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COMMUNICATION

Electrochemically Driven Bromochlorination of Alkenes

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Organic halides are vital in the synthesis of pharmaceutical, agrochemical, and materials. While conventional alkene dihalogenation uses active halogen reagents, we developed an electrochemical strategy for selective bromochlorination. This approach enables precise halogenation under mild conditions.

Organic halides are common structural motifs in many bioactive natural products,[1] pharmaceuticals,[2] commodity chemicals[3] and polymers.[3b, 4] Additionally, organic halides are utilized as important reaction intermediates in organic synthesis due to their ability to convert into various functional groups for creation of complex organic compounds.[5] Bromochlorides constitute a significant subset within the realm of organic halides, showcasing distinctive physiological activities (Figure 1a).[6] Moreover, bromochlorides containing two distinct halogen atoms can undergo sequential reactions to introduce two different molecular fragments, which significantly enhances the diversity and flexibility in the synthesis of complex molecules.[7]

The bromochlorination of alkenes represents an efficient and step-economical strategy for the incorporations of chlorine and bromine.[8] The key of this strategy involves the provision of two halogen intermediates with different electronic properties. In addition, the nucleophilic competition of halogen anions (Br-, Cl-), site selectivity, and stereoselectivity all increase the difficulty in obtaining a single bromochloride product (Figure 1b).[9] The traditional approach for bromochlorination of alkenes entails the direct addition of disparate halogen sources to the alkenes in the presence of well-designed catalysts (Figure 1c).[10, 11, 12] Nevertheless, a limitation of this methodology is the use of highly active reagents. Xie and colleagues have reported a photocatalytic shuttle strategy to realize bromochlorination of alkenes with perovskite quantum dots (QDs) as catalysts (Figure 1d).[13] However, an extra excess of 1,1,2,2-tetrachloroethane (TCE) was required to obtain bromochloride products under long time LED irradiation.

Electrochemistry can provide an effective and sustainable alternative to traditional chemical methods for organic redox transformations.[14] Lin's and Morandi's group have independently utilized Mn-catalyzed electrolysis to achieve the dihalogenation of alkenes by employing $MgCl_2$ and dihalogen ethane as halide sources (Figure 1e).[15, 16] Nevertheless, there is still a significant knowledge gap in utilizing electrochemistry for the bromochlorination of alkenes. Inspired by these precedents and our continued interest in alkenes functionalization,[17] we employed undivided cell to generate two distinct types of halogen intermediates through paired electrolysis (Figure 1f).[18] These intermediates were then reacted with alkenes, enabling the efficient synthesis of bromochlorides with high chemo-, regio-, and diastereoselectivity. Besides, the reaction was characterized by its simplicity, as catalyst or additive free condition. Initially, styrene **1a** was chosen as the model substrate for optimization (Table 1). With hexachloroethane (C_2Cl_6) as chlorine source, bromochloride **2a** was obtained as main product by using

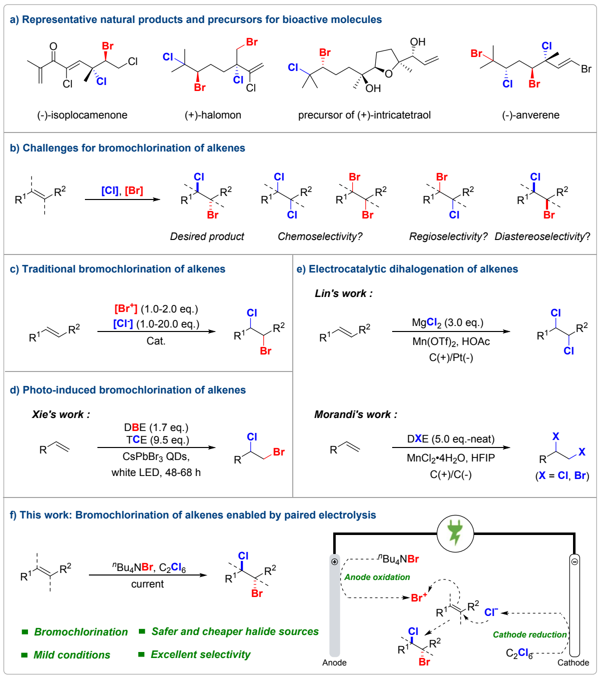

Figure 1. Representative vicinal bromochlorides and related syn-thesis from alkenes.

