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Harnessing C–H Activation and Photoredox Catalysis in Organic Synthesis: A Contemporary Review

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Abstract

C–H activation and photoredox catalysis have become complementary and are leading to the synergistic integration into a new potent approach to modern organic synthesis that is highly selective, efficient, and sustainable in its ability to transform molecules. Site-selective functionalization of inert C-H bonds is achieved through C-H activation, and the formation of reactive radical intermediates in mild conditions under visible light is achieved through photoredox catalysis. Their combination enables two-catalytic processes, which provides the possibility to build new bonds and functionalize functional groups late, as well as bring complex molecules, such as natural products, pharmaceuticals, and heterocycles, into easy reach. Recent developments include the emphasis on environmentally friendly procedures, widening the range of substrates, and reaction design that is guided by calculations. This review has outlined key principles, mechanistic understanding, applications, challenges and emerging trends in this field of synthetic chemistry with particular focus on its transformative nature through this dual approach.

Key words

C–H activation, photoredox catalysis, dual catalysis, visible-light reactions, late-stage functionalization.

Introduction

The strategic creation and conversion of carbon -hydrogen (C-H) bonds are some of the most common and inert bonds in organic molecules that have long been critical to organic synthesis. In the past, functionalization of organic compounds necessitated pre-activated substrates or multi-step sequences, and usually resulted in less atom economy, reduced complexity of synthetic pathways, and greater wastage [1]. Here, C-H activation has proved to be a groundbreaking one with chemists being able to directly convert C-H bonds to C-C, C-N, C-O, and other bonds in an efficient and selective fashion. The methodology does not only simplify synthetic paths but it also allows one to synthesize previously difficult or inefficiently synthesized molecules [2]. During the last 20 years, there has been a notable advance in the evolution of transition-metal-catalyzed C–H activation, and especially with palladium, rhodium, ruthenium and iridium catalysts that have shown exceptional regio- and chemoselectivity in the structure of complex molecules [3].

Coexisting with these developments, photoredox catalysis has also become an important instrument in the contemporary organic chemistry. Photoredox catalysis enables the use of visible light to drive single-electron transfer (SET) reactions to produce highly reactive radical intermediates in mild conditions by use of visible light along with photocatalysts typically transition-metal complexes or organic dyes [4]. This method has transformed the capability of undertaking redox transformations and has allowed new types of bond formation that are challenging to accomplish using thermal or metal-catalyzed redox transformations [5]. Photoredox catalysis is an extremely appealing approach to both research and practice in the academic sector and industry because of the mild reaction conditions, high-function-group tolerance, and its compatibility with sustainable energy sources [6].

The combination of C-H activation with photoredox catalysis is an important advancement in the synthetical protocol. The combination of these two methods allows chemists to combine the strengths of either method: site-selectivity and ability to form covalent bonds with C–H activation, and the ability to generate radicals and cover redox reactions of photoredox systems [7]. This synergy has given rise to new kinds of synthetic transformations, such as late-stage functionalization of complex molecules, direct arylation and alkylation of unactivated C H bonds, and easy access to heterocycles and bioactive molecules [8].

The objective of this review is to present an overview of recent developments in the field of C-H activation and photoredox catalysis together. We shall talk about some of the principles, some mechanistic insights, some of the applications in the synthesis of organic molecules and the emerging trends as well as the challenges that characterise this fast changing field. This review attempts to outline major breakthroughs to guide researchers in the development of effective and sustainable methods to complex molecular construction with a strong focus on the transformative nature of combining these two potent technologies [9].

Principles of C–H Activation

C–H activation is one of the greatest developments in contemporary organic synthesis, which allows direct functionalization of carbon-hydrogen bonds, without necessarily using pre-functionalized starting materials. Historically, C -H bonds were regarded as chemically inert because such bonds have high bond dissociation energies and are not polar, and the selective transformation of such bonds is extremely difficult [10]. Nevertheless, with the invention of transition-metal catalysis, chemists have been able to address these drawbacks, and now have methods to selectively cleave and functionalize C-H bonds with incredible specificity. This methodology has not only made the synthesis of pathways simplified, but has also led to an increase in atom economy, waste minimization, and the number of synthetic steps that are undertaken to produce complex molecules have also been reduced [11].

