

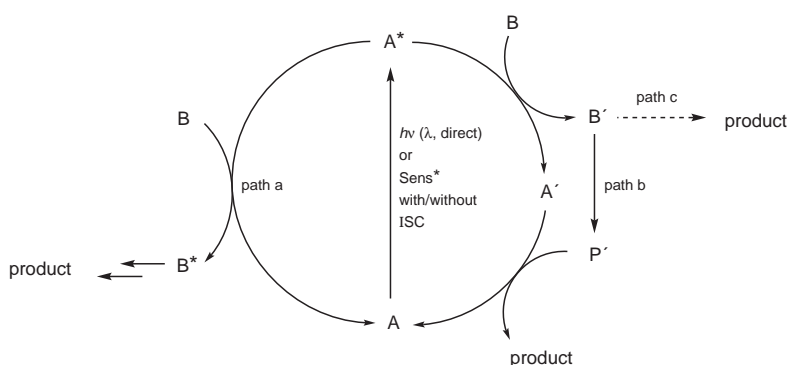
Abstracts

p 3

2 Photocatalysis: The Principles

F. Gaida, A. G. Griesbeck, and M. Vollmer

Understanding photocatalysis requires knowledge of the primary and secondary photochemical and photochemical processes: light absorption and emission, radiationless decay, energy and electron transfer, and hydrogen and group transfer. Photocatalysis is largely dictated by energy and spin restrictions that allow fast transfer of energy, electrons, or atoms. The kinetics of photoredox-initiated catalysis can be estimated from the redox properties of the electronic ground states as well as the excitation energies and spin properties of the excited states involved. These principles are demonstrated using three model processes: photochemical decarboxylation, fluorination/fluoroalkylation, and (molecular) oxygen-transfer processes.



Keywords: photocatalysis · photochemistry · photolysis · homogeneous catalysis · heterogeneous catalysis · asymmetric catalysis · transition-metal catalysis · ruthenium catalysts · iridium catalysts

p 101

3 Practical Aspects of Photocatalysis

E. Speckmeier and K. Zeitler

Visible-light photocatalysis has emerged as a versatile, important tool for organic synthesis, often allowing for complementary approaches to more traditional transformations. This chapter summarizes general practical aspects for the conduction of (visible light) photochemical and photocatalytic reactions, focussing on irradiation sources and experimental setups both for batch and flow reactions, including special equipment for NMR and EPR spectrometers, autoclaves, or ball mills. A short overview of typical experiments and approaches to elucidate basic mechanistic information is additionally provided.

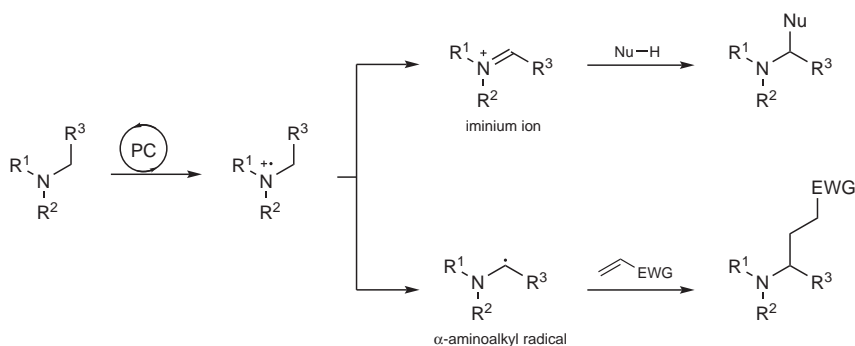


Keywords: photocatalysis · irradiation sources · reactors · flow chemistry · control experiments · quantum yield · electron transfer · LEDs · visible light · green chemistry · photochemistry · radicals

4 Photocatalytic Oxidative C–C Bond Formation

G. Pandey and R. Laha

This chapter summarizes some important examples of carbon–carbon bond-forming reactions at the α -position of tertiary amines using photoredox catalysis. The photocatalytic single-electron oxidation of tertiary amines leads to the generation of an amine radical cation, from which two highly reactive and synthetically useful intermediates, iminium ions and α -aminoalkyl radicals, can be produced. Iminium ion intermediates, being electrophilic in nature, react with a range of carbon nucleophiles forming new carbon–carbon bonds. On the other hand, the α -aminoalkyl radical, an electron-rich radical, adds efficiently to electron-deficient unsaturated systems resulting in carbon–carbon bond-forming reactions. This chapter also highlights some examples of carbon–carbon bond-forming reaction by nucleophilic/radical addition to photocatalytically generated arene radical cations.



