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Review Article

Advances in Green Bromination: Emerging Eco-Friendly Reagents and Methodologies

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ABSTRACT

In light of the growing emphasis on sustainable practices in modern chemistry, this review critically examines recent advancements in environmentally benign methods for the bromination of organic compounds. Bromination, a transformation of significant synthetic and industrial relevance, has traditionally relied on harsh reagents and conditions that raise environmental and safety concerns. This review focuses on "green" strategies developed for the selective introduction of bromine atoms into organic molecules, encompassing both direct bromination and oxidative bromination methodologies. Emphasis is placed on approaches that minimize hazardous waste, utilize safer brominating agents, and operate under milder reaction conditions. Particular attention is given to catalytic systems, solvent-free protocols, aqueous media, and the use of renewable feedstock's. Each method is evaluated not only for its synthetic efficiency and selectivity but also through the lens of sustainability metrics, including atom economy, energy efficiency, and environmental impact. By compiling and analyzing recent literature, this review aims to provide a comprehensive understanding of current progress and remaining challenges in the field of green bromination chemistry.

Keywords: Green Bromination, Eco-friendly Reagents, Sustainable Chemistry, Oxidative bromination, Selective halogenation, Catalytic bromination.

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INTRODUCTION

In organic synthesis, bromination is a basic transformation that is frequently used to add bromine atoms to organic compounds. The resultant brominated intermediates are extremely useful and crucial building blocks for the production of advanced materials, polymers, agrochemicals, and pharmaceuticals. Their usefulness results from bromine atoms' capacity to function as reactive handles, which permits further cross-coupling, substitution, and elimination reactions. Bromination is still a fundamental component of synthetic chemistry due to its strategic role, which has wide-ranging effects on both industrial production and scholarly study.

However, the increased focus on sustainability in recent years has led to a reexamination of conventional bromination techniques. Traditional techniques frequently use energy-intensive conditions, produce toxic byproducts, and depend on dangerous reagents like elemental bromine. The ideas of sustainable chemistry and green chemistry have become more well-known in the scientific community and in various chemical industry sectors in an effort to allay these worries. The urgent need for chemical processes that are both economically and environmentally sound is reflected in this paradigm shift. The Twelve Principles of Green Chemistry, a thorough manual for creating safer, cleaner, and more effective chemical transformations, were developed more than 20 years ago by Paul T. Anastas and John C. Warner, who laid the groundwork for this movement. These guidelines place a strong emphasis on tactics including atom economy, energy efficiency, waste reduction, using renewable feedstocks, and creating non-toxic products. Since their debut, they have sparked a variety of innovations, such as the creation of more environmentally friendly bromination techniques that combine enhanced sustainability and safety with synthetic utility.

Building upon this foundation, recent research has focused on applying green chemistry principles to halogenation reactions, particularly bromination, which plays a crucial role in the synthesis of pharmaceuticals, agrochemicals, and advanced materials. As critically reviewed by Sabuzi *et al.*, (2019), significant progress has been made in the development of more sustainable bromination techniques that reduce the use of hazardous reagents

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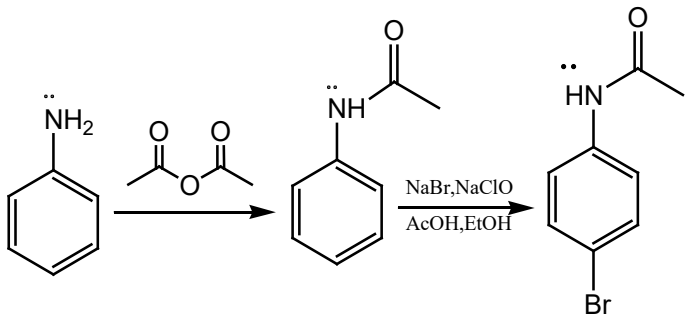
and minimize harmful by-products.[1] Their work offers a thorough evaluation of greener alternatives for the selective incorporation of bromine into organic molecules, encompassing both direct and oxidative bromination strategies within the context of green chemistry.

