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Photochemical Insights into Light: Responsive Heterocyclic Compounds

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Abstract

Heterocyclic compounds are significant in a wide range of chemical fields. They are crucial components of the structural makeup of bioactive substances. Such compounds can be conveniently transformed through photochemical processes. Chemical reagents are rarely utilized. It is possible for members of one compound family to change into members of another. There is discussion of three key categories of photochemical rearrangements involving heterocyclic compounds: Photochemical reactions involving hydrogen atom transfer (HAT), photochemical electrocyclization, and photochemical heteroatom isomerization involving heteroatoms and substituents. Heterocyclic system thermochemistry. Heterocyclic synthesis—both photoaddition and photocyclization—is quickly taking the lead as the preferred synthetic route. The processes of photochemical reactions are expounded upon in this chapter. When a molecule absorbs UV light, its energy increases to a point where bond breaking occurs. The molecule may so fragment and reorganize as a result. Based on ring size, the transformations are categorized and the impact on heterocycles is explored. There is also discussion of pyrazolines, heterocyclic dienes, and heteroaromatic compounds. In order to explore new molecular space, modern organic chemists are facing a major challenge: creating more complex and uncommon ring systems. Heterocyclic ring systems have been the subject of intense research into their biological functions. The research on organic photochemistry that has applications in organic synthesis was covered in this review. The synthesis of heterocyclic compounds was described in this review. Conventional methods are very cumbersome, expensive, or require specialist equipment that would not be useful to a synthetic organic chemist.

Keywords: Heterocycles, photochemistry, ultraviolet (UV) spectroscopy photochemical, six-membered rings, nitrogen

INTRODUCTION

By orthoannellating benzene, carbon compounds known as helicenes are created. These are phenanthrene's benzene analogs. This kind of benzene ring arrangement invariably results in face-to-face overlapping. Their great optical activity is one of these compounds' most distinctive features. Regarding a recent theoretical intervention. More recently, helicenes' vibrational circular dichroism (VCD) has been studied. The scope of this field's research has expanded to include helicene-like compounds with heterocyclic moieties or smaller carbocycles like cyclobutenes [1].

Numerous helicenes applications have been documented. Asymmetric synthesis has made use of helicenes because of their chiral characteristics. Various ligands for phosphine that contain a

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helicene moiety have been synthesized. The study of chemical reactions in molecules having one or more rings made of elements like carbon, nitrogen, oxygen, sulfur, etc. that are triggered by light is known as photochemistry in heterocyclic compounds. Because there are atoms other than carbon in the ring structure, these rings are known as heterocycles [2].

When heterocyclic compounds undergo photochemical reactions, a variety of transformations and products can result, many of which have distinct reactivities from their non-heterocyclic counterparts. Among the frequent photochemical processes in heterocyclic compounds are:

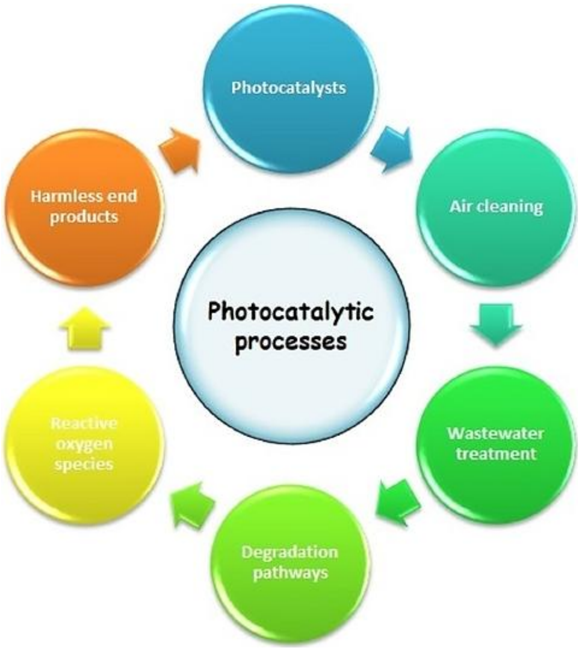

Figure 1. Shown: photocatalytic processes.