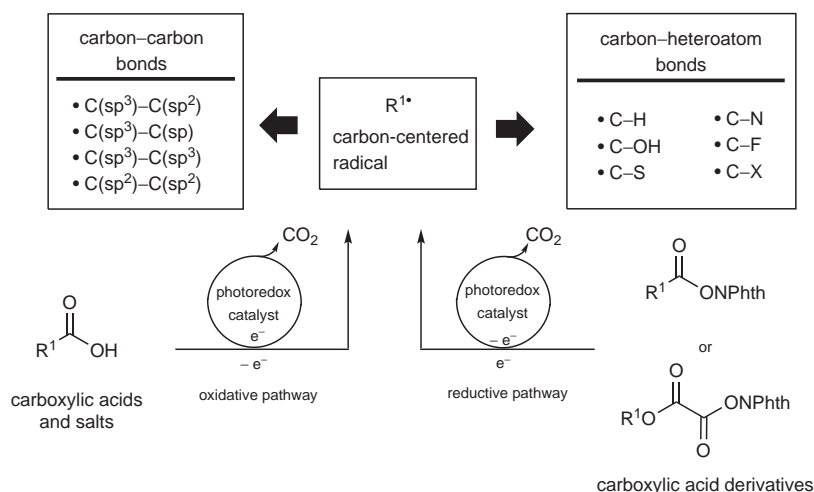
PC = photocatalyst; EWG = electron-withdrawing group; Nu = carbon nucleophile

Keywords: photocatalysis · photoredox catalysis · carbon–carbon bond formation · tertiary amines · iminium ions · α -aminoalkyl radicals · arene radical cations · cross coupling · aza-Henry reaction · Mannich reaction · Friedel–Crafts reaction · Strecker reaction · Sakurai reaction · radical addition · Michael addition · radical–radical coupling · heteroarylation · arylation · carbocyclization · acylation · alkylation

5 Decarboxylative Coupling Reactions

Q.-Q. Zhou, Y. Wei, L.-Q. Lu, and W.-J. Xiao

The radical decarboxylative functionalization of carboxylic acids and their derivatives using visible-light photoredox catalysis has been established as an efficient method for carbon–carbon and carbon–heteroatom bond formation. The generation of carbon-centered radicals through the single-electron oxidation or reduction process under mild reaction conditions, together with the further reaction with a variety of organic reagents, allows diverse transformations of readily available carboxylic acids and their derivatives. In this chapter, the most recent advances in the field of visible-light-photocatalytic decarboxylative coupling reactions are highlighted.

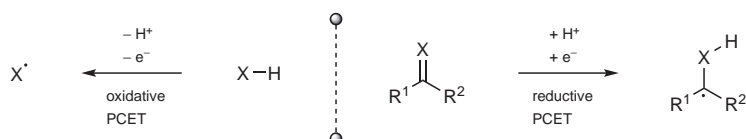


Keywords: photocatalysis • photoredox • carboxylic acids • carboxylates • esters • carbon–carbon bond formation • carbon–heteroatom bond formation • decarboxylative coupling

6 Proton-Coupled Electron Transfer

S. M. Thullen, M. A. Ashley, and T. Rovis

Proton-coupled electron transfer (PCET) enables the functionalization of prevalent organic moieties that are commonly regarded as energetically inaccessible. This chapter focuses on reductive and oxidative PCET in organic systems and the variety of catalyst systems that allow for the formation of ketyl and amidyl radicals for C–C and C–N bond-forming reactions.