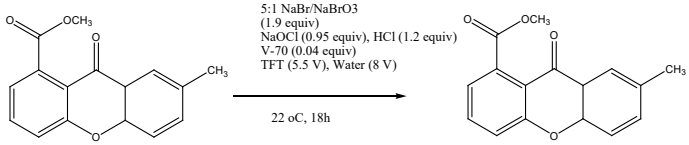
Green chemistry offers a forward-looking framework for chemical manufacturing by addressing the environmental and safety challenges associated with conventional chemical processes. Its core objective is to design innovative and efficient synthetic routes that enhance the formation of desired products while simultaneously minimizing or eliminating the generation of unwanted by-products. This approach not only improves the atom economy of reactions but also reduces the dependency on toxic reagents, hazardous solvents, and energy-intensive conditions. As highlighted by Li and Trost (2008), the application of green chemistry principles to chemical synthesis represents a transformative strategy that fosters both environmental sustainability and process efficiency in the development of new molecules.[2] By incorporating green chemistry principles at the earliest stages of synthetic planning, chemists can markedly reduce the ecological and human health impacts of chemical production, while simultaneously improving process efficiency and safety. Within this context, bromination reactions have garnered particular attention due to their widespread utility in the synthesis of organobromine compounds, which are frequently employed as intermediates in the development of pharmaceuticals, agrochemicals, flame retardants, and advanced materials. These organobromides are highly valued for their functional versatility, making them indispensable building blocks in a variety of organic transformations.

However, traditional bromination methods often rely on hazardous reagents such as molecular Bromine (Br_2), which poses significant risks related to toxicity, corrosiveness, and environmental persistence. In response to these concerns, researchers have sought to develop greener alternatives that offer both improved safety and sustainability. For instance, Van Kerrebroeck *et al.*, (2019) demonstrated that electrophilic bromination under continuous flow conditions offers a safer and more environmentally friendly approach compared to conventional batch processes that utilize molecular bromine.[3] Flow chemistry techniques not only enhance reaction control and minimize exposure to hazardous reagents but also align well with the goals of process intensification and green manufacturing. These advancements underscore the growing potential of sustainable bromination strategies to meet the demands of both modern synthesis and environmental stewardship.

In this synthetic approach, acetylation with acetic anhydride is used to first protect aniline's primary amino group. This safeguard is necessary to suppress the production of dangerous byproducts and avoid polysubstitution during subsequent halogenation. Free amino groups can produce hazardous and possibly explosive chloramine derivatives and are extremely reactive with sodium hypochlorite. The conversion of aniline to acetanilide improves selectivity in the bromination step by decreasing the nucleophilicity of the amino group. A safer and more environmentally friendly substitute for elemental bromine is then used to complete the bromination process. By reacting sodium hypochlorite with sodium bromide in an acidic environment, molecular bromine is produced in situ rather than by handling corrosive liquid bromine directly. In this system, sodium hypochlorite serves as the oxidising agent, converting bromide ions into bromine, which selectively brominates the acetanilide derivative's aromatic ring. This environmentally safe method has several benefits, including reducing the need for elemental bromine directly, streamlining the experiment, and enhancing lab safety. A noteworthy yield of roughly 75% was obtained for the brominated product, highlighting the method's effectiveness and usefulness. Crucially, characteristics like yield and ease of product isolation have a significant impact on the process's overall cost-effectiveness when assessing green alternatives, especially in situations involving scale-up. These approaches are both economically and environmentally feasible because they minimise reagent waste and require less time, labour, and resources due to their straightforward work-up and higher yields.[4]



There is a new bromination method that uses a salt-based system with sodium bromide and sodium bromate in a 5:1 molar ratio. Here, the reagent mixture-typically linked to the industrial cold-process synthesis of elemental bromine-acts as an *in situ* bromine generator when acidified. It is no longer necessary to handle corrosive liquid bromine directly because of the controlled release of molecular bromine from the acid-mediated redox reaction between NaBr and $NaBrO_3$.



