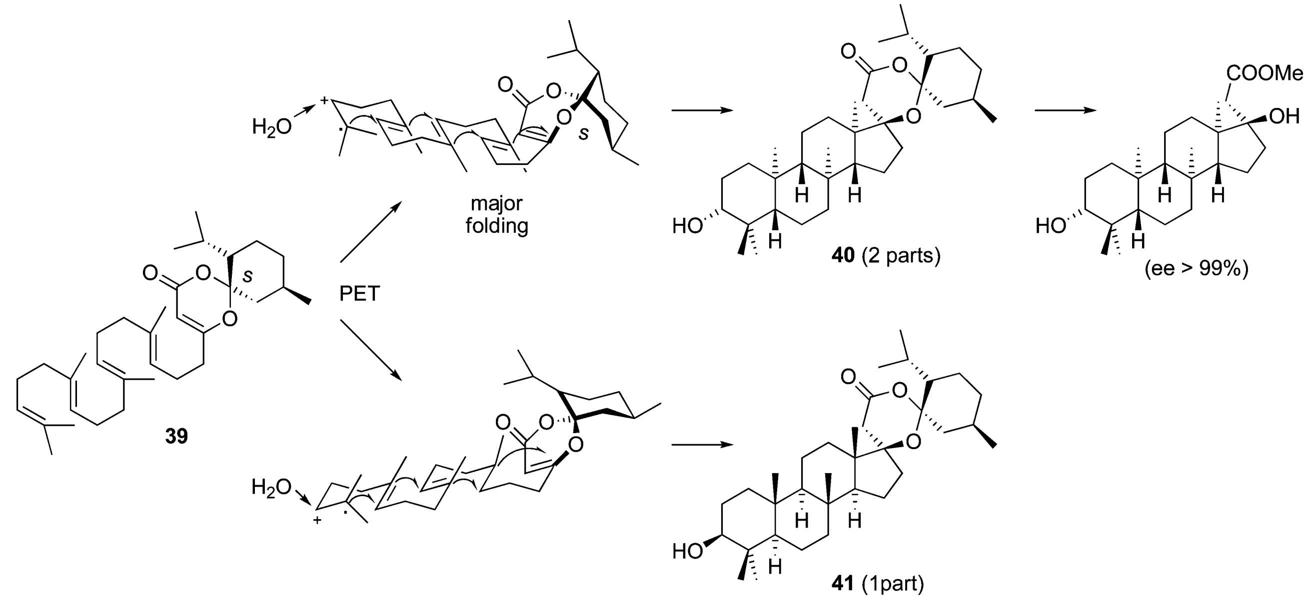
In the case of geraniol, in nonaqueous low-polarity medium such as methylene chloride, two isomeric five-membered ring derivatives (**42** and **43**) were formed upon photolysis in the presence of DCA (ca. 30% mol equiv), along with a small amount of an oxabicyclo[3.4.0]octane derivative **44** (Scheme 55).[238,239]

Cyclic ethers such as **44** arose from tandem C−C and C−O bonds formation and predominated when using 1,4-dicyanobenzene (DCB) in the place of DCA. With the latter photocatalyst, the intramolecular attack by the OH group was prevented by fast BET from $DCA^{\bullet-}$ to the radical cation intermediate.[239]

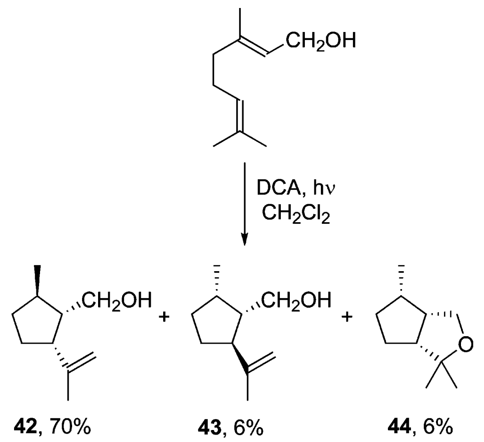
Organoselenium compounds (rather toxic, though) were shown to be versatile intermediates for the intramolecular C−C bond formation.[240] As an example, $PhSeSiR_3$ (e.g., SiR_3 = $SiPh_2$-*t*-Bu) was used to initiate a radical chain group transfer reaction[168,169,241] (Scheme 56, left part), when photocatalytically reduced by ^{1}DMN. The radical anion **45** thus formed fragmented, and the $R_3Si^\bullet$ radical obtained abstracted either a halogen or a PhSe group (X in the scheme) from the substrate, thus, leading to a cyclization. As for the $PhSe^-$ anion, this was oxidized by oxygen to diselenide PhSeSePh that participated in the termination step of the reaction after that intramolecular C−C bond formation, generally in the *5-exo*-trig mode, had taken place. The presence of ascorbic acid ensured the regeneration of DMN (40% mol equiv used with respect to the alkene, see further below).

Alternatively, the efficient DCN photocatalyzed one-electron oxidative dissociation of the selenium−selenium bond in PhSeSePh could be exploited.[242−245] In this case, an electrophilic species ($PhSe^+$) was generated and induced a cyclization step after addition onto various substituted C−C double bonds (Scheme 56, right part). As an example, both allyl propargyl ethers[243,245] and *ω*-hydroxyalkenes[244] were used as starting materials for this reaction and yielded phenyl selenyl substituted tetrahydrofurans. The phenyl selenide group was in every case incorporated in the end products.

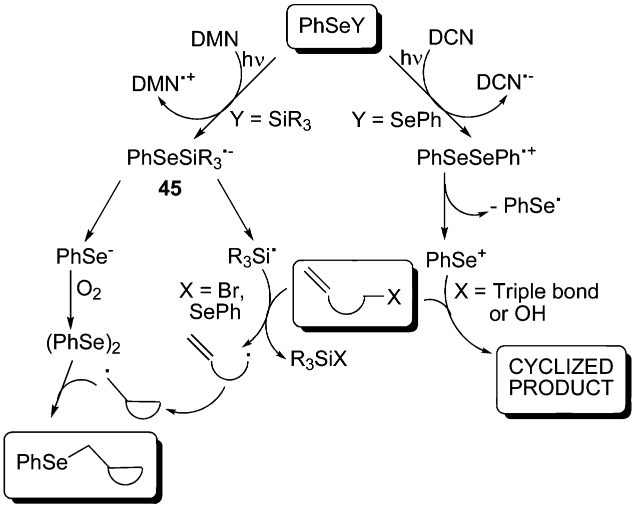
Scheme 54



Scheme 55



Scheme 56



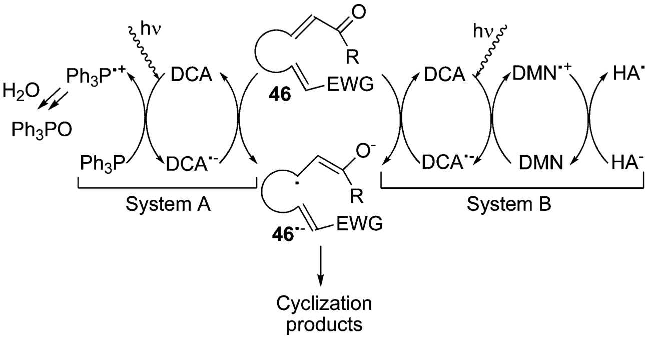
These compounds could be easily converted into the corresponding methyl ethers by a further photocatalyzed oxidation step in MeOH. This occurred via fragmentation of the carbon-selenium bond in radical cation $R'SeCH_2R^{\bullet+}$, assisted by the alcohol. The corresponding ether RCH_2OMe was finally isolated, and the overall process corresponds to a one-pot C−C bond formation, selenylation, and deselenylation reaction.[242] Alkyl phenyl selenides could be alternatively reduced by ^{1}DMN. In this case, $PhSe^-$ loss followed by a radical intramolecular addition onto a C═C bond occurred.[246]

