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Electrochemical electrophilic bromination/spirocyclization of *N*-benzyl-acrylamides to brominated 2-azaspiro[4.5]decanes†

Zhongyi Zhang,[a,b] Zhong-Wei Hou,*[a] Hao Chen,[a] Pinhua Li [b] and Lei Wang *[a,b,c]

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An electrochemical electrophilic bromination/spirocyclization of *N*-benzyl-acrylamides with 2-bromoethan-1-ol as the brominating reagent has been developed. The paired electrolysis employs low concentrations of bromine produced from both cathodic reduction and anodic oxidation as an electrophile, and realizes an H_2O-involved electrophilic spirocyclization. A number of unexplored brominated 2-azaspiro[4.5]decanes are obtained with satisfactory yields under mild conditions, and the reaction exhibits good efficiency at the gram-scale synthesis. In addition, this approach is further highlighted by late-stage transformations and synthetic applications in constructing cyclohepta[*c*]pyrrole-1,6-diones *via* debromination tandem cyclization of brominated 2-azaspiro[4.5]decanes.

Introduction

Spiro compounds are common scaffolds in natural products and bioactive molecules, and also can be used as pivotal synthetic intermediates in organic synthesis.[1] Among them, azaspiro compounds have attracted much attention as unique building blocks.[2] In recent years, noble-metal-involved spirocyclization of phenol derivatives containing allylic carbonates, difluorobromides or α-diazoacetamides is an efficient route to 2-azaspiro[4.5]decanes (Scheme 1a).[3] The intramolecular radical dearomatizing spirocyclization could be accomplished under dilauroyl peroxide-mediated, Et_3B/air-mediated or visible-light-induced iridium-catalysis conditions (Scheme 1b, top).[4] In addition, variously functionalized 2-azaspiro[4.5]decanes were also synthesized through photo-catalyzed and metal-mediated intermolecular radical addition/spirocyclization of *N*-benzyl acrylamides (Scheme 1b, bottom).[5] However, these reported methods often require the use of extra-oxidants and metal reagents, and anisoles or phenols as activated substrates. Moreover, hypervalent iodine-mediated intramolecular spirocyclization reactions have been explored by Zhang, Nevado, Chabaud and Guillou, providing a straightforward way to construct 2-azaspiro[4.5]decanes.[6]

Organic electrochemistry realizes redox reactions through anodic oxidation and cathodic reduction without the need for traditional chemical reagents.[7] Due to its safety, controllability and environmental friendliness, organic electrosynthesis is widely applied in organic chemistry.[8] Recently, electrochemical dearomatizing spirocyclization could be achieved for the synthesis of spiro compounds under oxidant-free conditions.[9] Guo and coworkers described an electrochemical selenation/spirocyclization of *N*-aryl alkynamides to give selenated 1-azaspiro[4.5]trienones.[10] Chen and Xu developed an electrochemical oxidative halospirocyclization of *N*-aryl alkynamides to synthesize 1-azaspiro[4.5]trienones.[11] However, a metal-free and oxidant-free method for the electrophilic functionalized spirocyclization of alkenes is still lacking.[12] Using 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) as an electrophilic reagent, You and co-workers reported electrophilic bromination initiated spirocyclization at −20 °C for the preparation of azaspiro[5.5]decanes.[13]

Based on the above progress and our previous reports on electrochemical bromination of (hetero)arenes,[14] we herein developed a metal- and oxidant-free approach for the electrochemical electrophilic bromination/spirocyclization of *N*-benzyl acrylamides with 2-bromoethan-1-ol as the brominating reagent for the synthesis of unexplored brominated 2-azaspiro[4.5]decanes, which could react with nucleophilic reagents to form cyclohepta[*c*]pyrrole-1,6-diones *via* a debromination tandem cyclization under simple basic conditions (Scheme 1c).