Waste Metrics for Original Bromination Procedure and New Bromination Procedure

A brominating reagent based on a 2:1 molar ratio of bromide to bromate has been developed, derived from the alkaline

intermediate typically formed during the standard industrial bromine recovery process. Upon in situ acidification, this reagent system generates hypobromous acid (HOBr), a highly reactive electrophilic species responsible for facilitating bromination reactions. The generation of HOBr under mild conditions enables efficient electrophilic substitution, thereby eliminating the need for elemental liquid bromine, which poses significant safety, handling, and environmental concerns.

This reagent exhibits broad applicability across a variety of organic substrates. Aromatic compounds such as phenols, anilines, aromatic ethers, and even unsubstituted benzene undergo smooth bromination in the absence of metal catalysts or external promoters. The method offers high regioselectivity and operational simplicity, aligning with sustainable and green chemistry practices.

In addition to aromatic bromination, the reagent demonstrates selective reactivity towards non-aromatic compounds bearing activated methylene groups, favoring monobromination under controlled conditions. Moreover, when applied to olefinic substrates, the system induces formation of bromohydrins in moderate yields, indicating its potential for functional group transformation via electrophilic addition pathways.

Conventional bromination methods usually use elemental Bromine (Br 2) which is very toxic, corrosive, and hard to deal with on a large scale. To overcome these issues, more environmentally friendly techniques have been invented that produce bromine on-site by reacting safer bromine sources like Sodium Bromide (NaBr) with an oxidizing agent like Sodium Bromate (NaBrO 3) or Sodium Hypochlorite (NaOCl). Such systems employ the generation of molecular bromine directly in the reaction mixture and react it at once with the substrate, eliminating the necessity to store or directly manipulate liquid bromine.[5]

The benefit of the *in situ* generation method is that it enhances safety in a number of ways:

- Reduced Exposure: Because Br 2 is not produced permanently and in small quantities, there is very little threat of accidental inhalation, spills or environmental release.
- Less Handling Hazards: Bromine does not require any special storage or transportation, making it easier to conduct laboratory and industrial processes.
- Controlled Reactivity: The bromine is slowly produced in the reaction medium thereby a better control of concentration and hence prevents overbromination and undesired side reactions.

A noteworthy advantage of this methodology is its cost-effectiveness and scalability. By utilizing the liquid bromine precursor in a controlled oxidation environment to generate the active reagent in situ, the process circumvents the direct use of hazardous bromine while still achieving high bromination efficiency. This innovation not only enhances safety but also contributes to the reduction of chemical waste and production costs, making it attractive for both laboratory and industrial applications.[6]

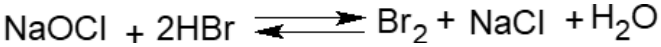
$$5NaBr + NaBrO3 + 6HCl\ 3Br2 + 3H2O + 6\ NaCl$$

$$5NaBr + NaBrO3 + 3NaOCl\ 4NaBr + 2NaBrO3 + 3NaCl$$

In the reported bromination protocol, hazardous brominating agents such as molecular Bromine (Br_2) or Potassium Hypobromite (KOBr) are not used directly but are instead generated in situ. This is accomplished through the reaction of a readily available oxidizing agent, such as Sodium Hypochlorite (NaOCl), with a bromide source-either Hydrobromic Acid (HBr) or Potassium Bromide (KBr). The *in situ* formation of the active brominating species is tightly coupled with the bromination step, ensuring controlled reactivity while simultaneously minimizing the risks associated with handling free bromine.

A notable advantage of this methodology lies in its ability to efficiently brominate both olefinic and aromatic substrates. The process has been demonstrated to be effective across a variety of solvent systems, showcasing its versatility and broad substrate compatibility. The reaction conditions enable selective polybromination without the need for metal catalysts or harsh reagents, making the process operationally simple and environmentally favorable.