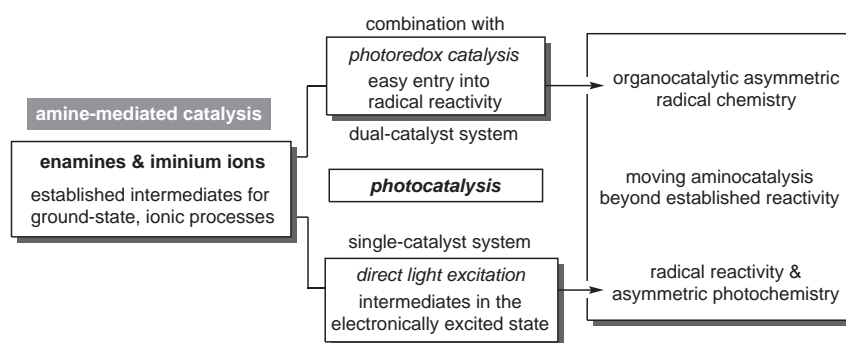


Keywords: photocatalysis • proton-coupled electron transfer • oxidative PCET • reductive PCET • amidyl radicals • ketyl radicals • homolysis • radical cyclization • [1,5]-hydrogen-atom transfer • asymmetric induction

7 Organocatalysis with Amines in Photocatalysis

Y. P. Rey, H. B. Hepburn, and P. Melchiorre

This chapter details recent advances in enantioselective amine-catalyzed reactions triggered by light. By presenting a selection of pioneering studies, the chapter highlights how the combination of photochemistry and amine-mediated catalysis has created exciting new opportunities in asymmetric synthesis while profoundly influencing different fields of modern chemical research, such as radical reactivity. The discussion focuses on the concepts of enamine and iminium ion mediated reactions and their combination with photochemical reactivity. The selected methods represent the state of the art in the rapidly evolving area of photochemical amine-catalyzed processes, which provides effective synthetic tools for making chiral molecules sustainably.

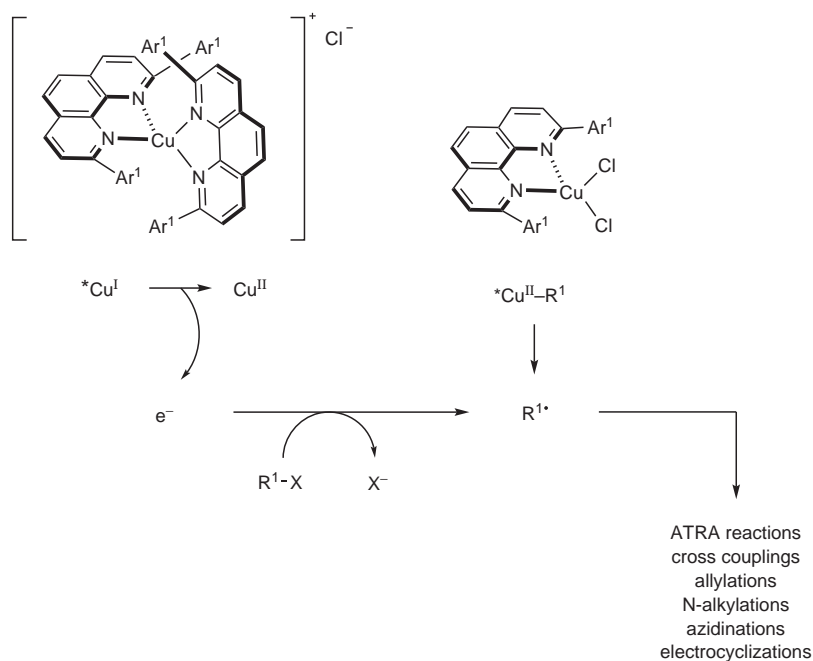


Keywords: photocatalysis · amines · asymmetric catalysis · enamines · iminium ions · electron transfer · organocatalysis · radical reactivity · photochemistry · redox processes

8 Copper-Based Photocatalysts for Visible-Light-Mediated Organic Transformations

P. Ehrnsberger and O. Reiser

Copper(I) and copper(II) complexes prove to be a powerful alternative to common photocatalysts based on ruthenium, iridium, or organic dyes. A distinct feature is their ability to interact with substrates beyond electron or energy transfer, allowing unique transformations that are otherwise not possible.

