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Electrochemical Halogenation/Semi-pinacol Rearrangement of Allylic Alcohols Using Inorganic Halide Salt: An Eco-friendly Route to Synthesis of β -halocarbonyls

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An efficient and eco-friendly electrochemical method involving halogenation/semi-pinacol rearrangement of allylic alcohols using inorganic halide salt as the halogen source to synthesize various β -halocarbonyls bearing an all-carbon α -quaternary center under mild reaction conditions has been developed (X = Br, Cl). Stoichiometric oxidants, metal catalysts, and even external electrolytes were avoided in this method. It was found that the whole reaction system was compatible with various common interfering ions in water and exhibited good selectivity for bromide ion. Furthermore, halogen resource can be efficiently extracted from simulated wastewaters to construct key intermediates for the syntheses of natural products (±)-galanthamine and (±)-crinamine. Additionally, this strategy may be promising to treat oil and gas wastewaters and desalt seawater.

Oil and gas wastewaters containing high concentrations of bromide do not easily adsorb on sediments and could enter surface water through a long-distance migration.¹ Therefore, more and more wastewaters around the world are becoming an urgent and severe challenge to ecological environment and human health. Many attentions have been paid to scientific research to treat the wastewaters avoiding environmental pollution.² The simplest method is direct discharge of brine, however, it not only contributes to serious threats to ecological environment, but also is enormous waste of halogen resources.³ On the other hand, organohalo compounds are particularly important and useful due to they are not only widely present in bioactive natural products especially marine natural products, but also reveal extensive synthetic utility.⁴ Accordingly, a number of efforts to develop the synthetic strategies for the formation of organohalo compounds have been made.⁵ Among them, electrophilic halogenated reagents such as Nchlorosuccinamide (NCS), N-bromosuccinamide (NBS), and bromine

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HO R¹ R² (mixture of Br, CI, etc.) (X=Br, CI) Electrochemical + brine • Green and efficiency • Green and efficiency • Green and efficiency • Green and efficiency • Green and efficiency

High chemical selective
potential to treat oil and gas wastewaters and desalt seawater Classic halogen sources • High cost and pollution A) NCS (\$25.4/100 g) B) NBS (\$31.2/100 g) (Br₂ (\$73.7/100 g, danger and toxic) D) Phi(OAc)₂(\$146/100 g)/NAX:

Application to the synthesis of natural product



Scheme 1 Approaches to β -halocarbonyls via electrochemical semipinacol rearrangement of allylic alcohols.

(Br₂) have most frequently emerged as halogen sources and the combination of halogen anion and stoichiometric strong oxidant were also developed recently. For example, our group has been focusing on halogenation/semi-pinacol rearrangement to synthesize β -halocarbonyls bearing a guaternary center which broadly exist in bioactive and pharmacological molecules, with different electrophilic halogenated reagents (Scheme 1).⁶ Recently, a halogen-salt-involved semi-pinacol rearrangement using stoichiometric PhI(OAc)₂ as the oxidant was also developed (Scheme 1).7 However, these two strategies are not ideal from the perspective of the cost and environmental protection. However, these two strategies are not ideal from the perspective of the cost and environmental protection. Considering the above two issues together, the development of a protocol which could recycle halogenion from wastewaters to environmentally friendly synthesize universal organohalo compounds is in high demand.

Electrochemical method has attracted significant attentions in organic synthesis due to environmentally friendly feature. Stoichiometric chemical oxidants are avoided in the electrochemical reaction while substrates are oxidized