Furthermore, the reaction system allows for the efficient quenching of any residual bromine formed during the reaction, thereby reducing the potential for overbromination and limiting the generation of hazardous waste. Reported yields for the brominated products range impressively from 78% to 99%, indicating high efficiency and reproducibility. This approach presents a safer, scalable, and greener alternative to traditional bromination methods, suitable for both academic research and industrial-scale applications.[7]



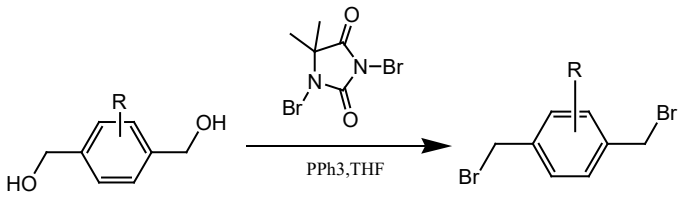
This study introduces a novel and efficient methodology for the selective dibromination of benzylic diols, offering a practical route to access valuable brominated intermediates. The developed protocol demonstrates broad substrate scope, affording moderate to good yields across a diverse array of aromatic systems-including electron-rich, electron-neutral, and electron-deficient arenes. This versatility underscores the robustness and generality of the method for synthetic applications.

A key feature of this strategy is the use of 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) as the brominating agent in Tetrahydrofuran (THF) as the reaction medium. Both the reagent

and solvent are considered environmentally benign compared to conventional bromination systems that typically involve elemental bromine or halogenated solvents. The adoption of DBDMH and THF aligns with green chemistry principles by reducing toxicity, improving safety, and minimizing environmental impact.

Selective bromination 1,3-Dibromo-5,5-Dimethylhydantoin (DBDMH) in THF is a green substitute to elemental bromine or halogenated solvents, with a wide range of substrate compatibility and lower toxicity. This methodology has been effectively used to produce omeprazole intermediates, which has shown operational simplicity, high regioselectivity as well as environmental compatibility.

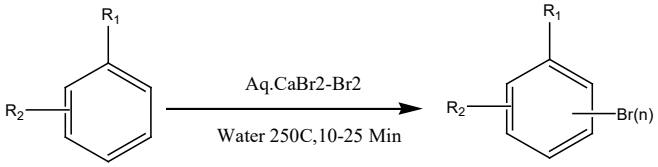
Importantly, this method has been successfully applied to a high-yielding step in the synthetic pathway of omeprazole, a widely used proton pump inhibitor, highlighting its potential relevance to pharmaceutical synthesis. The operational simplicity, eco-friendliness, and compatibility with structurally diverse substrates make this dibromination protocol a valuable addition to the toolbox of sustainable synthetic organic chemistry.[8]



Among various bromination strategies, the aqueous Calcium Bromide-Bromine ($CaBr_2$-Br_2) system has emerged as one of the most advantageous brominating agents. This system operates efficiently in water as the reaction medium, eliminating the need for hazardous organic solvents and aligning with green chemistry principles. The use of water not only simplifies the reaction setup and workup procedures but also significantly enhances safety and environmental compatibility.

The $CaBr_2$-Br_2 system provides a highly effective medium for the electrophilic bromination of a wide range of organic substrates, including aromatics, alkenes, and activated methylene compounds. It offers a clean reaction profile with minimal byproduct formation and enables easy control over bromine concentration, thereby improving selectivity and reducing the risk of overbromination. The CaBr2-Br2 system enables bromination of water hence avoiding the use of dangerous organic solvents. It offers a high degree of substrate versatility and purity of reaction with little or no byproduct and better selectivity as a result of regulated bromine levels. The method is especially applicable to the industrial-scale production of brominated compounds.