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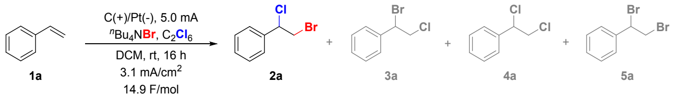
tetrabutylammonium bromide (^{n}Bu$_4$NBr) as electrolyte and bromine source in DCM (entry 1). Conducting the electrolysis without C_2Cl_6 resulted in a lower yield (entry 2). Replacing C_2Cl_6 with TCE as chlorine source was found to be slightly less effective in terms of activity and selectivity (entry 3). It was worth noting that when C_2Cl_6 was added, DCM typically only served as a solvent instead of chlorine source, which was further confirmed in subsequent mechanistic experiments (Figures 3D and 3E). Using DCE as both chlorine source and solvent resulted in poor selectivity of the reaction (entry 4). The use of alternative bromine sources, such as *N*-bromosuccinimide (NBS) or lithium bromide (LiBr), lowered the reaction efficiency with tetrabutylammonium hexafluorophosphate (^{n}Bu$_4$NPF$_6$) as the electrolyte (entries 5 and 6). The alteration of the ratio between ^{n}Bu$_4$NBr and C_2Cl_6 led to a significant decrease in yield and favored the formation of the undesired dichloride **4a** (entry 7). Solvents such as methanol (MeOH), acetonitrile (MeCN), and *N,N*-dimethylformamide (DMF) were screened as well, but lower yields were obtained (entries 8-10). The electrochemical reaction could also be performed when using glassy carbon (GC) electrode as the anode, although with a slight decrease in yield (entry 11). Severe corrosion of the lead cathode material occurred, which hindered the generation of chloride ions and thereby led to a decrease in both reaction activity and selectivity (entry 12). No desired reaction occurred in the absence of current (entry 13). Finally, under ambient air conditions, the electrochemical reaction could also be conducted (entry 14).

Table 1. Optimization of the reaction conditions.[a]



Entry	Variation	Yield[b] [%]			
		2a	3a	4a	5a
1	None	**91 (88[d])**	0	0	5
2	Without C_2Cl_6	43	0	0	8
3	TCE instead of C_2Cl_6	75	0	3	7
4	DCE instead of DCM, without C_2Cl_6	42	11	11	0
5[c]	NBS instead of ^{n}Bu$_4$NBr	19	0	0	12
6[c]	LiBr instead of ^{n}Bu$_4$NBr	24	0	4	0
7	^{n}Bu$_4$NBr (2.0 eq.), C_2Cl_6 (1.5 eq.)	29	0	24	7
8	MeOH instead of DCM	2	0	0	0
9	MeCN instead of DCM	59	10	6	0
10	DMF instead of DCM	30	0	0	6
11	GC(+)/Pt(-) instead of C(+)/Pt(-)	70	0	0	0
12	C(+)/Pb(-) instead of C(+)/Pt(-)	35	0	4	19
13	Without current	0	0	0	0
14	Under air	62	0	5	3

[a]Conditions: Unless otherwise noted, all reactions were performed with **1a** (0.20 mmol), ^{n}Bu$_4$NBr (1.5 eq.) and C_2Cl_6 (1.5 eq.) in DCM (4.0 mL) at room temperature for 16 h. [b]Yields were determined by GC-FID. [c]Adding ^{n}Bu$_4$NPF$_6$ (1.5 eq.) as electrolyte. [d]Isolated yield.