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selectively at the anode in different potentials.⁸ Numerous transition-metal-catalyzed electrochemical C-H functionalization reactions have been reported by Ackermann, Mei, and Lei etc., meanwhile radical transformations of alkenes initiated by electrocatalysis get great progresses, which are accomplished by Lin, Lei, Zeng, Xu, Stahl, Baran, and other groups.^{9,10} Indeed, electrochemical reactions involving halogen salt have been preliminarily investigated for the facile transformation of halogens to other function groups under economic and eco-friendly reaction conditions. For example, Lin group developed some Mn(II)-catalyzed electrochemical halogen-salt-involved alkene difunctionalizations in recent years,¹¹ while halogen salt can also be used as the catalyst in the electrochemical reactions.¹² Based on these advances and combined our research interest, we are desired to realize practical and economic electrochemical halogenation/semipinacol rearrangement of allylic alcohols directly using inorganic halide salts as the halogen source (Scheme 1b). To verify the feasibility of the above idea, we first carried out cyclic voltammetry studies, allylic alcohol 1a shows an oxidation peak at $E_{p/2} = 1.59$ V vs. SCE compared to MgBr₂·6H₂O $E_{p/2} = 0.95$ V vs. SCE or MgCl₂ E_{p/2} = 1.40 V vs. SCE, indicating that **1a** is workable to investigate a halogenation/semipinacol rearrangement reaction (for the details, please see SI). Next, we roughly tested the process for 1a, which involved constant-current electrolysis using a carbon felt as the anode and a Pt plate as the cathode, in an undivided cell containing MgBr₂·6H₂O in water at room temperature. To our delight, the desired product 2a was obtained in 59% yield (Figure 1). Encouraged by the preliminary success, we further studied the rearrangement reaction in detail. Herein, we are pleased to report electrochemical bromination and chlorination/semi-pinacol rearrangement of allylic alcohols with moderate to good yields. Furthermore, the reaction also proceeded smoothly no matter using simulated wastewaters or bittern, producing the desired β -halocarbonyls in moderate to excellent yields.



Figure 1 The preliminary study of electrochemical bromination/semipinacol rearrangement in water under open-air conditions.

We speculated that the relatively poor solubility of allylic alcohol **1a** in water resulted in the moderate yield (Figure 1 or Table 1, entry 1). To further improve the yield, the mixture of acetonitrile and water (2:1) was first chosen as the solvent. To our delight, a satisfying yield of desired product **2a** was obtained (79%, Table 1, entry 2). It should be noted that this reaction proceeded without external electrolytes for that MgBr₂·6H₂O was not only reactant but also electrolyte, and for this reason the cell potential increased gradually in the reaction. Next, other polar protic solvents (MeOH, AcOH) were also screened as co-solvent. The use of methanol as a co-solvent further increased the yield to 81%, while acetic acid gave 77% yield (entries 3-4). Trace amount of desired product was detected when acetonitrile was usell^O a⁵O.130 R/eff^C alonel, indicating that polar protic solvents may be crucial proton transfer medium in this electrochemical reaction (entry 5). Subsequently, we tested other bromine salts as halogen source in the reaction but no better result was obtained (entries 6-8). Finally, control experiment indicates that electricity is indispensable in the reaction (entry 9). Despite that a slightly higher yield was obtained when MeCN/MeOH were used as the solvent, MeCN/H₂O were identified as the promising solvent when economy and environmental friendliness were taken into accounts.

Table 1 Optimization.

	Ph HO Ph HO Ph HO Constant current (25 mA) bromine saits air, r.t, 1 h 1a undivided cell C (+) Pt (-) Ph Br O 2a	
entry	reaction conditions ^a	yield ^b
1	$MgBr_2 \cdot 6H_2O, H_2O$	59%
2	MgBr ₂ ·6H ₂ O, MeCN/H ₂ O (2:1)	79% ^c
3	MgBr ₂ ·6H ₂ O, MeCN/MeOH (2:1)	81% ^d
4	MgBr ₂ ·6H ₂ O, MeCN/AcOH (2:1)	77%
5	MgBr ₂ ·6H ₂ O, MeCN	<5%
6	NaBr, MeCN/MeOH (2:1)	34%
7	LiBr, MeCN/MeOH (2:1)	28%
8	MnBr ₂ , MeCN/MeOH (2:1)	78%
9	MgBr ₂ ·6H ₂ O, MeCN/H ₂ O (2:1), no	<5%
	current	

^a**1** (0.4 mmol), [Br] (8 equiv.), air, r.t, 1 h, carbon felt (1.0 cm × 1.0 cm) as the anode, and Pt plate (1.0 cm × 1.0 cm) as the cathode, constant current (25 mA), undivided cell. ^bisolated yield. ^cAnode potential starts from 1.42 V vs SCE, E_{cell} range from 3.29 V to 3.65 V, Faradaic efficiency 85% (2.35 F/mol). ^dAnode potential starts from 1.42 V vs SCE, E_{cell} range from 3.61 V to 4.02 V, Faradaic efficiency 86% (2.33 F/mol).