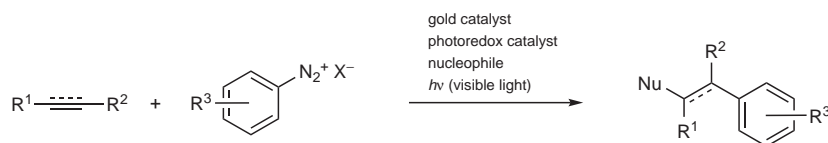


Keywords: photocatalysis · asymmetric synthesis · aziridines · cycloadditions · cyclobutanes · cyclopropanes · Diels–Alder · endoperoxides · Lewis acids · nitrenes · photochemistry · radical anion · radical cation · triplet state · visible light · [2+1] · [2+2] · [3+2] · [4+2] · [2+2+2]

9 Gold in Photocatalysis

M. N. Hopkinson and S. Dix

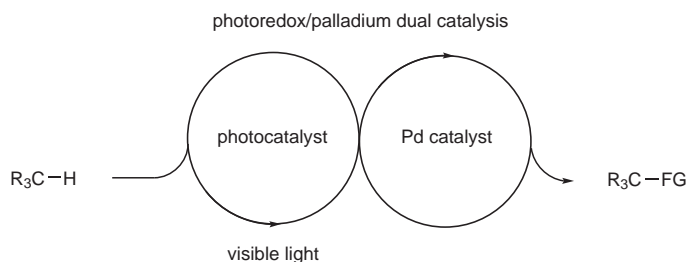
Dual catalytic systems combining gold and photocatalysis are capable of facilitating redox-neutral coupling reactions that are otherwise seldom observed using gold catalysts alone. The challenging oxidation of gold(I) to gold(III) in these processes is achieved through two single-electron-transfer steps involving photogenerated organic radicals derived most commonly from arenediazonium salts. In addition to analogues of some classical cross-coupling processes that are tolerant of halogen functionalities, arylation 1,2-difunctionalization reactions of π -systems, combining the traditional π -Lewis acidity of gold catalysts with coupling, are accessible. These processes can be performed on alkene, allene, and alkyne substrates with the unique mechanistic features of dual gold/photoredox catalysis allowing for improved selectivity for cross coupling compared to that observed in alternative oxidative gold-catalyzed coupling methodologies.



Keywords: photocatalysis · gold catalysis · photoredox catalysis · cross coupling · 1,2-difunctionalization · arylation · diazonium salts · dual catalysis · visible light · alkenes · allenes · alkynes · redox-neutral coupling · radical intermediates · aryl radicals

10 Palladium in Photocatalysis*M. Wang, P. Li, and L. Wang*

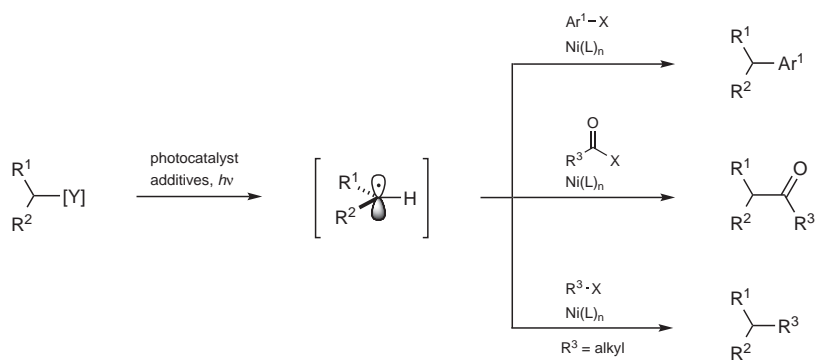
The concept of photoredox/transition-metal dual catalysis has been validated as a powerful platform for the construction of carbon–carbon and carbon–heteroatom bonds, and it illustrates the power of rational design in catalysis and the strategic use of mechanistic knowledge and manipulation for the development of novel synthetic methods. This chapter describes recent progress in the combination of visible-light photoredox catalysis with palladium catalysis, highlighting this as a valuable synthetic tool in accessing complex molecules in a rapid and modular fashion.