With the optimized conditions in hand, the scope of terminal alkenes was investigated (Figure 2A). Both electron-donating (**2b**-**2d**) and electron-withdrawing groups (**2e**-**2i**) at the *para*-position of the aryl ring were well tolerated, delivering the desired products in moderate to good yields with high selectivities. 1-Chloro-3-vinylbenzene also exhibited good activity and gave the bromochloride product in 87% yield (**2j**), although with a slight decrease in the chemoselectivity. However, the steric hindrance resulted in a noticeable decrease in both yield and chemoselectivity (**2k**). Besides, this protocol could be successfully extended to bromochlorination of heterocycle derived substrates (**2l-2m**). To our delight, the electrolytic process showed good compatibility with vinyl ester type alkenes (**2n**-**2o**).

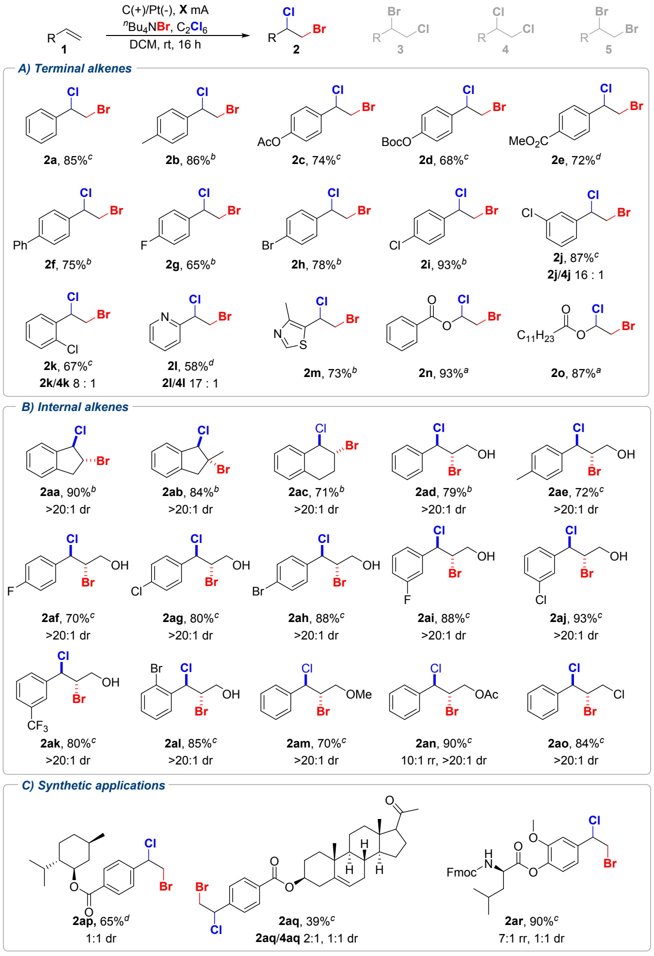


Figure 2. Substrate scope for bromochlorination of alkenes. [a]Reaction with 3.0 mA, 16 h (1.9 mA/cm^2, 8.9 F/mol). [b]Reaction with 4.0 mA, 16 h (2.5 mA/cm^2, 11.9 F/mol). [c]Reaction with 5.0 mA, 16 h (3.1 mA/cm^2, 14.9 F/mol). [d]Reaction with 6.0 mA, 16 h (3.8 mA/cm^2, 17.9 F/mol).

Additionally, the current electrochemical protocol was also suitable for the bromochlorination of internal alkenes (Figure 2B). It was observed that both five-membered (**2aa-2ab**) and six-membered (**2ac**) cyclic internal alkenes gave good results. Free hydroxyl groups were all compatible with this process, leading to the bromochloride products (**2ad-2al**) in high yields and selectivities. The reaction also demonstrated good tolerance for cinnamyl ether (**2am**) and cinnamyl chloride (**2ao**). Cinnamyl ester also exhibited good activity and gave the bromochloride product in 82% yield (**2an**), although with a decrease in regioselectivity. Finally, the electrolytic method successfully extended to alkenes bearing fragments of natural products (**2ap-2ar**), and these substrates could smoothly undergo bromochlorination with moderate to high yields (Figure 2C).