4.3.3. Via Electron-Withdrawing-Substituted Olefins

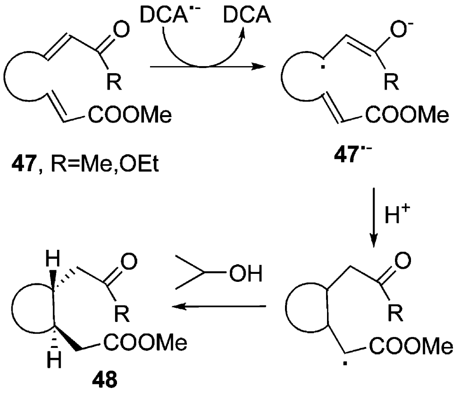
Pandey developed two photosystems for the monoelectronic reductively induced reaction at the β position of α, β-unsaturated esters or ketones. This involved the formation of carbon-centered radicals for the intramolecular C−C bond formation of 5- or 6-membered rings.[247,248] In both cases, visible light-absorbing DCA was used as the photocatalyst (Scheme 57). As the solvent, a mixture of DMF/*i*-PrOH/H_2O 88:10:2 was used; DMF was required to dissolve a sufficient amount of DCA so that an efficient catalysis could take place.

In both systems (**A** and **B** in Scheme 57), a sacrificial electron donor (Ph_3P or an ascorbate anion HA^-, respectively) was required to regenerate the photocatalyst. Suitable substrates (e.g., **46**) for the reaction were α, β-unsaturated ketones (or esters) tethered by an alkyl chain to an activated (electron-poor) olefin as illustrated in Scheme 58.

Scheme 57



Scheme 58

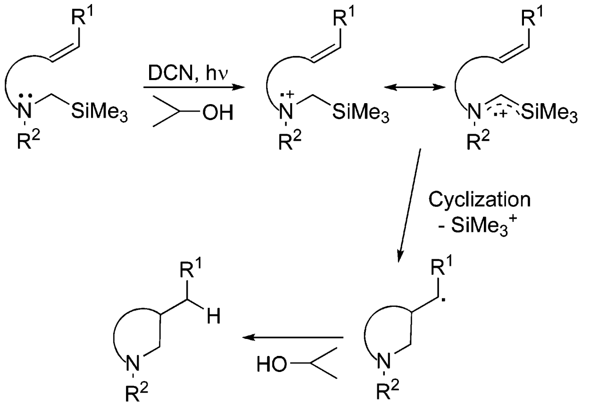


Accordingly, in the case of system **A**, ^{1}DCA oxidized Ph_3P (the amount of $Ph_3P^{\bullet+}$ formed was quenched by water forming Ph_3PO), and in turn, $DCA^{\bullet-}$ initiated the reaction by reduction of a carbonyl (carboxyl) moiety present in the precursor **47** (Scheme 58). The thus obtained enolate radical anion (**47**$^{\bullet-}$) underwent C−C bond formation via radical cyclization with a strong preference for *trans*-1,2-stereochemistry (**48**).[249−252] The last step was H abstraction from the solvent (*i*-PrOH) by the cyclized radical. Analogously, in system **B**, DMN was first oxidized (in the place of Ph_3P) and then restored to the neutral state by reaction with ascorbate anion. According to Scheme 57, DCA was recovered quantitatively at the end of the reaction. Efficient cyclization required activated olefins. Cyclization onto a double bond not bearing an EWG group occurred with poor efficiency indicating the moderate nucleophilic character of intermediate **47**$^{\bullet-}$. This notwithstanding, the reaction was recently applied in the synthesis of optically pure 6-phenyl-2,3-bis-methylenemethoxycarbonyl-[1,4]-dioxane, an interesting building block for the synthesis of biologically active compounds.[252]

4.3.4. Via (Silyl)amines

The PET oxidation of simple tertiary amines followed by proton loss could be expected to offer an appealing entry to α-amino radicals,[253] but α-deprotonation was usually slow in comparison to BET (see section 4.1.4.). To favor the fragmentation step, a better electrofugal group (Me_3Si^+ in the place of a proton) was used. In this case, the radical cation intermediate was delocalized thanks to the vertical overlap with both the filled C−Si orbital and the half-vacant nitrogen orbital. Accordingly, in the silylated radical ion, no assistance by the nitrogen lone pair was required and the cyclization step was facilitated. In fact, while the attempted cyclization of a free α-amino radical onto tethered olefins failed owing to the poor yield of radicals, irradiation of α-silylated amines in the presence of DCN in *i*-PrOH led to cyclization. In this way, pyrrolidine and piperidine rings, common subunits in many naturally occurring alkaloids, were formed (Scheme 59).[254,255] The more favorable *exo*-cyclization usually took place.

Scheme 59

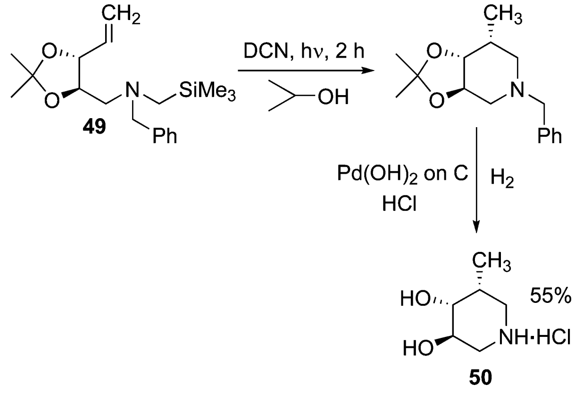


The reaction was completed by H abstraction from *i*-propanol used as the solvent ($DCN^{\bullet -}$ was reoxidized by O_2). Interestingly, α-amino radicals generated by the conventional thermal method mediated by Bu_3SnH/AIBN and starting from analogous precursors failed to cyclize and rather yielded the corresponding open-chain reduced amines.