Keywords: photocatalysis · palladium · visible light · photoredox · dual catalysis · C–H functionalization · C(sp²)–H arylation · C(sp²)–H acylation · intramolecular alkenation · intramolecular C–H amination · oxidative carbonylation · α -allylation of amines · decarboxylative allylation · acceptorless dehydrogenation

11 Nickel in Photocatalysis*C. B. Kelly, J. K. Matsui, J. P. Phelan, Á. Gutiérrez Bonet, S. B. Lang, and G. A. Molander*

Robust methods to forge C–C bonds selectively are treasured by the chemical community because of the inherent value of such processes in the convergent construction of complex molecules and the notorious challenges associated with creating such linkages. The advent of cross-coupling technologies (e.g., Suzuki, Negishi, and Heck processes) has revolutionized how synthetic chemists establish C(sp²)–C(sp²) bonds. However, the mechanistic features that make these transition-metal-catalyzed processes ideal for this type of transformation are the same ones that limit their abilities to involve C(sp³)-hybridized species. In this chapter, a recently developed solution to the underlying challenge of engaging C(sp³)-hybridized nucleophiles in cross coupling is outlined: nickel/photoredox dual catalysis. By proceeding through radical intermediates, the enthalpic penalty for two-electron transmetalation can be side-stepped, and cross coupling can proceed under mild, functional-group-tolerant conditions. Several variants of this dual catalytic process are presented which, taken together, demonstrate the breadth and scope of this new cross-coupling paradigm.



[Y]: BF_3^- , CO_2^- , bis(catecholato)silicate, 1,4-dihydropyridin-4-yl, H, OH, etc.
 photocatalyst = $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{bipy})]\text{PF}_6$, 4CzIPN, etc.
 X = I, Br, OTs, Cl, etc.

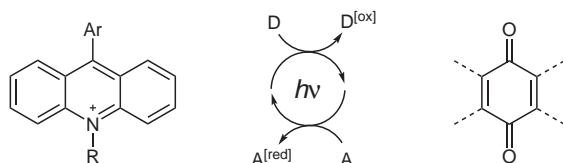
Keywords: photocatalysis • radicals • photoredox • cross coupling • single-electron transmetalation • nickel catalysis • single-electron transfer • hydrogen-atom transfer • visible light

p 371 —

12 Acridinium Dyes and Quinones in Photocatalysis

M. Brasholz

Acridinium dyes and quinones are two classes of powerful organic photooxidants. This chapter reviews the most important types of photocatalytic transformations mediated by these dyes, including photooxygenations, radical conjugate additions and cyclizations, radical cation cycloadditions, and oxidative C–H functionalizations.

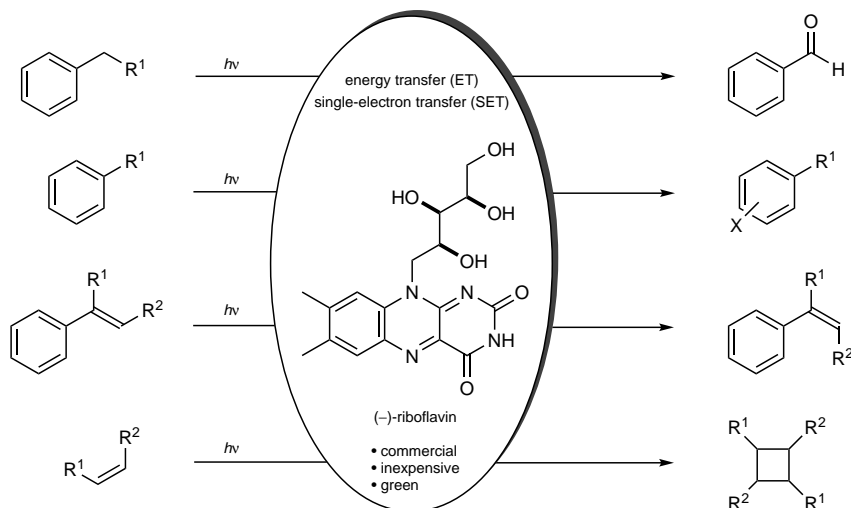


Keywords: photocatalysis • organic dyes • photooxidation • radical addition • cycloaddition • C–H functionalization