With the optimal conditions in hand, we examined a series of allyl alcohols for this electrochemical reaction. In general, the corresponding β -bromocarbonyls containing an all-carbon α quaternary center were produced with moderate to excellent yields (Table 2). Initially, various tertiary alcohols were subjected to the reaction for the synthesis of β -bromoketones (Table 2a). By contrast to the model substrate 1a, methyl group in the meta- or para-position obviously increased the yields, while in the ortho-position did not affect the yield (2b-d). The substrates with electron-donating substituents were welltolerated in this reaction and gave excellent yields (2f, g). It was found that 2-naphthyl substrate 1h was also suitable for this reaction delivering the corresponding product **2h** in 93% yield. To our delight, the moderate yields were obtained with excellent diastereoselectivities (dr>20:1) when tri-substituted alkenes were employed as the substrates (2i, 2j) and the relative configuration of 2i was determined by X-ray crystallography.13 It's worth mentioning that unactivated

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alkenes also reacted although resulting in some lower yields (**2k**, **2l**). Substrate with simple cyclopentanol **1m** led to an evident decrease in yield due to the relatively weak expansion ability of 5-member ring, while 9-fluorenol worked well giving 81% yield. Nicely, **1**,2-aryl and alkyl migrations were also accessible and afforded the corresponding products in middle to good yields (**2o-q**). We next examined some secondary alcohols as substrates in the reaction. A variety of β -bromo-aldehydes were afforded through electrochemical semi-pinacol rearrangement (**2r-u**). It is worth noting that the electron-rich phenyl migration group can result in a higher yield than electron-poor groups, which indicates a cation migration process involving in the tandem reaction.

(+) C | Pt (-) (25 mA)

- R1

Table 2 Substrate Scope of Allylic Alcohols^a



^{*o*}Reaction conditions: allylic alcohol (0.4 mmol), MgBr₂·6H₂O or MgCl₂ (4 equiv.), MeCN/H₂O (6 mL/3 mL), air, r.t, 1 h, carbon felt (1.0 cm × 1.0 cm) as the anode, and Pt plate (1.0 cm × 1.0 cm) as the cathode, constant current (25 mA), undivided cell. Isolated yield.

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Considering high chloride ion content of seawaters, and wersatile synthetic utility of organochlorides, we turned⁰ out⁹ attention⁵ to investigate electrochemical chlorination/semi-pinacol rearrangement of allylic alcohols. To our satisfaction, the desired chlorination product **3a** was obtained with 64% yield using MgCl₂ as the chlorine source. Next, a number of allyl alcohols were subjected to the reaction, affording the corresponding products with moderate to good yields (**3d-t**). Overall, the scope of bromination was all suitable for the chlorination although the yield is some lower.

To gain insights into this electrochemical halogenation reaction mechanism, some additional experiments were conducted. Addition of radical scavengers such as BHT and TEMPO results in the inhibition of the reaction, which indicates that radical species is involved in the process. Meanwhile, substrate with non-symmetric migration groups 1v was also tested and the product with electron-rich aryl group migration 2v was only obtained, which is identical to the product using NBS as the electrophilic halogen source (for the detail, please see SI). The outcome and the excellent diastereoselectivities of 2j and 2i conformably suggest that a cation migration process is involved in the tandem reactions. On the basis of the above results and previous works, a plausible mechanism was shown in Scheme 2. Halogen anion was oxidized to molecular bromine at the anode and then it promoted a classic electrophilic semipinacol rearrangement^{6g, 14} to form β -halocarbonyls.





It is well-known that bromine is described as "Ocean element" for that more than 99% of bromine on the earth exists in the ocean. Besides, there are abundant chlorine resources on the earth, such as industrial effluent from soda ash factory and sea water. The lower oxidation potential of MgBr₂·6H₂O than MgCl₂ provides the priority of bromine ion to chlorine ion to participate in the reaction, which could be used to split these two different ions. It was found that only β -bromoketone **2a** was detected when the equal amounts of MgBr₂·6H₂O and MgCl₂ were added in the reaction system. Next, we assumed that whether we can utilize bromine-rich brine as the halogen

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source, such as simulated dead sea water and bittern after making salt with seawater. To verify the idea, simulated solutions were prepared according to relative literature and were added into the reaction system (Table 3).¹⁵ Satisfyingly, the electrochemical reaction system offered good compatibility with common interfering ions in water, such as Na⁺, K⁺, Mg²⁺, Ca²⁺, SO₄²⁻, HCO₃⁻ and OH⁻. For simulated dead sea water and bittern after making salt with seawater, a good bromideselectivity (the ratio of [Br]/[Cl] is up to 5.1) was observed although bromide was far less than chloride, which showed a great efficiency to transform bromide ion from simulated brine to readily convertible function group in the product.