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To probe the mechanism of this electrochemically enabled bromochlorination, preliminary mechanistic investigations have been carried out (Figure S2, SI). Control experiments were conducted by individually adding MeOH or bulky ^{t}BuOH to the reaction system (Figure S2A, SI). The addition of MeOH gave bromochloride **2a** in 30% yield accompanied by bromoalkoxylation product **6a** in 21% yield (entry 2). Besides, the addition of ^{t}BuOH increased the yield of product **2a** to 56%, and a trace amount of bromoalkoxylation product **6b** was detected (entry 3). The above experiments suggest that a bromonium intermediate is involved in this reaction.[19] Furthermore, the scope of substrate was successfully conducted with high diastereoselectivities, which further supports our hypothesis.[20]

After adding BHT or TEMPO as a radical scavenger, a significant decrease in the yield of product **2a** was observed. HRMS analysis of the reaction mixture revealed no adducts of TEMPO or BHT. Moreover, when conducting radical clock experiment with (1-cyclopropylvinyl)-benzene **1p**, ring-opening product **7p** was afforded in 50% yield (Figure S2B, SI). These results suggest that bromine radical or cation may be involved in this reaction.[21]

In order to get insight into this electrochemical process, cyclic voltammetry (CV) studies were performed under different conditions (Figure S2C, SI). A sharp oxidation peak of styrene with $E_{1/2}$ = 2.06 V (vs. SCE) was observed (curve II). Besides, two distinct oxidation peaks of Br anion with $E_{1/2}$ = 0.98 V and $E_{1/2}$ = 1.4 V were exhibited respectively (curve III). A comparison between curves II and III indicates that Br anion is more susceptible to oxidation at the anode compared to styrene, and the generation of Br cation may undergo two-step anodization. In order to track the source of chlorine, CV studies of DCM and C_2Cl_6 were conducted (Figure S2D, SI). C_2Cl_6 showed a reduction peak with $E_{1/2}$ = -1.46 V (curve II) while DCM exhibited no apparent reduction peak from -3.0 to 0 V (curve III). Moreover, similar result was obtained when adding C_2Cl_6 and DCM (curve IV vs III). These results reveal that the chlorine mainly originates from the cathodic reduction of C_2Cl_6.

Kinetic studies were carried out to further gain mechanistic insight (Figure S2E, SI). The consumption of styrene and C_2Cl_6, as well as the generation of tetrachloroethylene (C_2Cl_4), exhibit a similar trend with a close-to-stoichiometric relationship. It further confirms that Br anion undergoes anodic oxidation to provide Br cation while C_2Cl_6 is reduced to produce Cl anion at the cathode. The desired bromochloride **2a** was not detected at the initial 1 h but then gradually increased. Throughout the entire process, the formation of side product **3a** was scarcely observed. The dibromide **5a** was quickly formed, reached the peak around 3 h and then gradually decreased. Although Cl anion had stronger nucleophilicity, the concentration of Br anion is much greater than that of Cl anion, resulting in similar rates of formation for bromochloride **2a** and dibromide **5a** at the early stage of reaction. As the reaction proceeded, the concentration of Cl anion gradually increased, favoring the formation of bromochloride **2a**, and dibromide **5a** also gradually converted to bromochloride **2a**. The dichloride **4a** was not detected at the initial 3 h, and then gradually increased until it reached the peak around 8 h. It is likely that dichloride **4a** results from the conversion of bromochloride **2a** or dibromide **5a**.