13 Flavins in Photocatalysis

J. B. Metternich, R. J. Mudd, and R. Gilmour

Inspired by naturally occurring biological processes, flavins have proven to be versatile organic frameworks for a wide variety of catalytic, photochemical procedures. Grounded in the photochemical activation mechanisms that are synonymous with flavins, this chapter surveys the photophysical and structural foundations of selected examples in flavin photocatalysis.

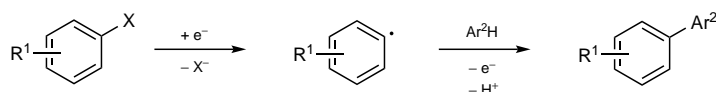


Keywords: photocatalysis • (–)-riboflavin • flavins • flavinium salts • biomimetic • energy transfer • electron transfer • photoredox • oxidation • halogenation • cycloaddition • isomerization • cyclization • benzylic alcohols • cyclobutanes • aryl halides • alkyl halides • α,β -unsaturated carbonyl compounds • α,β -unsaturated nitriles • coumarins

14 Organic Dyes in Photocatalytic Reductive C–H Arylations

I. Ghosh

In recent years, visible-light photoredox catalysis has gained enormous attention as an energy-efficient and versatile method for chemical synthesis. This chapter presents synthetically important C–H arylation reactions using inexpensive organic dyes (e.g., eosin Y, rhodamine 6G, perylene bisimides, etc.) under visible-light photoredox catalytic reaction conditions. Single-electron transfer to arenediazonium salts or aryl halides leads to the formation of aryl radicals, which, under the reaction conditions, react with (het)arenes to yield the respective C–H arylated products.

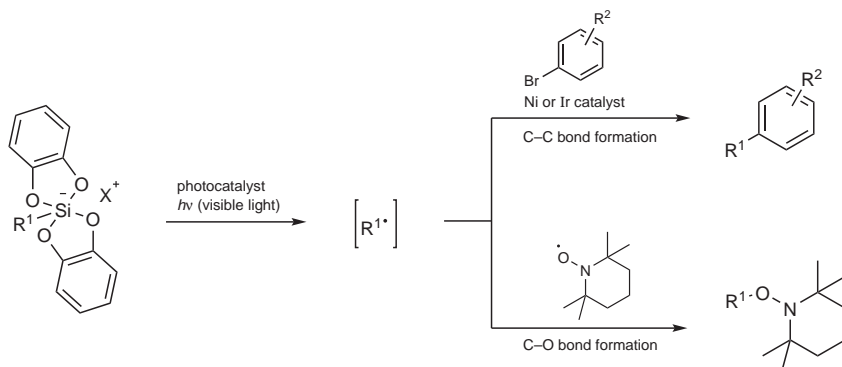
X = N₂⁺, I, Br, Cl, F

Keywords: photoredox catalysis • visible light • C–C bond formation • C–H arylation reactions • C–H heteroarylations • organic dyes • transition-metal free • aryl halides • arenediazonium salts • single-electron transfer • dehalogenation • consecutive photoinduced electron transfer (conPET) • radical reactions • chemoselective reactions

15 Silicates in Photocatalysis

V. Corcé, C. Lévêque, C. Ollivier, and L. Fensterbank

Bis(catecholato)silicates have emerged as robust alkyl radical sources under photocatalysis. This chapter describes the preparation of various silicates and their utilization under photocatalytic conditions for the formation of C–C and C–O bonds. The last section focuses on the use of silicates in photoredox/nickel dual catalysis.