 Table 3
 Compatibility of reaction system for simulated solutions

	HO D	C (+) Pt (-) (25 mA) Ph				
	1a	<i>simulated solu (<mark>A-D)</mark> 1 h, air, MeC</i>	tions Br O	+ CI 3a		
entry	scale of 1 (mmol)	simulated solution (Br :Cl)	calculation standard	total yield	Ratio (2a : 3a)	
1	0.055	A (1: 128)	Br, 4 equiv.	98%	5.1:1	
2	0.11	A (1: 128)	Br, 2 equiv.	85%	4:1	
3	0.4	B (1: 97)	Cl, 4 equiv.	54%	1:20	
4	0.07875	B (1: 97)	Br, 2 equiv.	96%	3:1	
5	0.4	C (0:100)	Cl, 4 equiv.	36%	0:100	
6	0.21	D (1:651)	Cl, 8 equiv.	62%	1:27	

Components of simulated solution:

A (Bittern after making salt with seawater, g/L): Br 5~7, MgSO₄ 13.51, MgCl₂ 452.18, NaCl 2.18, KCl 2.47.

B (Dead sea water, g/L): Cl⁻ (181.4), Br⁻ (4.2), SO₄²⁻ (0.4), HCO₃⁻ (0.2), Ca²⁺ (14.1), Na⁺ (32.5), K⁺ (6.2), Mg²⁺ (35.2).

C (Industrial effluent (producing Na₂CO₃), g/L): Cl⁻ 99-115, OH⁻ 1-2.7, SO_4^{2-} 0.1-1.2, Ca^{2+} 39-45, Na⁺ 18-25, NH₃ 0.01-0.03, Suspended solids 11-70, CaO 0.7-9.0, CaCO₃ 3.8-11, CaSO₄ 1.7-7.1, Others By difference, pH 11-12.)

D (Seawater, mg/L): Na⁺ 11061.28, Mg²⁺ 1330.23, K⁺ 410.17, Ca²⁺ 423.54, Cl⁻ 19891.90, Br⁻ 68.88, F⁻ 4.73, SO₄²⁻ 929.31.

As our initial goal was to synthesize useful organohalo compounds eco-friendly, we next demonstrated the application of this halogen-involved electrochemical semi-pinacol rearrangement. Two allyl alcohols **1w** and **1x** were prepared and employed in the reaction system while simulated bittern after making salt with sea water was used as halogen sources (Scheme 3). The desired β -bromoaldehydes **2w** and **2x** were obtained in 35% and 42% yield, respectively, which were key intermediates for the syntheses of Amaryllidaceae alkaloids, such as (±)-galanthamine and (±)-crinamine.¹⁶ It's worth mentioning that the desired **2x** was also produced with 41% yield only using simulated oil and gas wastewater without adding MeCN as the co-solvent, which may be promising to treat oil and gas wastewaters and afforded useful products.



^aReaction conditions: allylic alcohol (0.055 mmol), MeCN/simulated solution A, air, r.t, 1 h, carbon felt (1.0 cm × 1.0 cm) as the anode, and Pt plate (1.0 cm × 1.0 cm) as the cathode, constant current (3 mA), undivided cell. Isolated yield. ^{*b*}only using simulated wastewater based on Br concentration (1.7 g/L), isolated yield.

Conclusions

In summary, we have developed a simple and facile electrochemical method involving halogenation/semi-pinacol rearrangement of allylic alcohols to synthesize β -halocarbonyls (X = Br, Cl) with an all-carbon quaternary center using inorganic halide salt as the halogen source. This method features open-air and eco-friendly reaction conditions, moderate to excellent yields, high selectivity for bromide ion, and synthetic application in the formal syntheses of bioactive natural products (±)-galanthamine and (±)-crinamine. Further studies are underway to efficiently treat the oil and gas wastewaters.

Conflicts of interest

There are no conflicts to declare.

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