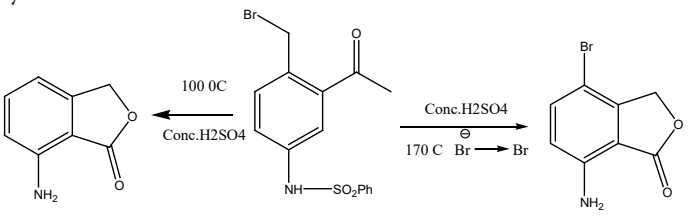
This method has proven particularly useful for the synthesis of commercially and industrially relevant brominated compounds. The operational simplicity, combined with cost-effectiveness and environmental safety, makes this aqueous bromination system a practical and sustainable alternative to conventional bromination methods that rely on corrosive bromine or organic solvent-based systems.[9]



In this method, a novel synthetic approach has been developed for the preparation of bromo-substituted 7-amino-phthalides and 7-amino-3-hydroxy-phthalides under acidic conditions at elevated temperatures. This protocol enables regioselective bromination and cyclization reactions, resulting in the efficient formation of structurally valuable phthalide derivatives.

The methodology demonstrates significant synthetic utility, particularly for the generation of bromo-substituted aryl amines, which serve as key intermediates in pharmaceuticals, agrochemicals, and materials science. The reaction conditions are optimized to promote both bromination and ring closure in a single step, enhancing the atom economy and simplifying the overall process. A new protocol allows a regioselective bromination and cyclization of 7-amino-phthalides and 7-amino-3-hydroxy-phthalides under acidic conditions at high temperatures. The single-step procedure enhances atom economy as well as simplifying the access to functionalized bromoaryl aryl amines that are useful intermediates in pharmaceuticals, agrochemicals and materials science.

This strategy offers a practical and scalable route for accessing functionalized bromo-aryl amine scaffolds. The use of high temperatures and acidic media facilitates the activation of substrates and improves the overall reaction efficiency, making it a valuable addition to modern heterocyclic and aromatic synthesis.[10]

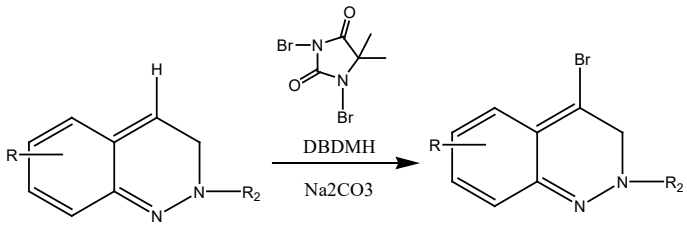


Bromoaryl compounds are gaining considerable importance in modern organic synthesis, particularly as key intermediates in the development of pharmaceuticals and bioactive molecules. In this context, a robust and efficient bromination strategy has been reported for the site-selective functionalization of indazole derivatives via direct C-H bond activation. This method enables regioselective bromination at the C3 position of the indazole core, yielding structurally defined 3-bromoindazoles that serve as valuable precursors for further synthetic elaboration.

The reaction employs 1,3-Dibromo-5,5-Dimethylhydantoin (DBDMH) as a stable and efficient bromine source. DBDMH exhibits broad substrate compatibility, effectively brominating

a wide range of indazole derivatives without the need for pre-functionalization. The transformation proceeds under ultrasound-assisted conditions, which enhance mass transfer and reaction kinetics, allowing the bromination to be completed within just 30 min under relatively mild reaction parameters. A mild, selective and rapid, example of an ultrasound-assisted bromination of the C3 position in indazole derivatives was illustrated with the use of the DBDMH. The technique is broadly compatible with substrates, does not involve functionalization before treatment, and brominates in less than 30 min, being therefore a very useful tool in pharmaceutical and heterocyclic chemistry.