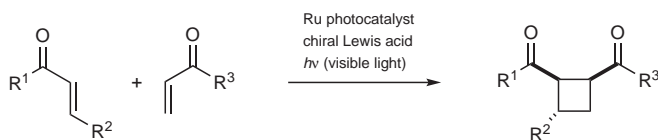


Keywords: photocatalysis • bis(catecholato)silicates • silicates • photoredox/nickel dual catalysis • photooxidation • C–C bond formation • C–O bond formation • alkyl radicals

16 Photocatalytic Cycloadditions

A. G. Amador, S. O. Scholz, K. L. Skubi, and T. P. Yoon

Photochemical cycloadditions are powerful tools for the rapid construction of molecular and stereochemical complexity. Recent advances in visible-light photocatalysis have provided novel methods involving the generation of radical ion, neutral radical, and triplet excited-state intermediates that can participate in a variety of cycloaddition processes. This chapter highlights recent methods in this area for the synthesis of three-, four-, five-, and six-membered-ring systems.

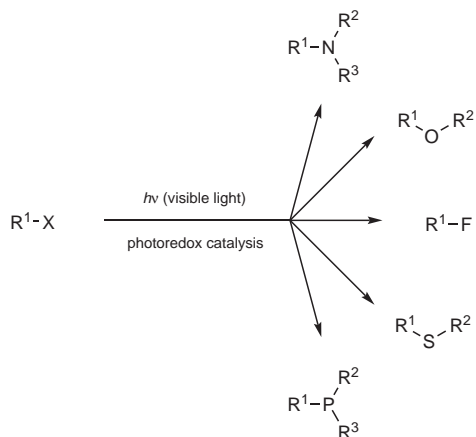


Keywords: photocatalysis • asymmetric synthesis • aziridines • cycloadditions • cyclobutanes • cyclopropanes • Diels–Alder • endoperoxides • Lewis acids • nitrenes • photochemistry • radical anion • radical cation • triplet state • visible light • [2 + 1] • [2 + 2] • [3 + 2] • [4 + 2] • [2 + 2 + 2]

17 Photocatalytic Carbon–Heteroatom Bond Formation

A. Ruffoni and D. Leonori

This chapter summarizes recent developments in the field of visible-light-mediated photoredox catalysis in the context of carbon–heteroatom bond formation. The discussion is organized by heteroatom, with further subgroups based on specific functionalities. Emphasis is placed on the scope and limitations of the reactions described.

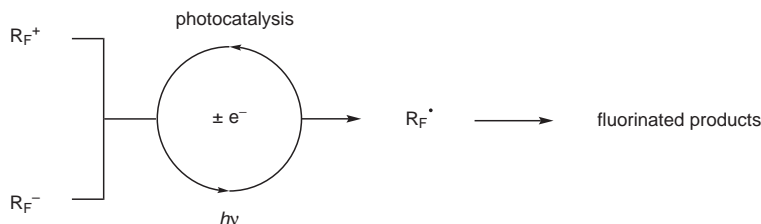


Keywords: photocatalysis · arylation · carbon–heteroatom bonds · carbon–nitrogen bonds · carbon–oxygen bonds · carbon–phosphorus bonds · fluorination · free radicals · photochemistry · radical cyclization · radical reactions · radicals

18 Photocatalytic Introduction of Fluorinated Groups

T. Koike and M. Akita

Fluorinated groups are prevalent in pharmaceutical and agrochemical compounds as they significantly influence the absorption, distribution, metabolism, and excretion properties of a molecule in biological systems. Photocatalytic radical processes enable the facile introduction of fluorinated groups into various organic skeletons. This chapter presents recent representative works and standard procedures to achieve such processes.