Cycloadditions Photochemical cycloaddition reactions are common in heterocyclic compounds, leading to the formation of cyclobutane rings. For instance, cyclobutane derivatives can be formed from reactions involving furans or pyrroles. In Figure 1 shown: Photocatalytic Processes. The economic prosperity brought by industrialization is associated with the dramatic degradation of the environment (i.e., water and air pollution, loss of natural resources, climate change, etc.). The uncontrolled release of numerous hazardous contaminants, such as dyes, chemicals, heavy metals, organic solvents, petroleum products, and solid wastes, is strongly contaminating the environment [3].

Isomerization Photoisomerization processes, such as E-Z isomerization in molecules containing double bonds within the heterocyclic ring, are observed. For example, azobenzene derivatives undergo trans-cis isomerization under light irradiation. Cleavage and Fragmentation Photochemical cleavage of bonds within the heterocyclic ring can occur, leading to fragmentation and the formation of smaller molecules. For instance, photolysis of certain heterocyclic compounds can lead to the release of nitrogen or other heteroatoms [4].

Photooxidation Heterocyclic compounds containing electron-rich centers can undergo photooxidation reactions upon exposure to light and atmospheric oxygen. These reactions often lead to the formation of oxidized products [4].

Photodimerization Some heterocyclic compounds can undergo photochemical dimerization reactions, where two molecules combine to form a dimeric product. For example, thymine and uracil can undergo photodimerization under UV light [5].

The study of photochemistry in heterocyclic compounds is important for various applications in fields such as organic synthesis, materials science, pharmacology, and environmental chemistry. Understanding the mechanisms and reactivity of these photochemical processes can facilitate the development of new synthetic methodologies, the design of photoresponsive materials, and the elucidation of biological processes involving heterocyclic compounds [5].

Photochemistry in heterocyclic literature encompasses a vast array of studies and applications, reflecting the importance and versatility of heterocyclic compounds in various fields of chemistry. Here are some key aspects of photochemistry in heterocyclic literature:

LITERATURE

Synthetic Methodology Many research articles focus on the development of new photochemical reactions involving heterocyclic compounds as key substrates. These studies often aim to devise efficient and selective methods for the synthesis of complex heterocyclic frameworks. For example, photoredox catalysis has emerged as a powerful tool for the functionalization and construction of heterocyclic motifs. Applications in Materials Science Heterocyclic compounds exhibit diverse photophysical properties, making them valuable components in the design of photoresponsive materials. Literature in this area explores the use of heterocyclic chromophores and photoactive motifs for applications such as organic light-emitting diodes (OLEDs), photovoltaics, photonic devices, and molecular switches [6].

Biological and Medicinal Chemistry: Heterocyclic compounds play a central role in drug discovery and medicinal chemistry due to their prevalence in pharmaceutical agents. Photochemical approaches are employed to synthesize bioactive heterocycles, modulate biological activity through photoactivation, and develop phototherapeutic agents for applications in photodynamic therapy (PDT) and photopharmacology [7].

Environmental and Green Chemistry Photochemical methods offer opportunities for sustainable and environmentally benign synthesis of heterocyclic compounds. Literature in this area explores photocatalytic processes, solar-driven reactions, and photochemical transformations under mild conditions, aiming to minimize waste generation and energy consumption [8].

Photostability and Photoinduced Toxicity Understanding the photostability and phototoxicity of heterocyclic compounds is essential for their safe handling and application in various fields. Studies investigate the photodegradation pathways, photoproduct formation, and potential adverse effects of heterocyclic compounds upon exposure to light [9].

Literature on photochemistry in heterocyclic compounds reflects the interdisciplinary nature of this research area, spanning synthetic chemistry, physical chemistry, materials science, medicinal chemistry, and environmental science. Continued advancements in photochemical methodologies and applications hold promise for addressing complex challenges and driving innovation across multiple disciplines [10].

Approach

Another molecule (e.g., an alkene) approaches the excited heterocyclic compound. The excited state of the heterocycle facilitates the reaction by lowering the activation energy required for the cycloaddition. Cycloaddition- The excited heterocyclic compound and the alkene undergo a cycloaddition reaction, resulting in the formation of a cyclobutane ring [11].

Product Formation The cyclobutane product is formed, incorporating atoms from both the heterocyclic compound and the alkene [12].

Relaxation and Rearrangement The cyclobutane product may undergo relaxation processes to return to the ground state, accompanied by any necessary rearrangements to achieve a stable conformation [12].

Photochemistry plays a significant role in heterocyclic methodology, offering unique and efficient pathways for the synthesis of diverse heterocyclic compounds [13].