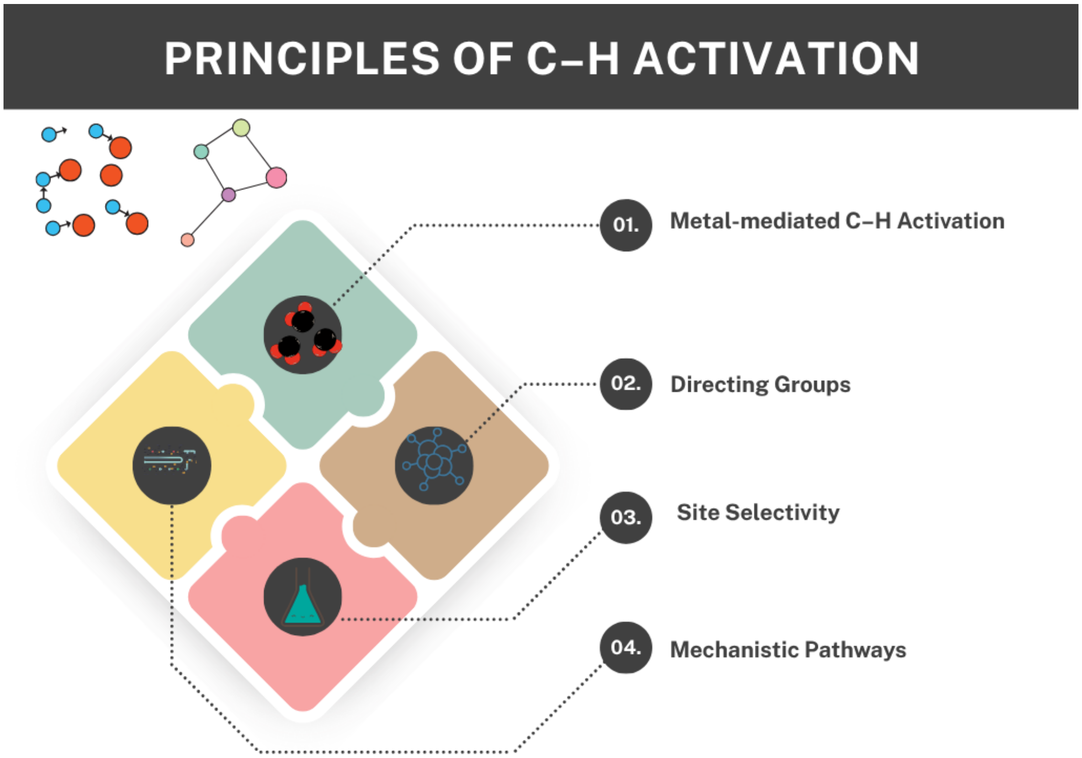

Figure: 1 showing principles of C-H activation

Mechanistically: C -H activation is frequently dependent on a metal catalyst forming a transient bond of metal with the substrate. Palladium, rhodium, ruthenium, iridium, and cobalt (transition metals) have been studied widely because of their unusual electronic characteristics, permitting them to catalyze either oxidative addition, or σ-bond metathesis, or concerted metalation-deprotonation reactions [12]. These routes allow the breaking of otherwise inert C-H bonds, and the further conversion to C-C, C-N, C-O or C-X (halogen) bond. Metals, ligands and reaction conditions are critically determined to affect reactivity and selectivity of the reaction enabling site-specific functionalization of complex molecules [13].

This is one of the main issues in C–H activation: selectivity. The existence of different C-H bonds with close electronic and steric surfaces tends to cause competing pathways thus regioselective functionalization becomes challenging. To overcome this, chemists have been able to come up with the concept of directing-group reaction in which an organizing functional group directs the metal catalyst to a given C–H bond, thus giving a high degree of positional selectivity [14]. Also, ligand design, steric tuning and transient mediators have also broadened the range of selective C–H functionalization enabling the elements of earlier inaccessible molecular architectures to be achieved [15].