This ultrasound-assisted protocol represents a significant advancement in selective halogenation, offering operational simplicity, high regioselectivity, and excellent functional group tolerance. The approach holds promise for rapid generation of bromo-substituted heterocycles, particularly useful in drug discovery and heterocyclic chemistry.[11]



They have created a more efficient and greener electrochemical process to selectively brominate the side-chain of acetophenone, using an undivided electrochemical cell with Platinum electrodes (Pt/Pt). This protocol works in soft, room temperature conditions and uses an environmentally friendly reagent system. The Ammonium Bromide (NH 4 Br) in the presence of a catalytic amount of Sulfuric Acid (H_2SO_4) is converted to bromonium ions in situ, where Sulfuric Acid (H_2SO_4) also serves as a supporting electrolyte. The choice of reaction medium, which is a 1:1 blend of water and acetonitrile (H_2O:CH 3CN) also conforms to the principles of green chemistry due to the reduced consumption of dangerous solvents.

It takes 2 Fardays (2F) of electricity per mole of substrate to become highly efficient and selectively form 3,4-bromoacetophenone with isolated yields as high as 80%. Remarkably, benzylic bromination is performed with great selectivity, and there is very little overbromination or unwanted aromatic bromination. Electrochemical approaches allow the production of bromonium ions on-site using bromide salts, and therefore it does not need any external oxidants, minimizing environmental impact. These techniques have been used in selective α-bromination of acetophenones, dibromination of alkenes, bromolactonization and tribromide-mediated aromatic bromination.

Limitations and Considerations

Although there are benefits, a number of drawbacks of electrochemical bromination should be identified:

Energy Consumption: Despite electricity being a clean reagent, energy input may be important in long reactions, or when loading substrates. Current density, voltage and reaction time/duration must be optimized to minimize energy consumption.

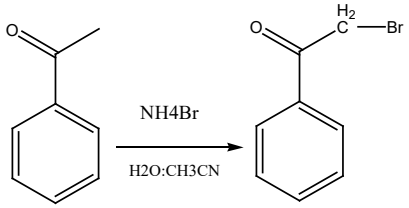
Electrochemical Cell Efficiency: The efficiency of reaction depends on electrode material, cell configuration and mass transport. Poor cell design may cause incomplete conversion, side reaction, or overbromination, which has an overall impact on atom economy.

Substrate and Solvent Limitations: Certain substrates can spontaneously undergo unwanted oxidation at an electrode surface, and solvent selection (e.g., aqueous-organic mixtures) can restrict the solubility of nonpolar substrates.

Scalability and Equipment Requirements: Scaling up will require close attention to the distribution, electrode contamination or heat loss to achieve selectivity and yield. High-level electrochemical equipment might be required which may push up the initial expense.

Operational Consideration: Even though electrochemical bromination helps to reduce the use of hazardous reagents, it cannot be effective without technical expertise to regulate the reaction parameters and assure reproducibility.

In general, electrochemical bromination is one of the most promising green technologies. This strategy offers environmentally compatible, scalable bromination, optimized cell design, energy input and reaction parameters. Its relative simplicity of operation, mild conditions, and lack of dangerous agents such as brominating agents turn into a useful tool both in laboratory and industrial processes in the synthesis of 2-brominated building blocks.[12]



A pivotal contribution in this area is the review by Sabuzi *et al.*, (2019), which comprehensively evaluates the use of environmentally benign brominating agents. The authors focus on reagents such as N-Bromosuccinimide (NBS), 1,3-Dibromo-5,5-Dimethylhydantoin (DBDMH), and bromine generated in situ from systems like NaBr/$NaBrO_3$ or NaBr/NaOCl. These systems allow the bromine to be released under controlled conditions, minimizing exposure and reducing the risk of over-bromination. The study highlights the role of water or alcohols as reaction media and stresses the importance of atom economy, reaction selectivity, and ease of product isolation. These

Table 1: Comparative Analysis of Bromination Strategies.