Cyclization Reactions Photochemical cyclization reactions are widely used for the construction of various heterocyclic rings. These reactions often involve the activation of π bonds or functional groups in the substrate under UV or visible light irradiation, leading to ring closure and formation of the heterocyclic scaffold. Examples include the synthesis of benzofurans, benzothiophenes, pyrroles, and furans via photochemical cyclization of appropriate precursors [14].

Isomerization Reactions Photoisomerization reactions involving heterocyclic compounds can be exploited for the synthesis of isomeric products with distinct chemical and physical properties . For example, photoisomerization of azobenzene derivatives leads to the formation of cis-trans isomers, which find applications in molecular switches and photomechanical devices [15].

Photooxidation and Photoreduction Photooxidation and photoreduction reactions can be employed for the synthesis of heterocyclic compounds from readily available starting materials. Photooxidation of heteroatoms or π systems can lead to the formation of heterocyclic rings, while photoreduction of functional groups can generate reactive intermediates for subsequent cyclization or functionalization reactions [16].

Functionalization Reactions**:** Photochemical functionalization reactions enable the introduction of functional groups into heterocyclic compounds under mild conditions. Functional groups such as halogens, alkyl groups, or aryl groups can be selectively added to heterocycles via photoredox catalysis or radical-mediated processes, expanding the synthetic versatility of heterocyclic scaffolds [16].

Pericyclic Reactions Certain pericyclic reactions, such as electrocyclization and sigmatropic rearrangements, can be promoted by photochemical activation. These reactions proceed through concerted processes involving cyclic transition states, leading to the formation of complex heterocyclic structures with high stereo- and regioselectivity [17].

Overall, photochemical methodologies offer unique opportunities for the synthesis of diverse heterocyclic compounds with high efficiency, selectivity, and atom economy. Continued advancements in photoredox catalysis, photocatalyst design, and reaction engineering are expected to further expand the scope and utility of photochemistry in heterocyclic synthesis [17].

"*Photochemistry has numerous applications"* in the field of heterocyclic chemistry, spanning various domains including organic synthesis, materials science, medicinal chemistry, and environmental chemistry [18].

Synthetic Chemistry Photochemical methods provide efficient routes for the synthesis of complex heterocyclic compounds. Reactions such as photocyclization, photooxidation, and photorearrangement enable the construction of diverse heterocyclic scaffolds with high regio- and stereocontrol. These methodologies are valuable for accessing natural product analogs, pharmaceutical intermediates, and functional materials [18].

Materials Science Heterocyclic compounds are integral components in the design of photoresponsive materials. Photochromic dyes, photopolymers, and photoswitchable molecules based on heterocyclic motifs find applications in optical devices, data storage, sensors, and smart materials. Photochemical processes also facilitate the fabrication of organic thin films, nanoparticles, and nanostructures with tailored optical and electronic properties [19].

Medicinal Chemistry Heterocyclic compounds constitute a significant proportion of pharmaceutical agents, owing to their diverse biological activities and drug-like properties. Photochemical methods are employed for the synthesis and functionalization of heterocyclic drug candidates, as well as for the development of photoactivatable prodrugs and photodynamic therapy (PDT) agents. Photochemical reactions can modulate the pharmacokinetics, targeting specificity, and therapeutic efficacy of heterocyclic drugs, leading to improved treatments for various diseases including cancer, infectious diseases, and neurological disorders [19].

Photoinduced Bioorthogonal Chemistry Photochemical reactions offer a non-invasive and temporally controlled approach for bioconjugation and biomolecule labeling in living systems. Heterocyclic photoactivatable groups, such as diazirines, benzophenones, and aryl azides, enable site-specific modification of biomolecules under mild conditions upon light irradiation. These strategies are employed in chemical biology, proteomics, and drug discovery for studying biomolecular interactions, protein function, and cellular signaling pathways [20].

Phenol: Overview of Uses and Properties One well-known pollutant that is constantly added to the environment by industry and human activity is phenol. Colorless to light-pink, phenol is an aromatic chemical with a peculiar smell and burning flavor. It dissolves in most organic solvents, less so in aliphatic hydrocarbons, and moderately in water. When plants and microbes break down organically, phenols are created. Compared to other soil organic matter, phenols are released into the soil gradually. The predominant method for producing phenol is by far the oxidation of cumene (Hock process). As a pollutant of priority concern, the phenol was classified by the US Environmental Protection Agency (USEPA). In addition to being extremely genotoxic and skin irritating, repeated exposure to it can lead to infertility and weight loss, disrupt hormones, and harm the liver, kidneys, and neurological system. A maximum allowable content of phenol in drinking water is 2 mg L^{-1} according to recommendations made by the World Health Organization (WHO). However, contamination of drinking water supplies poses a risk to human health even at extremely low quantities, as it directly impacts the wellbeing of ecosystems [20].