The effect of C-H activation is not only limited to mere changes of bonds. It has allowed functionalization of complex natural products and pharmaceuticals at later stages, allowing fast diversification of lead compounds and faster drug discovery [16]. Moreover, it has established access to sustainable synthesis through decreasing the use of pre-activated substrates and minimizing dangerous reagents. Simply, C-H activation offers a flexible and potent tool kit, which has become a pillar of contemporary organic chemistry, especially in combination with complementary techniques like photoredox catalysis, as a result of which the synthetic capabilities can be expanded further [17].

Photoredox Principles of Catalysis

This photoredox catalysis has become an innovative approach to organic synthesis that has provided a new way to control chemical reactivity never before possible, utilizing the energy of visible light to catalyze redox transformations. The photoredox catalysis, in contrast to the traditional thermal or metal-catalyzed reaction, takes place under relatively mild conditions, usually at room temperature and atmospheric pressure, increasing the tolerance of functional groups to reactants and decreasing the energy usage [18]. Photoredox catalysis relies on the basic mechanism given that the presence of light triggers photocatalyst absorption to produce an excited state that can undergo single-electron transfer (SET) reactions to form highly reactive radical intermediates that can react in a wide variety of bond-forming reactions [19].

Photocatalysts employed in such reactions mostly belong to two broad categories, namely, transition-metal complexes and organic dyes. Much more general are transition-metal complexes (e.g., ruthenium, iridium) in which the high-lying excited states, redox potentials which are tunable, and efficient light absorption are used [20]. The eosin Y, acridinium salts, and flavins are organic photocatalysts and provide a similar reactivity but without any metal, which is usually desired in green chemistry. When the photocatalyst is light excited, the photocatalyst will change its oxidative or reductive potential and become excited, which has either stronger reduction or oxidation ability compared to the ground state. This has made it easier to produce reactive radical species out of stable organic substances and diverse transformations take place like C-C, C-N and C-O bonding [21].

Among the major benefits of photoredox catalysis, one can note the possibility to regulate reaction routes, which cannot be reached with the help of conventional techniques. Selective production of radicals enables chemists to conduct extraordinarily site-selective reactions, such as the functionalization of unactivated C-H bonds, cross-coupling, as well as two-step reactions [22]. In addition, photoredox processes can generally be used with other catalytic systems, including organocatalysis, transition-metal catalysis, and, in particular, C-H activation, allowing reaction designs that are synergistic and thus increase the range of synthetic options [23].