In this way, the photochemical synthesis of (±)-epilupinine,[256,257] (±)-isoretronecanol,[256,257] and (−)-retronecanol[258] was easily accomplished by forming quinolizidine and pyrrolizidine rings by cyclization onto suitable tethered π-functionalities. Noteworthy, in the last cases, the cyclization step involved nonactivated olefins (i.e., not bearing an electron-withdrawing group), despite the nucleophilicity of the attacking radical. The indolizidine skeleton was accessible in the same way.[259]

PET-promoted cyclizations were also used in the synthesis of 1-*N*-iminosugar type compounds which were known to be strong inhibitors of glycosidases and to possess a high chemotherapeutic potential in the prevention of a variety of diseases, including AIDS.[260−263] The viability of this strategy was demonstrated in the synthesis of both enantiomers of isofagomine.[260,261] Recently, galactose type derivatives were likewise obtained from chiral-silylated amine **49** under PET conditions. A single diastereomer **50** was formed in 55% yield (Scheme 60).[262,263]

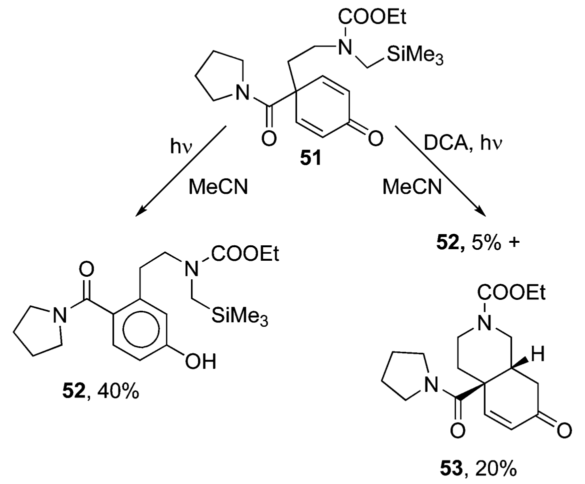
Scheme 60



Although benzophenone was no convenient photocatalyst for generating α-amino radicals from tertiary amines (see section 4.1.4.), it was used in the last step of the synthesis of some indolizidine alkaloids (21% yield).[264]

Mariano and co-workers explored the possibility to form substituted dihydroisoquinolines by PET-catalyzed photocyclizations of silylamino and silylamido 2,5-cyclohexadienones (Scheme 61).[265]

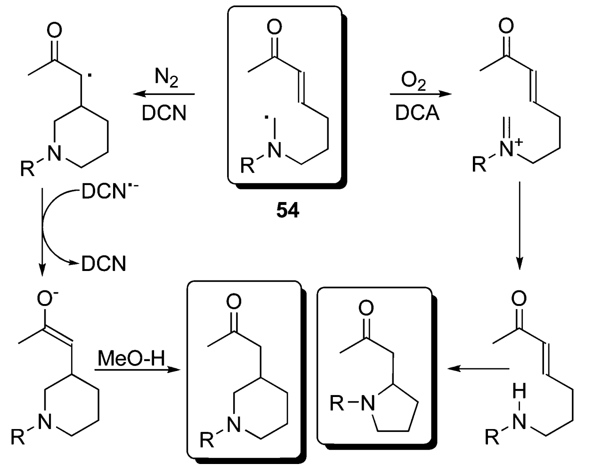
Scheme 61



Interestingly, direct irradiation of enone **51** afforded uncyclized phenol **52** in 40% yield. On the contrary, photocatalysis by DCA (10% mol equiv) gave **53** in a modest yield (20%) but in a highly stereoselective fashion. The formation of a small amount (5%) of phenol **52** was attributed to a partial competitive absorption of the starting enone (Scheme 61).[265] Various piperidines were synthesized in a similar way and employing α-silylaminoenones and -ynones as the substrates.[266]

Furthermore, a α-silylamido-cyclohexadienone was used for the synthesis of yohimbanes.[267] Interestingly, it was possible to direct the reaction either toward the aminoradical path or toward the iminium ion path by a sensible choice of conditions, as demonstrated by Mariano and co-workers and illustrated in Scheme 62.[268−270]

Scheme 62



Under deareated conditions and using a photocatalyst (e.g., DCN) that was not able to oxidize the α-aminoalkyl radical **54** before cyclization, a piperidine ring was formed. The process occurred via enolate anion (arising from the reduction of the α-keto radical by the reduced photocatalyst) followed by MeOH-induced protonation. On the contrary, when the reaction was carried out in the presence of oxygen and using DCA (which was a better oxidant than DCN in the ground state), an iminium ion was formed and a carbon unit was lost, thus, inducing the intramolecular aza-Michael addition of the secondary amine onto the enone moiety.[268−270]

Iminium cations have also been exploited in various intramolecular addition onto a malonate moiety, thus, affording various heterocyclic ring systems.[271]

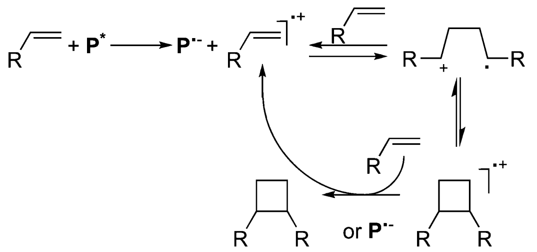
4.4. Cycloaddition

Just as in the case of cyclization reactions, photocatalysis via the ET (generally oxidative) mechanism has been exploited for a varied series of cycloadditions. Work in this direction has significantly contributed, along with thermally oxidative initiation, to enlarging the scope of this all-important class of reactions.[55,272,273]

4.4.1. Formation of a 4-Membered Ring

The synthesis of 4-membered rings has been easily accomplished by head-to-head [2 + 2] cycloaddition of alkenes after an initial photocatalyzed oxidation step as illustrated in Scheme 63. **P** was regenerated by BET from $P^{\bullet-}$ to the cyclobutane radical cation. Alternatively, this cation oxidized the initial alkene and initiated a (short) chain process.

Scheme 63



The first example of this type of reaction was the photocyclodimerization of *N*-vinylcarbazole reported by Ellinger in 1964.[274] This dimer was later obtained using DCB[275] as the photocatalyst. In this case, the yields were significantly improved under aerated conditions by adding a cocatalyst such as perylene. In such a way, polymerization of *N*-vinylcarbazole was prevented, and the overall turnover number of the photocatalyst was over 8000. Furthermore, the dimerization occurred efficiently under heterogeneous conditions using a CdS dispersion.[276] Chloranil and fluorenone were used with some success as photocatalysts.[277]

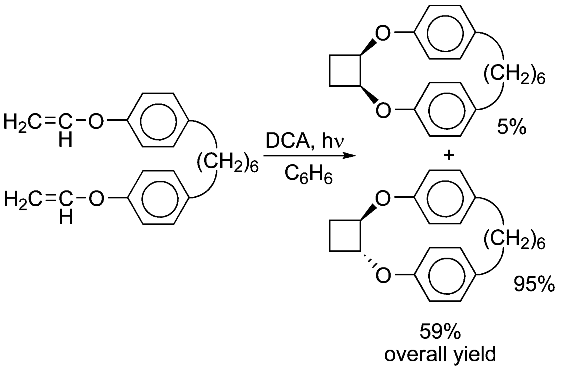
However, the most extensively studied [2 + 2] cyclodimerization involved phenyl(aryl) vinyl ethers.[278−285] Thus, parent phenyl vinyl ether (PVE) gave the corresponding cyclobutane derivatives (30% yield, isomer ratio 3:4) when photocatalyzed by 1,4-dimethyl terephthalate (DMP, 40% mol equiv) in MeCN.[278,279] The reaction was not thought to involve free radical ions but rather a complex between the $\pi\pi^*$ singlet excited DMP and the ground state of the ether. Interestingly, polyethylene terephthalate could be used as well and gave comparable amounts of the dimer with respect to DMP. The polymeric photocatalyst could be easily filtered out after reaction, washed, and re-used, although its effectiveness decreased strongly after each run.[280] The dependence of the quantum yield and of the *cis*/*trans* isomer ratio of the cyclobutanes formed on the PVE concentration (from 2×10^{-3} to 2 M) was investigated in the DCA photocatalyzed reaction in MeCN.[281] The reaction quantum yield decreased when decreasing the PVE concentration, while formation of the *cis* isomer was largely preferred (ca. 9:1), a selectivity not observed with [PVE] above 0.01 M.