Environmental Chemistry Photochemical processes play a crucial role in the fate and transformation of heterocyclic pollutants in the environment. Heterocyclic compounds present in industrial effluents, pesticides, and pharmaceuticals can undergo photodegradation and photooxidation in natural waters, soils, and atmospheric aerosols, leading to the formation of photoproducts with altered toxicity and environmental impact. Understanding the photochemistry of heterocyclic pollutants is essential for assessing their environmental fate and developing remediation strategies for water and air purification [20].

photochemistry in heterocyclic applications continues to advance interdisciplinary research and innovation, offering versatile tools for addressing complex challenges in chemistry, biology, and materials science. Continued exploration of photochemical methodologies and their applications holds promise for addressing emerging societal needs and driving scientific progress [20].

CONCLUSIONS

The most versatile photochemical reaction for the synthesis of helicenes is the cyclization of stilbene subunits followed by an oxidation. This reaction is frequently applied to the preparation of carbohelicenes as well as helicenes containing heterocyclic moieties. In many cases, the formation of helicene structures efficiently competes with the formation of isomeric conjugated oligoarenes even when the formation of the latter once is thermodynamically favored. Pollutant elimination by only photocatalysis is a highly demanding task and difficult to carry out. Therefore, combining photocatalysis with other techniques is imperative. Photocatalysis as a depollution method has limited efficacy, but from the environmental point of view, it has great significance because the sun is a cheap and endless source. In fact, in nature, all the existent pollutants are exposed to solar irradiation. Oxide materials (e.g., minerals) are slowly degrading pollutants under solar light, and the fate of intermediates is less known. Thus, the photocatalytic pollutant degradation mechanism in laboratory experiments is very important because it is relevant to the natural depollution processes.