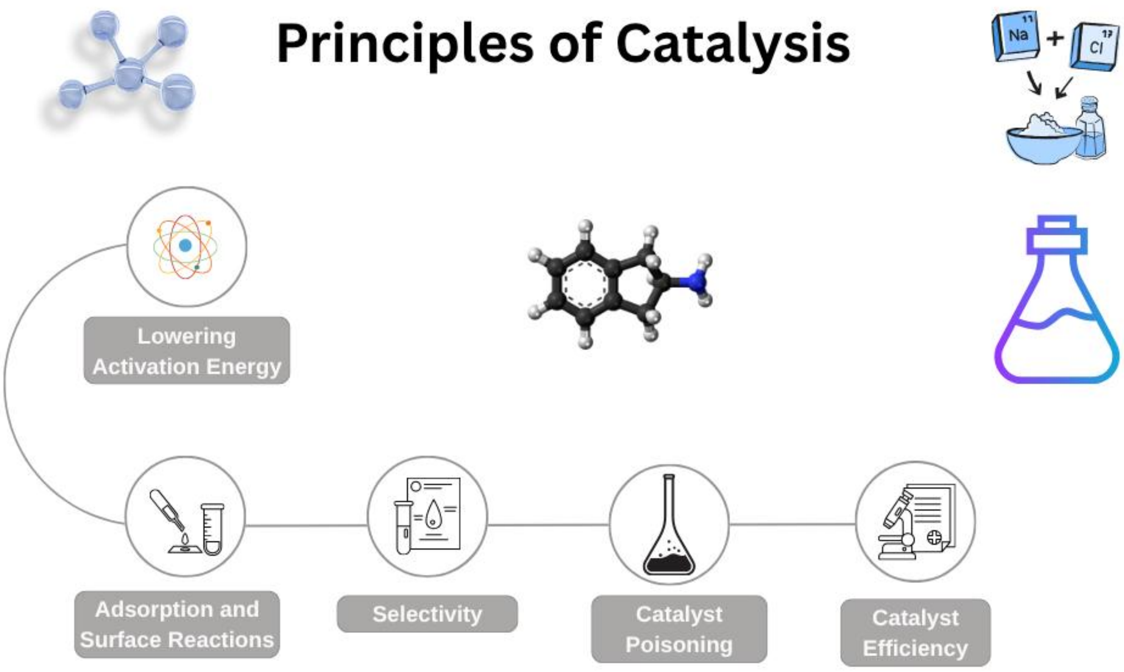

Figure: 2 showing principles of catalysis

Sustainability and energy efficiency have also been the subject of recent developments. Photoredox catalysis can be applied to comply with the principles of green chemistry, as visible lights produced by cheap LEDs or even sunlight can be used, eliminating the need to use potentially dangerous reagents and high energy sources. There are also mechanistic studies such as time-resolved spectroscopy and computational models that have given a more in-depth understanding of radical generation, electron-transfer processes and catalyst design and enable rational optimization of reaction conditions and improved selectivity [24].

Altogether, the field of photoredx catalysis provides a flexible and efficient framework of current organic synthesis. Its mild operating environment, its suitability with various functional groups and capability to produce reactive radical intermediates makes it a good choice of complementary strategies including C-H activation, to enable new directions of constructing the molecules efficiently and sustainably [25].

Synergistic CH Activation and Photoredox Activation

C-H activation + photoredox catalysis is a particularly exciting development in modern organic synthesis, complimenting the abilities of two otherwise very versatile methods to produce transformations once difficult or not possible. Whereas C -H functionalization can be performed with site-selectivity on unactivated C -H bonds by using C -H activation, photoredox catalysis is a mild, light-based method to form reactive radical intermediates. Combined with each other, these methods allow making accurate bonding with environmentally friendly conditions, enhancing efficiency and sustainability in synthetic chemistry [26].

Mechanistically, the synergy between C -H activation and photoredox catalysis tends to be two independent catalytic cycles acting in tandem. In an ideal situation, a transition-metal catalyst is used in the selective cleavage of a C-H bond, to produce a metal-carbon intermediate. At the same time, a photocatalyst can absorb visible light and be excited to the active state, which can be capable of single-electron transfer (SET) reactions [27]. The resulting radical species then reacts with the metal-bound intermediate or enters into other steps involved in bond formation and essentially connects the two catalytic cycles. This complementary process permits a wide variety of transformations, such as arylation, alkylation, amination and oxygenation, and regio- and chemoselectivity is frequently high [28].

Among the main benefits of the dual method, it is possible to functionally mimic complex molecules in late stages. Pharmaceuticals, natural products and other bioactive compounds can be targeted to undergo substitution at positions that would otherwise be inert or sterically impeded to hasten drug discovery and development. Also, the mild conditions used in photoredox catalysis avoid degradation of delicate functional groups which can be a drawback with many traditional C-H activation technologies [29].