As in the case of *N*-vinyl carbazole, inorganic semiconductors (ZnO, CdS) were effective for the reaction.[283,284] Surprisingly, some samples of CdS caused the dimerization to occur in the dark as well,[284] a fact that illustrated how difficult it was preparing samples of semiconductor sulfides that gave reproducible results. When arylalkenes and the photocatalyst were included within NaX zeolites,[286] the dimer ratios differed from those observed in solution (e.g., in the case of *trans*-anethole the *cis*/*syn* cyclobutanes were formed preferentially).

[2 + 2] Cyclodimerization was also applied to aliphatic vinyl ethers. Thus, ethyl vinyl ether (100 mmol) in a benzene solution afforded the expected cyclobutanes in 39% yield upon photocatalysis by DCN (5 mmol).[287] A triplex (viz., an excited complex involving **P** and two molecules of the ether) mechanism rather than the intermediacy of the free radical cations was invoked in this case. Other photocatalytic systems such as Phen/DCB or pyrilium salts could be conveniently used in the dimerization of α-methylstyrene[288] and of (dialkyl)indene,[289] whereas *p*-methoxystyrene gave only the *trans*-head-to-head cyclodimer in a low yield (13%) when irradiated in the presence of DCB.[290] Aromatic enamines were reported to form cyclodimers in the presence of a wide range of photocatalysts (e.g., aromatic ketones, pyrilium salts), provided that oxygen was present in solution and prevented undesired polymerization.[291]

Interestingly, the intramolecular version of the reaction was used for synthesizing macrocyclic 2,ω-dioxabicyclo-[*n*.2.0] ring systems as shown in Scheme 64.[292]

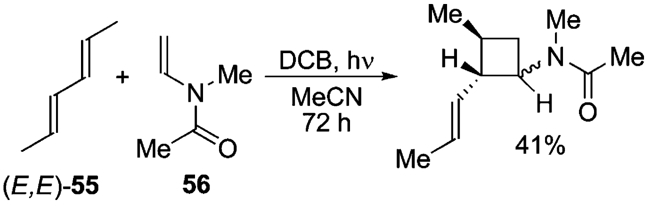
Scheme 64



The stereoselectivity of the process strongly depended on the solvent employed. In most cases, the *cis* isomer was predominant in MeCN and the *trans* isomer in benzene. The DCN-photocatalyzed intramolecular [2 + 2] cycloaddition of di- and tetra-allylsilanes was also carried out and gave silabicyclo[3.2.0]heptanes in good yields.[293] Worth noting, when an open chain allyltrimethylsilane was subjected to the same irradiation conditions, no cycloadduct was formed. Analogously, 2-silacyclobuta[2.3]cyclophanes were synthesized starting from dimethyl-bis(4-vinylphenylmethyl) silanes.[294] As for the latter reaction, the same photocatalytic conditions were able to induce cycloreversion to give back the starting material.

The cross cycloaddition between two different olefins is of obvious importance. However, when a mixture of an alkyl and a phenyl vinyl ether was irradiated in MeCN in the presence of DCB, a significant amount of cross adducts was obtained only by using a large excess of one of the ethers.[295] Most reported examples involved a diene as one of the partners. Thus, a [2 + 2] cycloadduct between 1,1′-dicyclopentenyl and ethyl vinyl ether was formed in a high yield upon DCB (35% mol equiv) photocatalysis, but the ether was used in a 12-fold amount with respect to the diene.[296] However, a clean reaction took place when one (or both) of the partners was not itself liable to dimerization, as it was the case in the reaction shown in Scheme 65.

Scheme 65



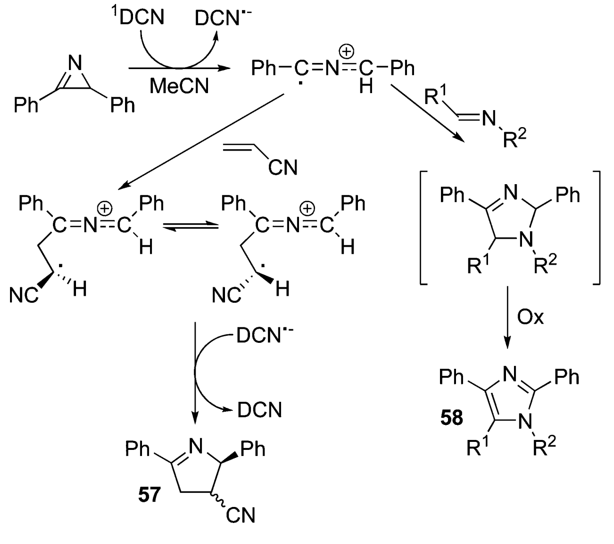
The unusually clean reaction between the diene **55** and *N*-methyl-*N*-vinylacetamide **56** implied that the radical cation of the more easily oxidized term (the diene) reacted preferentially with **56** rather than with neutral **55**.[297] This behavior was attributed to the powerful stabilization of the positive charge at an adjacent carbocationic center by the amide function.

4.4.2. Formation of a 5-Membered Ring

The PET-induced ring opening of 3-membered ring derivatives (oxiranes, azirines, or cyclopropanes) followed by reaction with a double bond offers a convenient access to 5-membered ring compounds.

Azirines were extensively studied in [3 + 2] cycloaddition reaction under PET conditions.[298−303] A 2-azaallenyl radical cation was suggested as the intermediate (Scheme 66).