REFERENCES

1. Friedmann, D.A. General overview of heterogeneous photocatalysis as a remediation technology for wastewaters containing pharmaceutical compounds. *Water* 2022, *14*, 3588.
2. Dutschke, M.; Schnabel, T.; Schütz, F.; Springer, C. Degradation of chlorinated volatile organic compounds from contaminated ground water using a carrier-bound TiO_2/UV/O_3-system. *J. Environ. Manag.* 2022, *304*, 114236.
3. Fiorenza, R.; Spitaleria, L.; Perricelli, F.; Nicotra, G.; Fragalà, M.E.; Scirè, S.; Gulino, A. Efficient photocatalytic oxidation of VOCs using ZnO@Au nanoparticles. *J. Photochem. Photobiol. A Chem.* 2023, *434*, 114232
4. Zhang, Y.; Zhao, G.; Chen, Z.; Lian, H.; Gan, L.; Pan, M. Hierarchically nanostructured Ag/ZnO/nBC for VOC photocatalytic degradation: Dynamic adsorption and enhanced charge transfer. *J. Environ. Chem. Eng.* 2022, *10*, 108690
5. Ramalingam, G.; Perumal, N.; Priya, A.K.; Rajendran, S. A review of graphene-based semiconductors for photocatalytic degradation of pollutants in wastewater. *Chemosphere* 2022, *300*, 134391.
6. Kang, W.; Chen, S.; Yu, H.; Xu, T.; Wu, S.; Wang, X.; Lu, N.; Quan, X.; Liang, H. Photocatalytic ozonation of organic pollutants in wastewater using a flowing through reactor. *J. Hazard. Mater.* 2021, *405*, 124277.
7. Preda, S.; Umek, P.; Zaharescu, M.; Anastasescu, C.; Petrescu, S.V.; Gifu, C.; Eftemie, D.-I.; State, R.; Papa, F.; Balint, I. Iron-modified titanate nanorods for oxidation of aqueous ammonia using combined treatment with ozone and solar light irradiation. *Catalysts* 2022, *12*, 666.
8. Mirsadeghi, S.; Zandavar, H.; Rajabi, H.R.; Sajadiasl, F.; Ganjali, M.R.; Pourmortazavi, S.M. Superior degradation of organic pollutants and H_2O_2 generation ability on environmentally–sound constructed Fe_3O_4-Cu nanocomposite. *J. Mater. Res. Technol.* 2021, *14*, 808–821.
9. Qu, Y.; Chen, Z.; Duan, Y.; Liu, L. H_2O_2 assisted photocatalysis over Fe-MOF modified BiOBr for degradation of RhB. *J. Chem. Technol. Biotechnol.* 2022, *97*, 2881–2888.
10. Binas, V.; Venieri, D.; Kotzias, D.; Kiriakidis, G. Modified TiO_2 based photocatalysts for improved air and health quality. *J. Materiomics* 2017, *3*, 3–16.
11. Denny, F.; Permana, E.; Scott, J.; Wang, J.; Pui, D.Y.H.; Amal, R. Integrated Photocatalytic Filtration Array for Indoor Air Quality Control. *Environ. Sci. Technol.* 2010, *44*, 5558–5563.
12. Humayun, M.; Raziq, F.; Khan, A.; Luo, W. Modification strategies of TiO_2 for potential applications in photocatalysis: A critical review. *Green Chem. Lett. Rev.* 2018, *11*, 86–102.
13. Chen, W.; Wang, Y.; Liu, S.; Gao, L.; Mao, L.; Fan, Z.; Shangguan, W.; Jiang, Z. Non-noble metal Cu as a cocatalyst on TiO_2 nanorod for highly efficient photocatalytic hydrogen production. *Appl. Surf. Sci.* 2018, *445*, 527–534.
14. Gocearenco, E.; Morjan, I.P.; Dutu, E.; Scarisoreanu, M.; Fleaca, C.; Gavrila-Florescu, L.; Dumitrache, F.; Banici, A.M.; Teodorescu, V.S.; Anastasescu, C.; et al. The effect of noble metal addition on the properties of oxide semiconductors nanoparticles. *J. Solid State Chem.* 2022, *307*, 122817.
15. Fukuhara, D.; Joseph, M.T.; Loumissi, T.; Zhang, C.; Itoi, T.; Zhang, H.; Izumi, Y. Local silver site temperature critically reflected partial and complete photooxidation of ethanol using Ag-TiO_2 as revealed by extended X-ray absorption fine structure Debye−Waller factor. *J. Phys. Chem. C.* 2021, *125*, 14689–14701.
16. Haselmann, G.M.; Baumgartner, B.; Wang, J.; Wieland, K.; Gupta, T.; Herzig, C.; Limbeck, A.; Lendl, B.; Eder, D. In situ Pt photodeposition and methanol photooxidation on Pt/TiO_2: Pt-loading-

dependent photocatalytic reaction pathways studied by liquid-phase infrared spectroscopy. *ACS Catal.* 2020, *10*, 2964–2977.

17. Preda, S.; Anastasescu, C.; Balint, I.; Umek, P.; Sluban, M.; Negrila, C.; Angelescu, D.G.; Bratan, V.; Rusu, A.; Zaharescu, M. Charge separation and ROS generation on tubular sodium titanates exposed to simulated solar light. *Appl. Surf. Sci.* 2019, *470*, 1053–1063.
18. Anastasescu, C.; Zaharescu, M.; Angelescu, D.; Munteanu, C.; Bratan, V.; Spataru, T.; Negrila, C.; Spataru, N.; Balint, I. Defect-related light absorption, photoluminescence and photocatalytic activity of SiO_2 with tubular morphology. *Sol. Energ. Mater. Sol. Cells* 2017, *159*, 325–335.
19. Raciulete, M.; Papa, F.; Negrila, C.; Bratan, V.; Munteanu, C.; Pandele-Cusu, J.; Culita, D.C.; Alkinson, I.; Balint, I. Strategy for modifying layered perovskites toward efficient solar light-driven photocatalysts for removal of chlorinated pollutants. *Catalysts* 2020, *10*, 637.
20. Raciulete, M.; Papa, F.; Kawamoto, D.; Munteanu, C.; Culita, D.C.; Negrila, C.; Atkinson, I.; Bratan, V.; Pandele-Cusu, J.; Balint, I. Particularities of trichloroethylene photoatalytic degradation over crystalline $RbLaTa_2O_7$ nanowire bundles grown by solid-state synthesis route. *J. Environ. Chem. Eng.* 2019, *7*, 102789.