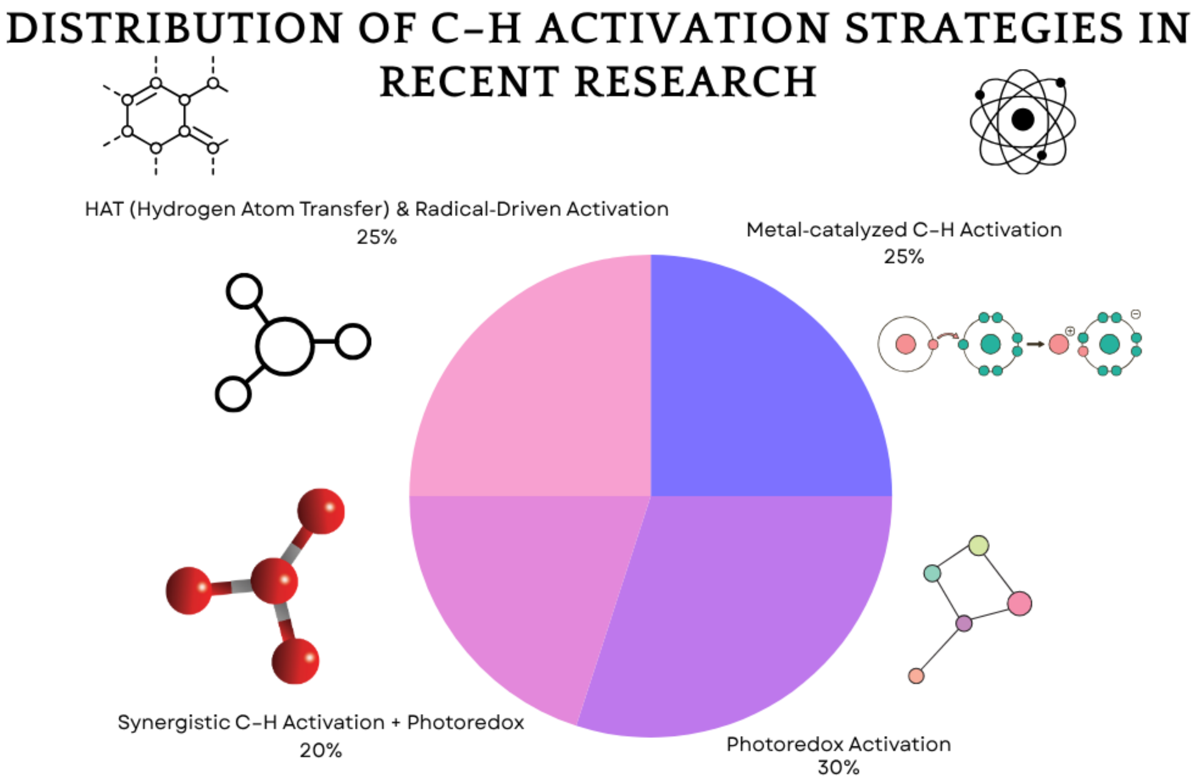

Figure: 3 showing distribution of C-H activation strategies in recent research

Recent work has seen a broad spectrum of useful applications, such as remote C–H functionalization using radical relay, direct cross-coupling of unactivated C-H bonds with heteroaryl or alkylic partners, and stereoselective metathesis using chiral ligands in the metal-catalyzed cycle. Computational and mechanistic investigations have also helped to understand these systems further, and have made known factors that affect selectivity, reaction efficiency, and radical stability [30]. The combination of C–H activation and photoredox catalysis is also in keeping with the concept of green chemistry. The synergistic method of synthesis is sustainable because it involves minimal pre-functionalization, less waste, use of visible light as a renewable energy source and so on. In general, the dual catalysis paradigm is one of the potent paradigms in contemporary organic chemistry, which allows the generation of efficient, selective, and environmentally friendly routes to complex molecular structures that broadens the scope of synthetic tools accessible to chemists [31].

Applications of Organic synthesis, Molecular scale and Reactor scale

Combination of CH activation and photoredox catalysis has greatly broadened the scope of organic synthesis by allowing transformations that are highly selective, efficient and in complex molecular scaffolds. It is most evidently used in the synthesis of the complex molecules and natural products. Direct functionalization of unactivated C -H bonds enables chemists to make complex molecular structures with minimal synthetic operations, requiring fewer pre-functionalized substrates and protecting groups [32]. This simplified method saves time, resources, as well as enhances the efficiency of the entire atom economy, and thus, synthetic routes become more sustainable and less costly. The versatility and wide applicability of the strategy have been demonstrated in recent studies that have shown it useful in the total synthesis of alkaloids, terpenes, and other bioactive natural products [33].