Scheme 66



Addition to acrylonitrile, ring closure, and BET led to didhydropyrroles **57**. Since the reaction occurred in two steps and involved an odd-electron species, it differed from the thermal-concerted 1,3-dipolar cycloaddition. Moreover, the 2-azaallenyl radical cation was able to add to the C−N double bond of imines leading to 1-substituted imidazoles **58** via the spontaneous rearomatization of first formed imidazolines (Scheme 66).[298−300]

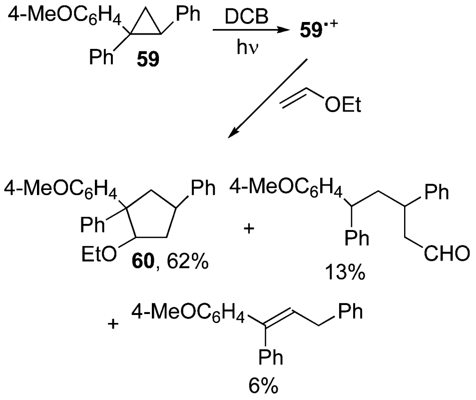
When bicyclic azirines were used in the reaction with imines, [*n*](2,4)imidazolophanes were obtained. The polymethylene bridge must contain at least five units for making the reaction successful.[301] Further expanding this strategy, four azirine moieties were built on a cyclododecane ring, and PET-induced photocatalysis was exploited for opening the 3-membered rings and add alkynes. In this way, a new synthesis of porphyrin systems was accomplished.[302]

C_{60} fullerene was a suitable trap for the 2-azaallenyl cation. 1,9-(3,4-Dihydro-2-5-diphenyl-2*H*-pyrrolo)fullerene-60 was isolated from the reaction with diphenylazirine, although the concomitant formation of oligoadducts was detected.[303]

2,3-Diphenyloxirans likewise gave tetrahydrofurans on DCN photocatalysis in the presence of α,β-unsaturated nitriles and esters.[304] The stereochemistry of the products depended on that of the oxirans, in accord with mechanistic studies showing that the *exo,endo* and *exo,exo* forms of carbonyl ylides were produced in significantly different ratios from *cis* and *trans*-oxides.[305] This indicated the intermediacy of distinct, nonequilibrating, ring-opened radical cations in the two cases. The reaction was extended to other epoxides bearing one to three aryl groups, although tetraphenyloxirane gave no adducts, probably due to steric hindrance.[306−309]

Triarylcyclopropanes **59** likewise underwent [3 + 2] cycloadditions after PET reaction with DCB in the presence of vinyl ethers. A cyclopentane derivative **60** was formed in 62% yield along with two byproducts in non-negligible amounts (Scheme 67).[310] The reaction required the use of an equimolar amount of the photocatalyst, but this was >80% recovered at the end of the reaction.

Scheme 67



α,α'-Bis-(trimethylsilyl)-amines underwent two sequential desilylation processes following two single-electron-transfer steps (DCN was the photocatalyst). In this way, a nonstabilized azomethine ylide was formed (see Scheme 11).[311,312] These ylides were the key intermediates in 1,3-dipolar cycloaddition reactions. Dipolarophiles such as aromatic ketones, α,β-unsaturated esters, and amides were used, obtaining in every case the corresponding 5-membered cyclic adducts.[311,312]

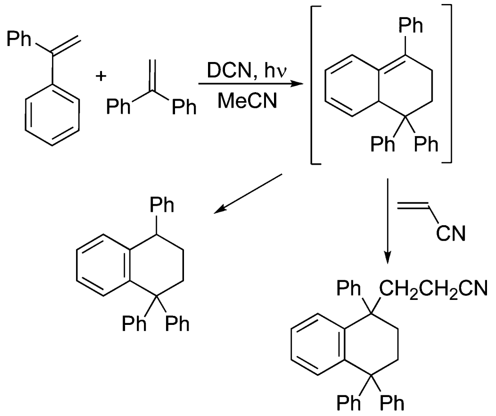
4.4.3. Formation of a 6-Membered Ring

As it is well-known, the Diels−Alder (DA) reaction does not apply to the case when both diene and dienophile components are electron-rich compounds. However, photocatalysis offers a way for the *Umpolung* of one of the reagents, thus, allowing the reaction to occur.

Several examples were reported in the literature concerning the photocatalyzed DA reactions. The mechanism was similar to that proposed for the photocyclodimerization, and actually, in some cases, the two reactions occurred competitively (vide supra). Photocatalysis was generally preferable to ET thermally induced DA reactions, such as those initiated by ground-state acceptors such as triarylaminium salts (e.g., Ar$_3$N$^{\bullet+}$SbF$_6^-$), since, in the latter case, a large excess of dienophile was required and underwent competitively isomerization or polymerization under these conditions.

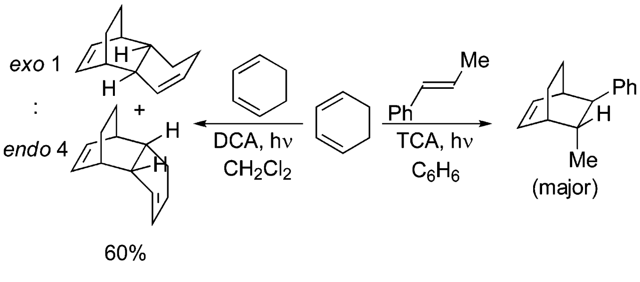
Thus, 1,1-diphenylethylene, upon oxidative photocatalysis by an aromatic nitrile, led to the formation of a tetrahydronaphthalene via attack of the radical cation onto a neutral molecule.[313−315] BET from the photocatalyst radical anion and rearomatization of the thus formed triene completed the sequence. It was also possible to trap the intermediate via an ene reaction, for example, by using acrylonitrile as depicted in Scheme 68.[315]

Scheme 68



Schuster extensively investigated the use of cyclohexadienes as dienophiles (dienes that lacked a rigid s-*cis*-arrangement of the double bonds were usually reluctant to react). A triplex mechanism was invoked in this case. Accordingly, the exciplex formed by the excited singlet state of **P** (usually a cyanoarene, e.g., 2,6,9,10-tetracyanoanthracene, TCA) and a dienophile was trapped by a diene to give a triplex that finally evolved to the cycloadduct.[316−319] *β*-Methylstyrene[316−318] and indene[319] were also used as dienophiles (see Scheme 69, right side).

Scheme 69



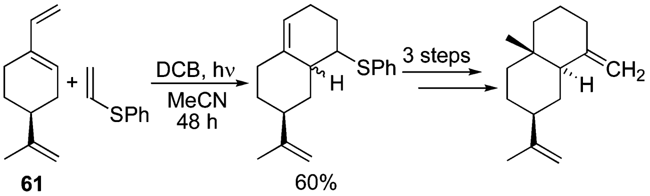
In the former case, the *endo*−*trans* isomer was largely preferred, and the selectivity was not affected when using a chiral catalyst such as (−)-1,1′bis(2,4-dicyanonaphthalene).[318]

Cyclohexadiene was also used in the DCA photocatalyzed [4 + 2] cyclodimerization in CH$_2$Cl$_2$ (Scheme 69, left part), which afforded a mixture of *endo*- and *exo*-dimers in more than 60% isolated yield.[320] Interestingly, the same reaction carried out under thermal conditions gave poor yields, whereas the concomitant formation of [2 + 2] cycloadducts was observed by changing the photocatalyst.[320,321]

2,4,6-Triphenylpyrylium tetrafluoroborate in CH$_2$Cl$_2$ was found to be particularly effective for inducing the Diels−Alder reaction of cyclohexadiene derivatives, since only 0.1−1.5% mol equiv of the photocatalyst was required, light with wavelength >345 nm could be used, and the irradiation time was dramatically reduced with respect to the reaction catalyzed by cyanoarenes.[322,323] Triphenylpyrylium salts could also be incorporated inside zeolites. Under these conditions, the 1,3-cyclohexadiene dimerization proceeded at a pace slower than that in homogeneous solution, and the *endo*[4 + 2] adduct was the major product.[324] 1-Methoxy-1,3-cyclohexadiene likewise underwent a cycloaddition reaction (70% yield) when irradiated in MeCN in the presence of 25% mol equiv of DCB,[325] while in the thermal Ar$_3$N$^{\bullet+}$-catalyzed reaction, polymerization predominated.