Study/Approach	Reagent/System	Key Features	Advantages	Limitations
Sabuzi *et al.*, (2019)	NBS, DBDMH, NaBr/$NaBrO_3$	Green reagents, in situ Br_2	Low toxicity, scalable, water as solvent	May require controlled conditions
Jiang *et al.*, (2023)	KBr-Oxone, $NaBrO_3$-HCl	Oxidative bromination	Metal-free, mild, selective C-H activation	Oxidants can be costly
Electrochem (2023)	Electrooxidation of Br^-	Electrochemical bromination	Clean energy source, high selectivity	Requires electrochemical setup
Kim *et al.*, (2014)	NH_4Br/KBr in 2-phase cell	Benzylic bromination	High yield, scalable, Br_2-free	Limited to alkyl aromatics
J. Org. Chem. (2024)	Br_3^- species in 200% cell	Electrophilic arene bromination	Mechanistic control, high precision	Advanced instrumentation needed
Kiplinger *et al.*, (2016)	Br_2, PBr_3, BrCl, NBS	Comprehensive overview	Classical + modern methods	Involves hazardous reagents
Front. Chem. (2022)	General electrosynthesis	Tutorial perspective	Sustainable, wide applicability	Introductory level only

improvements translate into lower E-factors and better alignment with green chemistry principles, making them attractive for industrial applications.[13]

Expanding on this, Jiang, Wu, and Cui (2023) have detailed the recent progress in oxidative bromination techniques involving arenes and heteroarenes. Their review surveys the development and application of bromide/oxidant systems such as KBr-Oxone, $NaBrO_3$-HCl, and TBAB-based protocols, which facilitate site-selective C-H bond activation. These methodologies function efficiently without the need for transition metal catalysts or stoichiometric halogenating reagents, offering high substrate tolerance and excellent yields. Mechanistic pathways for these transformations, including radical and electrophilic mechanisms, are thoroughly discussed. The review provides extensive examples illustrating how bromination can be leveraged to functionalize complex aromatic and heteroaromatic frameworks under mild and sustainable conditions.[14]

The role of electrochemical techniques in bromination chemistry is increasingly recognized, as evidenced in a 2023 review published in *Electrochem* that outlines strategies for electrochemical bromofunctionalization. This paper discusses how electrochemical oxidation of bromide sources (e.g., NaBr, Bu_4NBr) can generate bromonium ions in situ, which are subsequently used for transformations such as alkene dibromination, bromolactonization, and bromoetherification. These reactions are typically carried out in acetonitrile or aqueous-organic solvent systems under ambient temperatures. The key advantages of electrochemical methods include the elimination of external oxidants, low energy requirements, high selectivity, and the use of electricity as a clean and controllable reagent. These characteristics make electrochemical bromination highly suitable for green and scalable synthetic processes.[15]

A more application-focused perspective is offered by Kim *et al.*, (2014), who reported the electrochemical bromination and oxidation of alkyl aromatic compounds via two-phase electrolysis using NH_4Br or KBr. Their undivided electrochemical cell enabled benzylic bromination of substrates like toluene and ethylbenzene with high selectivity and yields reaching up to 98%. The system is particularly attractive for scale-up because it eliminates the use of elemental bromine and minimizes the formation of undesired polybrominated byproducts. The use of a biphasic solvent system further aids product isolation and reduces cross-contamination between electrodes.[16]

An advanced mechanistic study published in *The Journal of Organic Chemistry* (2024) describes the use of a "200% cell" configuration to control the speciation and reactivity of bromine in the form of tribromide (Br_3^-) ions. This setup allows for precise electrochemical modulation of the reaction environment, enabling selective aromatic bromination via electrophilic substitution pathways. The study provides valuable insights into how tribromide equilibrium and electrode potentials influence reaction selectivity and yield. This work underscores the growing sophistication of electrochemical approaches in achieving chemoselective halogenation with minimal environmental impact.[17]

In a broader context, Kiplinger *et al.*, (2016) published a foundational review in *Chemical Reviews*, presenting a detailed account of bromine chemistry in organic synthesis. This exhaustive review covers both classical reagents such as Br_2, PBr_3, and BrCl, as well as more modern bromination tools like DBDMH, NBS, and ionic liquids. It includes mechanistic discussions, reactivity trends, and applications in the synthesis of pharmaceuticals, dyes, and advanced materials. The authors also explore safety considerations, industrial-scale challenges,

and regulatory perspectives, making it an essential resource for synthetic chemists.[18]