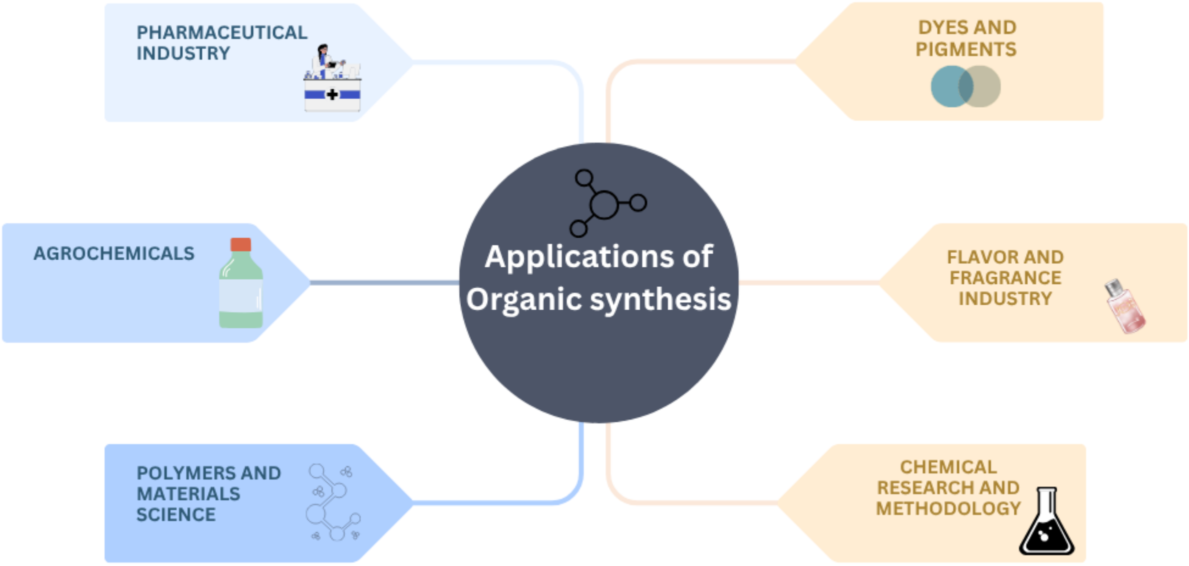

Figure: 4 showing Applications of organic synthesis

The other significant application area is late-stage functionalization that has gained greater importance in drug discovery and medicinal chemistry. Chemists, by selectively altering C H bonds in complex pharmaceuticals, can produce analogs to be used in structure-activity relationship (SAR) studies, without having to synthesize them de novo [34]. Photoredox-based C

-H functionalization allows the functionalization of diverse functional groups - aryl, alkyl, amino, oxygen-containing - and mild conditions both retain sensitive functional groups and stereochemistry. The ability is of importance especially in the optimization of the biological activity and exploration of chemical space quickly with modification of drug candidates [35].

Dual C–H activation and photoredox activation methods have been also used in the synthesis of heterocycles in the pharmaceutical and material chemistry of relevant structural motifs in drugs, agrochemicals and functional materials. The methodology allows the functionalization of C-H with direct catalysis to form five and six-membered heterocycles with subsequent cyclization, usually ambient conditions. Also, it has been used to prepare complex polymeric structures, organic dyes, and molecular cages with specific functionalization patterns, and has also shown its use in other areas, such as the synthesis of small molecules [36].

Moreover, the selective and mild nature of these transformations permits functional group tolerance, compatible with alcohols, amines, carboxylic acids and other sensitive moieties which are frequently not compatible with the classic C-H functionalization methods. Together with the principles of green chemistry (e.g. activation by visible light, reduced production of waste) these methodologies add to the environmental friendliness of synthetic operations [37]. In general, C–H activation and photoredox catalysis can be applied in organic synthesis in endless ways that include total synthesis and late-stage functionalization, drug discovery and material science. The combination of selectivity, efficiency, and sustainability makes this dual method one of the foundations of modern organic chemistry, and new ways to quickly and conveniently design complex molecular structures are created [38].