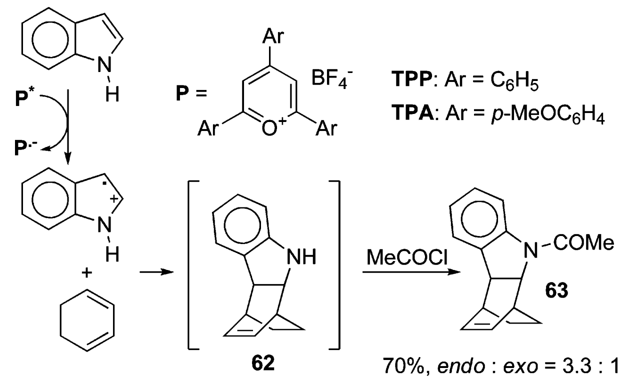
A precursor of the sesquiterpene (−)-*β*-selinene was obtained in 60% yield by photochemical reaction of diene **61** and phenyl vinyl sulfide (Scheme 70),[326] in one of the few examples of the synthesis of a natural product by photocatalyzed DA reaction.

Scheme 70



Useful applications of [4 + 2] photocatalyzed cycloadditions were developed by Steckhan's group starting from indole derivatives.[327−335] Although the 2,3-double bond of these substrates can be considered an electron rich 2*π* partner, only a few reactions between indoles and electron-poor heterodienes have been reported.[336] On the other hand, monoelectronic oxidation of (substituted) indoles was conveniently obtained by irradiation in the presence of 5% mol equiv of triphenylpyrylium salts, and the radical cation thus formed behaved as an electron-poor dienophile, smoothly reacting with dienes in a cycloaddition process (Scheme 71).

Scheme 71

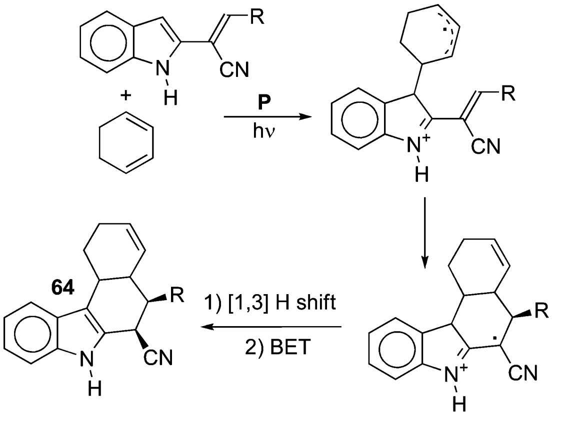


As a matter of fact, the photochemical path broadened the synthetic scope of the DA reaction and was applied for the synthesis of elaborated indole derivatives having biological activity.

As an example, the indole radical cation underwent a cycloaddition with cyclohexadienes. However, product **62** was more easily oxidized than the starting indole, and thus, it reacted further to give a complex mixture. This shortcoming was overcome, and amide **63** was prepared in a satisfactory yield when the reaction was performed in the presence of acetyl chloride, which functionalized the indoline as soon as it was formed and precluded further transformation.[327] A triplex was again invoked as the intermediate, and indeed calculations supported a nonsynchronous-nonconcerted reaction, involving a relatively stable intermediate.[327−331] This evidence could explain the complete regioselectivity observed, that is, a substituent in the 1-position (2-position) of the cyclohexadiene moiety was found in the 1-position (3-position) of the carbazole formed. The reaction was inefficient with indoles carrying a substituent on the 2,3-double bond (probably for steric reasons) and when open-chain dienes were employed. Furthermore, exocyclic dienes could be used in some cases, as it was shown in the 2,4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate photocatalyzed reaction with (1,2)oxazinan-2-yl derivatives as dienes.[330,331]

Another class of suitable substrates for [4 + 2] cycloaddition reactions was shown to be that of 2-vinylindoles.[332−335] In this case, the indole derivatives reacted as the diene, and the course of the reaction was different. The first step was the oxidation of the indole, followed by addition of the radical cation onto cyclohexadiene, cyclization, [1,3] H shift, and BET. This finally yielded carbazole **64** (Scheme 72). The use of chiral dienophiles led to a single isomer.

Scheme 72



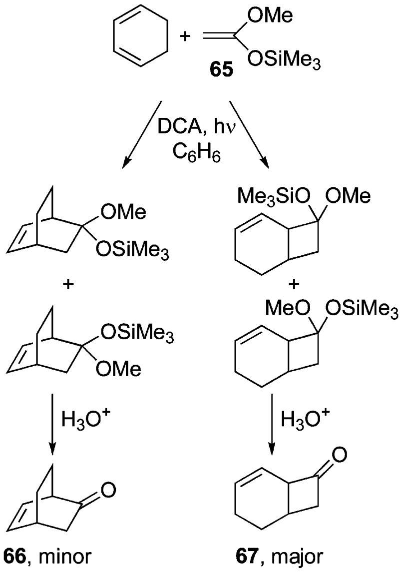
One of the limitations of this reaction was that it required that the difference between the oxidation potentials of the two starting materials did not exceed 0.5 V.[332] As an example, substituted enamines were suitable dienophiles for this reaction, since they had exactly the same oxidation potential of the above-mentioned vinylindoles.[334] Moreover, vinylindoles gave pyrido[1,2*a*]indoles in the reaction with *β*-enamidoesters or -nitriles by using 2,4,6-tri-(*p*-anisyl)-pyrylium tetrafluoroborate (TPA) as the photocatalyst.[335] Unlike vinylindoles, 2-vinylbenzofurans mainly reacted as dienophiles, and their reaction with cyclohexadiene showed a predominant *endo*-selectivity.[337]

Furan behaved as a dienophile in the DCN-photocatalyzed reaction with indene. The reaction gave both the photocycloadduct and a substituted indene. The former product was the preferred one only when the furan ring had no substituent; a methyl group in the 2-position dramatically enhanced the yield of the substitution product.[338]

The intramolecular version of the PET Diels−Alder reaction was rarely employed, although this path removed the requirement of high dienophile concentrations to prevent the diene dimerization. As an example, the reactions of cyclohexadienyl derivatives bearing a flexible alkyl chain containing a double bond was investigated by Schuster[339] and co-workers. The [4 + 2] cycloadditions yielding the *endo-trans*-tricyclic compounds occurred to a variable extent depending on the photocatalyst used, since competing [2 + 2] reactions might take place. The highest [4 + 2]/[2 + 2] ratio (ca. 7) was observed in DCA-catalyzed experiments.