Electrosynthesis continues to evolve as a green alternative to traditional organic transformations. A tutorial review published in *Frontiers in Chemistry* (2022) outlines the basic principles of electrochemical organic synthesis, including halogenation reactions. It provides practical guidance on electrode materials, electrolyte selection, cell design, and parameter optimization. The review emphasizes how electricity can serve as a sustainable oxidant and outlines case studies where electrochemical bromination offers distinct advantages in terms of atom economy and environmental impact.[19]

In summary, the field of bromination chemistry is undergoing a paradigm shift toward cleaner, safer, and more sustainable practices. Innovations in reagent design, electrochemical techniques, and in situ bromine generation have greatly expanded the synthetic utility of bromination reactions while aligning them with the core principles of green chemistry. These advancements not only improve reaction efficiency and selectivity but also enhance the environmental compatibility of bromination protocols, making them suitable for modern synthetic and industrial applications (Table 1).[20,21]

CONCLUSION

In summary, the field of bromination chemistry is undergoing a paradigm shift toward cleaner, safer, and more sustainable practices. Innovations in reagent design, electrochemical techniques, and in situ bromine generation have greatly expanded the synthetic utility of bromination reactions while aligning them with the core principles of green chemistry. These advancements not only improve reaction efficiency and selectivity but also enhance the environmental compatibility of bromination protocols, making them suitable for modern synthetic and industrial applications.

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ABBREVIATIONS

NBS: N-Bromosuccinimide; **DBDMH:** 1,3-Dibromo-5,5-dimethylhydantoin; **NaBr/$NaBrO_3$:** Sodium Bromide/Sodium Bromate system; **KBr-Oxone:** Potassium Bromide-Oxone system; **$NaBrO_3$-HCl:** Sodium Bromate-Hydrochloric Acid system; **Electrooxidation of Br^-:** Anodic oxidation of bromide ion to reactive bromine species; **NH_4Br/KBr in 2-phase cell:** Ammonium or Potassium Bromide in a biphasic electrochemical setup; **Br_3^-species in 200% cell:** Tribromide ion formed in enhanced electrochemical cell configuration; **Br_2:** Molecular Bromine; **PBr_3:** Phosphorus Tribromide; **BrCl:** Bromine Monochloride; **General Electrosynthesis:** Broad term for electrochemical synthesis using electric current as a reagent.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

FUNDING

The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.

SUMMARY

Bromination plays a crucial role in organic synthesis, particularly in the development of pharmaceuticals, agrochemicals, and functional materials. Conventional bromination techniques typically involve hazardous reagents such as molecular bromine and often require harsh reaction conditions, which pose safety and environmental risks. This review highlights recent progress in the development of green bromination methodologies that emphasize sustainability, safety, and synthetic efficiency.

Recent innovations include the use of eco-friendly brominating agents like N-Bromosuccinimide (NBS) and 1,3-Dibromo-5,5-Dimethylhydantoin (DBDMH), along with in situ generation of active bromine species from systems such as NaBr/NaOCl and NaBr/$NaBrO_3$. Electrochemical bromination has emerged as a powerful alternative, offering high selectivity, operational simplicity, and scalability. Strategies such as two-phase electrolysis, tribromide-mediated transformations, and the use of advanced electrochemical cell designs have shown significant promise in achieving efficient and selective bromination without the need for external oxidants.

This review also explores the adoption of catalyst-free protocols, solvent-minimized systems, and aqueous media, all of which contribute to the alignment of bromination chemistry with green chemistry principles. Mechanistic perspectives-including radical and electrophilic substitution pathways-are discussed to provide insights into the factors influencing reactivity and selectivity.

Overall, the review illustrates the transformation of bromination chemistry through greener approaches, making it more compatible with the demands of modern synthetic and industrial applications.

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