Recent Innovations and New Trends

Recent years have seen remarkable improvement of the field of CH activation coupled with photoredox catalysis following the increased interest in creating sustainable, efficient, and highly selective synthetic methods. Among the most prominent ones is the combination of visible-light photoredox catalysis with transition-metal-mediated C–H activation that enables chemists to form some bonds previously inaccessible [39]. This bifunctional catalytic approach uses the site-selectivity of C H activation with the weak radical-generating power of photoredox systems to effect transformations in ambient conditions, with high levels of functional group tolerance. Such improvements have facilitated the creating new reactions such as remote C H functionalization, radical relay reactions as well as direct cross-coupling of unactivated C H bonds with heteroaryl or alkyl partners [40].

One more new tendency is the emphasis on green and sustainable approaches. To align with the environmentally friendly practices, researchers are using metal-free organic photocatalysts, renewable light sources, which might include LEDs or sunlight, and solvent-minimizing strategies. Green photoredox catalysis with C-H functionalization further decreases the use of dangerous reagents as well as the generation of waste which is especially relevant in large-scale pharmaceutical and industrial processes [41]. Further, it is now possible to design reactions and optimize them more rationally due to progress in mechanistic understanding primarily made possible by computational modeling and time-resolved spectroscopies, which have given insights into radical formation, reaction kinetics and selectivity [42].

The recent research articles have also shown the application of dual-functional ligands and transient directing groups to improve regio- and chemoselectivity in C-H activation reactions. These technologies enable the functionalization (of complex molecules) such as natural products, pharmaceuticals and functional materials to be precisely functionalized without requiring pre-functionalization. Also, the integration of asymmetric photoredox catalysis has provided access to enantioselective reactions, which have enabled the construction of high-stereocontrolled chiral centers [43].

The other significant development is the integration (synergistically) with computational and AI-assisted methods. To determine the best reaction conditions, predict reactive sites during C H functionalization and develop new photocatalysts, machine learning and predictive modeling are becoming common. This integrative approach of synthetic methodology and computational tools is increasing the rate of new transformations and efficiency of optimization of reactions [44]. On the whole, these new developments and trends signify a swift transformation of the sphere with its focus on efficiency, selectivity, sustainability, and innovation. The discovery of novel catalysts, reaction design, and computational methods ongoing contributes to extending the spectrum of C H activation and photoredox catalysis and supports them as transformative technology in contemporary synthetics in the organic area [45].

Difficulties and Future Discussions

Although C–H activation and photoredox catalysis have achieved great success, there are still a number of issues that restrict the application of the two techniques in complex organic synthesis. Regio- and chemoselectivity are one of the major challenges. Most organic molecules have multiple C bonds on the organics which have similar steric and electronic environments thus are difficult to selectively functionalize [46]. Though directing groups and ligand-directed methods have enhanced site selectivity, the development of general methods that can react with particular C -H bond in even very challenging molecules is still a persistent challenge. The selectivity is extremely important and without heavily modifying its substrates, a researcher is still trying to reach a pinpoint selectivity [47].

Other issues include the stability and compatibility of the catalysts. When the photoredox and the transition-metal catalyst are used in dual catalysis, they have to work in concert without affecting the activity of one another. The degradation of photocatalysts of long-term exposure to the light, and deactivation of catalysts through side reactions may decrease the effectiveness and reproducibility of the reaction. The important challenge in scaling up such reactions to industrial use is the development of strong and long-life catalysts that are able to keep a high activity over a wide variety of substrates and reaction conditions [48].

Reaction efficiency and scope of substrates are also problematic. Although these reactions are shown to transform well in laboratory environments, the scaling up of these reactions typically faces limitations on the form of low yield, extended reaction time, or intolerance of functional groups in typical conditions. It is still important to improve the assortment of substrates and utilize more various and sterically hindered molecules [49]. In the future, it is a promising solution that computation and AI-assisted methods can help address a great number of these problems. Machine learning models may forecast the position of reactive sites, optimize the conditions of the reaction, and create new photocatalysts, which may lower the trial and error linked to the development of reactions. Integration of experimental findings and computational forecasts will shorten the process of identifying effective, selective, and sustainable C H functionalization reactions [50].