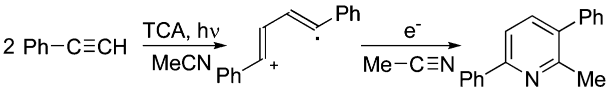
As a matter of fact, [2 + 2] cycloadducts or open chain dimers were often formed as side products in photocatalyzed Diels−Alder reactions.[296,340−345] A representative example is shown in Scheme 73. Thus, irradiation of a benzene solution of DCA (2×10^{-2} M) containing cyclohexadiene (0.21 M) and 1-(trimethylsilyloxy)-1-methoxyethene (**65**, 0.86 M) gave a mixture of *endo* and *exo* [2 + 2] and [4 + 2] cross-coupling cyclized products along with the cyclohexadiene dimers.[345] Acidic hydrolysis of the silicon-containing products yielded ketones **66** and **67** in a 1:3 ratio.

Scheme 73



Finally, in the attempted cyclodimerization of phenylacetylene in MeCN, a diphenylpyridine was isolated as the main product. This compound was envisaged as arising from trapping by the solvent of the dimeric radical cation intermediate (Scheme 74).[346]

Scheme 74



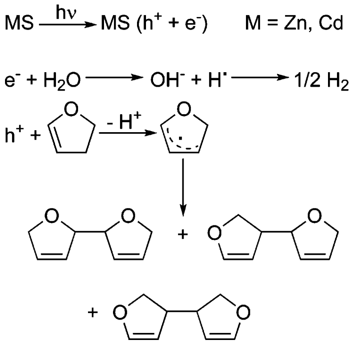
4.5. Radical Coupling

In previous sections, a few cases have been presented in which the C−C forming step involves two radicals or radical ions. However, (at least) one of such intermediates was generated from the reduction of a C−C or C−X multiple bond (see, e.g., Scheme 45), and such reactions have been discussed in the section reviewing additions to such bonds. In other instances that will be reviewed in the present section, the C−C bond is formed by coupling of radicals, both of which arise from the activation of sp^3 carbons according to eq 3.

$$\text{R-X} + \text{R}'\text{X}' \rightarrow \text{R-R}' \qquad (3)$$

Thus, semiconductor-photocatalyzed oxidation of organic substrates ($RX \rightarrow RX^{\bullet +}$) represented an easy access to carbon-centered radicals via deprotonation (for $X = H$) or fragmentation of another σ C−X bond. When the radicals were persistent and conditions favorable to accumulation, dimerization and formation of a C−C bond was a main process. Most of the reactions pertaining to this class involved dihydrofuran or -pyran as organic substrates. The process was often studied in water, where a concomitant evolution of hydrogen took place (actually, this was the main target of the study, the organic substrate being the 'sacrificial' donor, compare section 1).[347−351] The general mechanism is depicted in Scheme 75.

Scheme 75

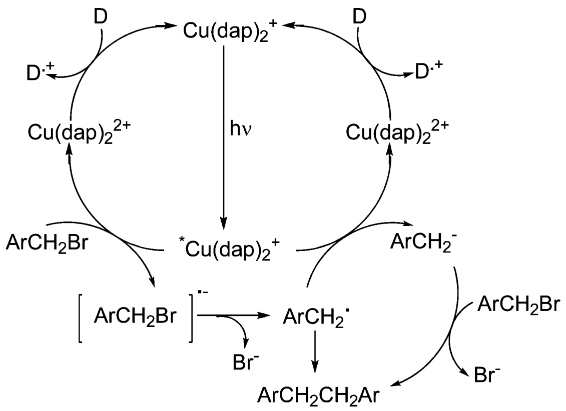


The use of semiconductor sulfides MS (M = Cd,[347] Zn[348−351]) made possible, as mentioned before, both electron (e^-) and hole (h^+) transfer upon photolysis (compare Scheme 2). The former species reduced water to hydrogen, whereas the latter gave rise to a dihydrofuran radical via hole transfer oxidation-deprotonation sequence. As a result, a statistical mixture of regioisomeric dehydrodimers was isolated at the end of the reaction (type A in the classification by Kisch, see section 4.2.). In the case of ZnS, a heterogeneous mixture of aqueous ZnS suspension could be used, and turnover numbers were usually high (ca. 3000). When using cyclohexene, the reaction likewise gave the dimer in position 3,3′.[350] On the other hand, dimers of cyclohexene or other cycloalkenes were also obtained under homogeneous rather than heterogeneous conditions by using TBADT as the photocatalyst (MeCN as the solvent).[352] In this case, an allylic hydrogen abstraction was envisaged as the first step, and TBADT was regenerated by reaction with heterogeneous oxidants such as RuO_2. In some cases, the photocatalyst was in turn prepared by photolysis of a metal complex as it was the case for metal dithiolenes that were used as ZnS precursors.[353]

TBADT was also able to abstract a α-hydrogen from dimethylsulfide. 1,2-Bis(methylthio)ethane from the dimerization of the thioether α-carbon radicals was detected as the major product (ca. 90% of the total products).[354]

Bibenzyls were an obvious target to be obtained by a radical dimerization process. Benzyl radicals could be generated by ET photocatalysis, both reductive and oxidative. In the former case, benzyl halides (usually bromides) were generally used as substrates in the presence of inorganic redox photocatalysts, as depicted in Scheme 76.

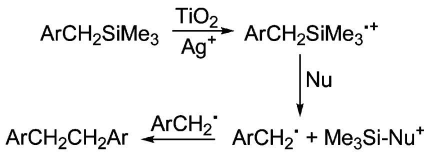
Scheme 76



Thus, the excited $Cu(dap)_2^+$ cation [dap = 2,9-bis(*p*-anisyl)-1,10-phenanthroline] gave benzyl radicals by reduction of benzyl bromides and bromide loss. These radicals either dimerized yielding bibenzyls or possibly were reduced to anions, which in turn reacted with the starting bromide.[355] In this way, (4,4′-di-*p*-nitro)bibenzyl was prepared in 47% yield with a turnover number of the catalyst of ca. 30. The initial copper complex was restored by reduction by a sacrificial donor (triethylamine, D in Scheme 76) present in excess in solution. Other inorganic photocatalysts such as $[Au_2(\mu\text{-dppm})_2]^{2+}$[356] and $[Ru(bpy)_3]^{2+}$ (the latter in the presence of 1-benzyl-1,4-dihydronicotinamide as secondary donor[357]) gave similar results.