In order to demonstrate conversion between the products and establish their conversion relation, control experiments were conducted by replacing styrene **1a** with bromochloride **2a** or dibromide **5a** as starting material under standard conditions (Figure S2F, SI). A trace amount of bromochloride **2a** was transformed into dichloride **4a** (left, entry 1). However, when using tetrabutylammonium chloride (^{n}Bu$_4$NCl) as electrolyte, the yield of dichloride **4a** increased to 18% (left, entry 2). The yield of dichloride **4a** was 8% without electricity (left, entry 3). No formation of dibromide **5a** was observed under the above conditions. When using dibromide **5a** as substrate, bromochloride **2a** was obtained in 6% yield while dichloride **4a** was not detected (right, entry 1). However, when employing ^{n}Bu$_4$NCl as electrolyte, the yield of bromochloride **2a** increased to 53% accompanied by dichloride **4a** in 5% yield (right, entry 2). In the absence of electricity, the yield of bromochloride **2a** was 14% along with trace amount of dichloride **4a** (right, entry 3). The above results indicate that, in the presence of Cl anion, bromochloride **2a** and dibromide **5a** can be further transformed into dichloride **4a** and bromochloride **2a** respectively. Notably, electricity could accelerate the corresponding transformation. And direct conversion of dibromide **5a** to dichloride **4a** is slow.

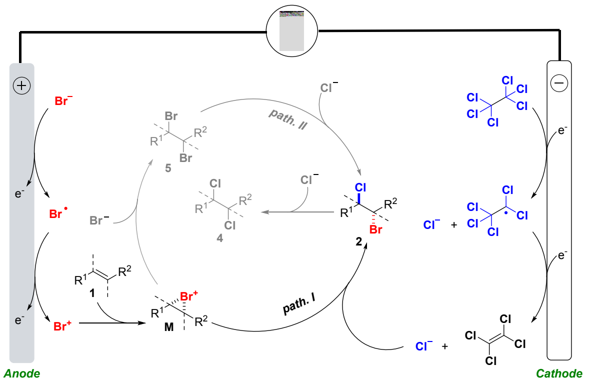

Figure 3. Proposed mechanism.

Based on the aforementioned experiments, a possible mechanism of this electrochemically driven bromochlorination of alkenes is proposed (Figure 3). At the anode, Br anion undergoes two-step oxidation to form Br cation. Simultaneously, C_2Cl_6 is reduced to generate Cl anion and C_2Cl_4 at the cathode. Br cation then reacts with the alkene **1** to form a bromonium intermediate **M**, which subsequently reacts with Cl anion to obtain the desired product **2** (Path I). Besides, Br anion can also react with the bromonium intermediate **M** to form dibromide product **5**. With the promotion of electricity, dibromide product **5** can gradually convert into desired product **2** (Path II). Meanwhile, a small amount of product **2** can transform into dichloride product **4**.

To further demonstrate the synthetic utility of this protocol, scale-up reaction and derivatizations have been performed (Figure S7, SI). Gram-scale preparation of cinnamyl alcohol **1ad** was carried out to afford the bromochloride **2ad** (1.5 g) in 75% yield with excellent diastereoselectivity (>20:1). Next, the esterification of bromochloride **2ad** could occur and the configuration of halogenated ester **8** was further confirmed through single crystal X-ray diffraction.[22] Furthermore, reactions of bromochloride **2ad** with various nucleophilic reagents were conducted to synthesize 1,3-diol **9** and ester **10** respectively.[23] Notably, these reactions could maintain high diastereoselectivities (>20:1). Finally, the elimination reaction of bromochloride **2ad** was performed, yielding the chlorinated allylic alcohol **11** (>20:1 *E/Z*) in 66% yield.

In conclusion, we developed an efficient electrolytic method for the catalyst-free bromochlorination of alkenes with high selectivities. C_2Cl_6 as halogen sources and demonstrates compatibility with multifarious functional groups such as free hydroxyl group.

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Mechanistic studies revealed that the reaction undergoes Br cation and Cl anion via paired electrolysis. Most importantly, the formation of bromonium intermediate results in high selectivities. Besides, diverse synthetic elaborations have been successfully achieved with high selectivities. We anticipate that this mild, efficient, and highly selective bromochlorination strategy will propel the development other dihalogenations (such as bromofluorination), thereby providing a new paradigm for precise electrochemical synthesis of organic halides.

Conflicts of interest

There are no conflicts to declare.

Data Availability Statement

The data underlying this study are available in the article and its SI.

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