The future trends would be marked with enantioselective conversions, novel approaches towards remote and late-stage functionalization, and creation of green and metal-free systems that would respond to the principles of sustainable chemistry. Scatter. The use of novel light sources, reactor design and continuous-flow photochemistry will increase the scalability and efficiency of operation further. The area of C.H. activation and photoredox catalysis is promised to evolve further despite the existing challenges [51]. By solving these drawbacks by creative catalyst design, mechanistic knowledge, and incorporation of computational methods, the generalizability of these methodologies will be extended, further supporting the role of such approach as a groundbreaking strategy in the contemporary process of organic synthesis [52].

Conclusion

The interplay between C–H activation and photoredox catalysis is the new frontier of contemporary organic synthesis, which gives chemists unparalleled access to selective, efficient, and sustainable molecular synthesis. Both of the methodologies have developed over the last 20 years to tackle significant issues in synthetic chemistry. C–H activation has made it possible to functionalize unactivated carbon-hydrogen bonds directly, which avoids the use of pre-functionalized substrates and simplifies the synthesis. In the meantime, photoredox catalysis has used visible light to produce highly reactive radical intermediates in mild and environmentally-friendly conditions. The combination of the two as a synergetic strategy has significantly extended the synthetic toolkit to allow more complex building of bonds, which could not be built in the traditional fashion.

This review has brought to light the principles of both C H activation and photoredox catalysis including the mechanism involved, catalyst development, and optimization of the reaction. C–H activation Reactive C–H bonds are broken in a highly regio- and chemoselective reaction of inert C–H bonds with transition-metal catalysts, typically directed by some form of directing group or ligand modification. In contrast, photoredox catalysis makes use of photocatalysts (either metal complexes or organic dyes) to catalyze single-electron transfer processes that produce radical intermediates, which can then undergo a wide range of transformations including C–C, C–N and C–O bond formation. A combination of the two techniques enables radical products produced by photoredox catalysis to react selectively with metal bound products and provides opportunities to run dual-catalytic cycles to improve reaction efficiency, selectivity, and scope.

There are wide and effective uses of this dual approach. These strategies allow more atom economy and fewer steps to be used in constructing complex natural products and bioactive molecules in total synthesis. Late-stage functionalization has proven to be a very potent method in medicinal chemistry because drug candidates can be selectively modified and structure-activity relationship studies can be easily done without the need to resynthesize the compound in large amounts. Also, the dual method has been used in material chemistry, such as in the synthesis of heterocycles, molecular cages, polymeric architectures, showing that the technology is not restricted to the synthesis of small molecules.

The latest developments indicate an increase in the significance of sustainability and green chemistry, such as metal-free photocatalysts, eco-friendly light sources, and solvent-efficient procedures. Computational modeling and reaction design with the help of AI also turned into a part of the package, which provided predictive possibilities of reactivity, selectivity, and optimum reaction conditions. These inventions are not only making the discovery of new transformations quicker, but also making scalable, environmentally conscious processes, which can be applied to industries.

Although a great breakthrough has been made, much work still needs to be done, such as the realization of universal regioselectivity, increased substrate range, increased catalyst durability, and scalability. It will be necessary to overcome these weaknesses through further innovation in the design of catalysts, their mechanistic insights, and the incorporation of computational tools. Moreover, new directions as enantioselective C–H functionalization, remote C–H activation, and hybrid photochemical methods are of significant potential in the future.

To sum up, a combination of C -H activation and photoredox catalysis has developed a new dimension of modern organic synthesis. These methodologies are able to merge selectivity, efficiency, and sustainability to create complex molecules with great accuracy. This dual-catalytic strategy will be an invaluable instrument in academia and industry as mechanistic insights become increasingly challenging to ignore and new technologies get incorporated, and it will become the basis of innovations in pharmaceuticals, natural product synthesis, and materials science. The current developments of this discipline highlight its potential of changes and the critical significance of this field in determining the future of synthetic chemistry.

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