An oxidative pathway was conversely adopted in the synthesis of diarylethanes from alkylbenzenes, aryl-2-propanols, or benzyltrimethylsilanes.[358,359] Photocatalysis using TiO_2 in the presence of silver sulfate gave the best results with the silyl derivatives (50−74% yield of bibenzyl), due to the easy elimination of the $SiMe_3^+$ cation in this case (Scheme 77).[358]

Scheme 77



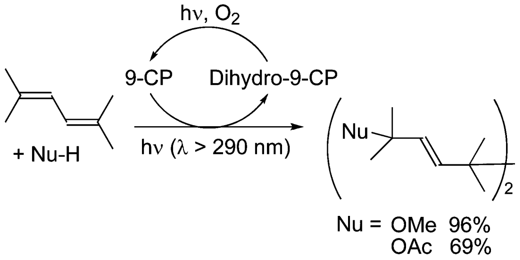
Silver salts were required to trap the valence electrons, so that internal electron return in the semiconductor was slowed down. Oxygen was found to be a less efficient oxidizing agent. In some cases, the benzyl radicals abstracted hydrogen from the solvent (acetonitrile) or were further oxidized to benzyl cations originating byproducts.[359]

Another class of stabilized radicals that underwent dimerization is that of α-amino radicals, easily produced by photoinduced ZnS oxidation of tertiary amines, as reported by Yanagida et al.[360] Thus, irradiation of a suspension of ZnS in a triethylamine/water mixture gave 2,3-bis(diethylamino)butane in a low yield besides other byproducts.

Recently, Mizuno reported an interesting PET dimerization of 2,5-dimethyl-2,4-hexadiene occurring under photocatalysis (ca. 30% mol equiv) by 9-cyanophenanthrene (9-CP, Scheme 78).[361]

The monoelectronic oxidation of the diene followed by nucleophilic addition (e.g., by an alcohol or an acid) afforded a stabilized allylic (and tertiary) radical, which in turn dimerized. Variable amounts of alkylated 9-CP were also observed in some cases. The presence of a small amount of oxygen was crucial for the success of the reaction, which was inefficient both in the absence of O_2 and in the presence of a large amount of it. Interestingly, the photocatalyst was

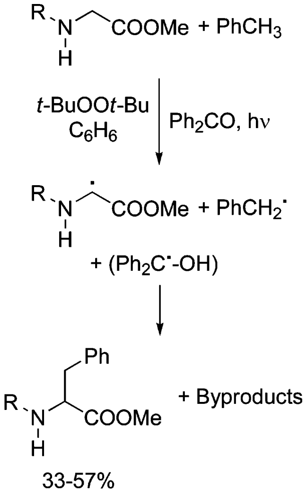
Scheme 78



regenerated by a further photochemical step since dihydro-9-CP formed in the reaction was thermally quite stable, but was readily photooxidized.[361]

A case of radical heterocoupling, though by no means through a clean reaction, was also reported and involved the photoalkylation of aminoacids or peptides.[362−365] The strategy was based on the photochemical H abstraction from the α position of the aminoacid and subsequent reaction either with a double bond (compare section 4.1.4.) or, more often, with another photogenerated radical to obtain branched aminoacids. After the pioneering studies by Elad and Sperling,[362] where the photocatalyst (acetone) was used as the solvent, recently BP (up to 5 mol equiv) was used for this purpose. Thus, irradiation of a mixture containing a glycine derivative, toluene, *t*-butyl peroxide, and benzophenone in benzene afforded phenylalanine derivatives in a modest yield besides other radical coupling products (Scheme 79).[364,365]

Scheme 79



Notice also that in some photocatalyzed alkylations of a C=X bond, carbon−carbon bond formation actually involved a radical heterocoupling. Since here attention is given to the overall reaction rather than to mechanism, these examples have been presented in section 4.2.

5. Conclusions and Outlook

Most of the topics presented here have been previously reviewed separately, although the term photocatalysis in the meaning defined here has been rarely applied to such reactions. We do think that all the processes gathered here have something in common and have an analogy with thermal catalysis that is worthwhile appreciating, and thus, that it is appropriate to present all of them under the common heading of photocatalytic methods.

We feel that this class of reactions represents an important contribution photochemistry can give to 'green' organic synthesis, and the viability of some of the processes considered is credible at this stage. Examination of the potential environmental impact of comparable photocatalyzed and thermal reactions indicates that the former ones are in most cases largely preferable.[366] Such reactions are often less expensive, since they feature shorter reaction sequences, better atom economy, mild conditions, and simple work up. Phosphor-coated lamps for the near-UV are efficient and unexpensive, and the cost of lamp alimentation and maintainance is usually not a concern. Furthermore, having recourse to solar irradiation has been demonstrated to be a sensible choice in several cases.[367,368] The apparatus required for gram-scale synthesis is simple and inexpensive, and thus, the use of photocatalyzed steps in exploratory syntheses appears to suffer from no limitation.

The only concern seems to be that photochemical reactions are usually carried out under dilute conditions, in order to make light absorption (relatively) uniform throughout the solution. This requires that solvent recovery is accurately planned, a requirement, however, that is nowadays common to all chemical processes and is in part compensated for by avoiding the toxic and aggressive reagents all-to-common in thermal syntheses. At any rate, improvements to solve this problem have been proposed, such as the use of falling film reactors, where more concentrated solutions are used and exposed to strong light sources,[369] or continuous flow reactors that are more versatile and are better suited for scaling-up and potentially for separating the product while it is formed.[370] Scaling-up introduces more complex issues, as indeed for every industrial process. However, every time that this problem has been confronted with a photoinduced reaction, sensible solutions have been found, indeed, even using solar light.[371]

It is therefore reasonable to expect that photochemistry will develop its synthetic potential in the near future and in particular photocatalysis for C−C bond formation will be more extensively applied as the environmental cryteria become determining factors. Indeed, the above-mentioned characteristics of photocatalyzed reactions should be compared with the conditions, generally deemed mild, of transition metal catalysis, usually requiring a sophisticate operation, control of temperature, air exclusion, and so forth. This makes it possible to generate highly active intermediates in the absence of aggressive (or labile) reagents and, thus, allows a much better control of the process and a versatile application. On the other hand, the same characteristics make these processes much more environmentally friendly.

6. Abbreviations

BET	Back electron transfer
BP	Benzophenone
9-CP	9-Cyanophenanthrene
DA	Diels−Alder
DCA	9,10-Dicyanoanthracene
DCB	1,4-Dicyanobenzene
DCN	1,4-Dicyanonaphthalene
DCTMB	1,4-Dicyano-2,3,5,6-tetramethylbenzene
DMN	1,4-Dimethoxynaphthalene
DMP	Dimethyl terephthalate
ET	Electron transfer
NMQ	*N*-Methylquinolinium
PET	Photoinduced electron transfer
Phen	Phenanthrene

PVE	Phenyl vinyl ether
TBADT	Tetrabutyl ammonium decatungstate
TCA	2,6,9,10-Tetracyanoanthracene
TCB	1,2,4,5-Tetracyanobenzene
TMPM	Tetramethyl pyromellitate
TPP	2,4,6-Triphenylpyrylium tetrafluoroborate
λ_{irr}	Irradiation wavelength

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8. Note Added in Proof

The photocatalytic generation of acyl radicals from aldehydes and their addition to electrophilic alkenes has been reported (compare Sec. 4.1.5).[372] An account on the synthetic application of photocatalytically generated α-amino radicals has been published (compare Sec. 4.1.4 and 4.3.4).[373] The photocatalyzed alkylation of some phenylcyano-*N*-benzoylimines by cycloalkenes has been obtained by using CdS but only when supported on ZnS (compare Sec. 4.2).[374]

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