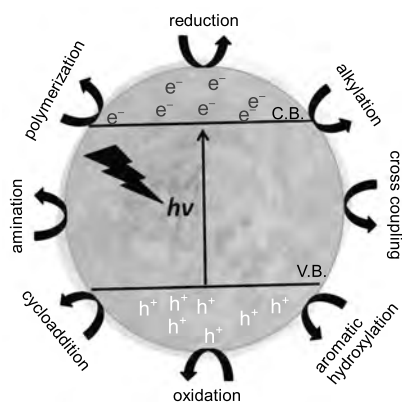


Keywords: photocatalysis · fluorine · alkenes · alkynes · enamines · isocyanides · arenes · thiols · alkanes · trifluoromethyl · difluoromethyl · monofluoromethyl · fluorination · difluoroalkyl · monofluoroalkyl

19 Heterogeneous Photocatalysis in Organic Synthesis

J. Albero and H. García

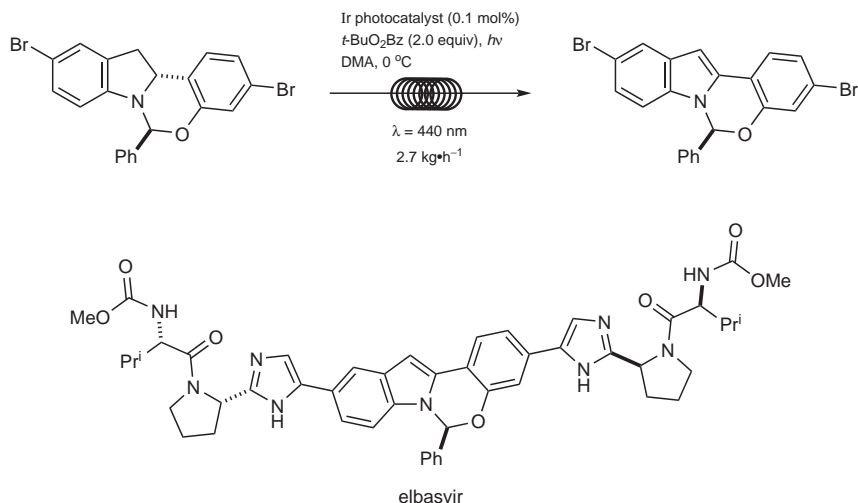
In recent years, heterogeneous photocatalysis has emerged as a very appealing approach, not only for the degradation of pollutants, but also for the synthesis of chemicals. Although the main use of heterogeneous photocatalysis so far has been the mineralization and complete degradation of organic compounds, interest in the application of heterogeneous (photo)catalysts in organic synthesis is growing due to their potential application in the fabrication of renewable fuels as well as in the preparation of compounds and intermediates especially valuable to the chemical industry, such as pharmaceuticals or polymers. The synthesis of organic molecules assisted by heterogeneous photocatalysts has been dominated by the use of inorganic metal oxide semiconductors, especially titanium(IV) oxide; the use of other semiconductor materials, such as inorganic chalcogenides, carbon-based semiconductors, or metal–organic frameworks has been less explored. In this chapter we show that, in spite of the potential and the large number of heterogeneous photocatalysts already studied, the state of the art of heterogeneous photocatalysis in organic synthesis is still unsatisfactory and much below expectation, particularly in reactions other than oxidation and reduction, such as cross couplings, oxidative decarboxylations, and cycloadditions.



Keywords: photocatalysis • heterogeneous catalysis • semiconductors • metal oxides • titanium(IV) oxide • charge separation • metal–organic frameworks (MOF) • graphene • oxidation • reduction • cross coupling • cycloaddition

20 Photocatalysis in the Pharmaceutical Industry*D. A. DiRocco and D. M. Schultz*

Applications of visible-light-photocatalyzed transformations utilized throughout drug development are highlighted. Specifically, transformations that proceed on both small and large drug-like targets, provide direct access to unique derivatives, and are amenable to scale up are discussed. Moreover, several industrial-academic collaborations are presented to showcase the development of new photochemical methodologies to address current synthetic challenges.



Keywords: photocatalysis · radicals · hetarenes · Minisci · methylation · oxidation · met-
allaphotoredox · dual catalysis · Smiles · oxyfunctionalization · decatungstate · flow ·
deuteration · tritiation · formylation · sulfonylation · decarboxylation · macrocyclization ·
perfluoroalkylation · fluorination · dehydrogenation