[a]*Advanced Research Institute and College of Pharmaceutical Sciences, Taizhou University, Jiaojiang, Zhejiang, 318000, P. R. China.*
E-mail: zhongwei.hou@tzc.edu.cn, leiwang88@hotmail.com
[b]*Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, P. R. China*
[c]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai 200032, P. R. China*

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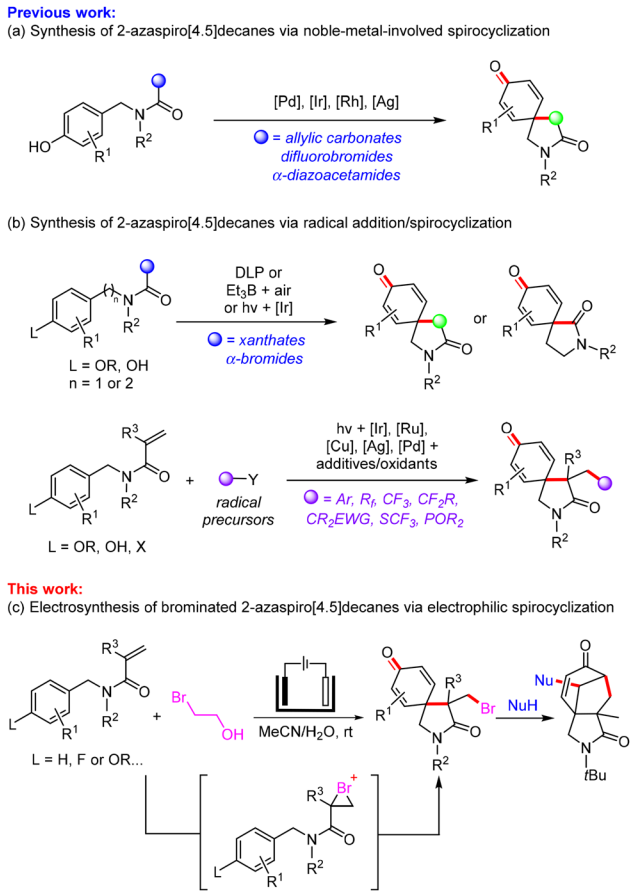
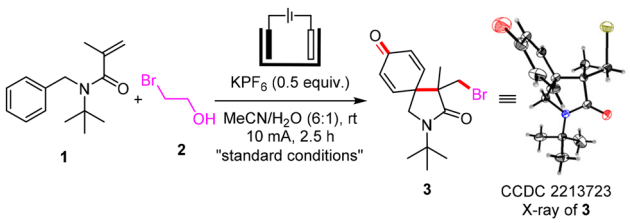


Scheme 1 Synthesis of 2-azaspiro[4.5]decanes.

Table 1 Optimization of the reaction conditions[a]



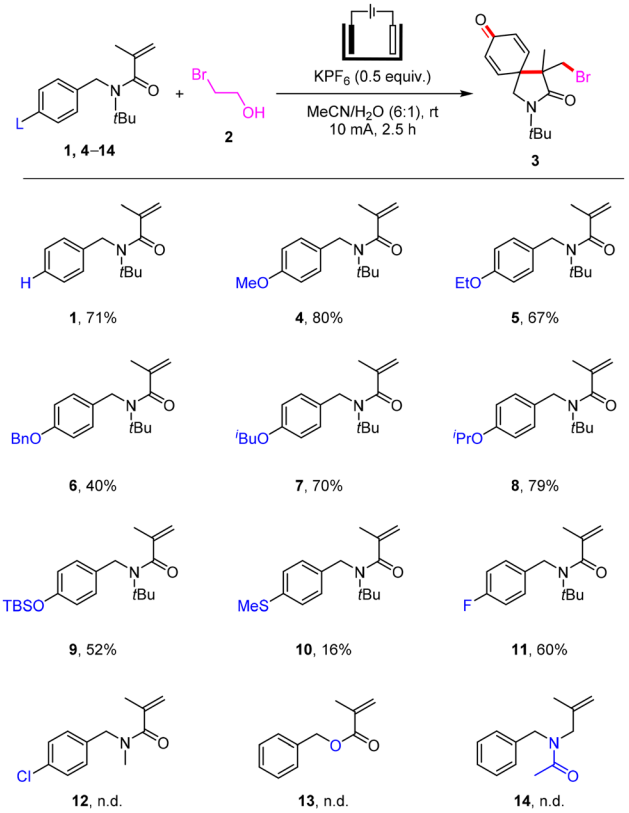
Entry	Variation from the standard conditions	Yield[b] (%)
1	None	73 (71)[c]
2	BnBr instead of **2**	40
3	CH_2BrCN instead of **2**	66
4	CH_2BrNO_2 instead of **2**	55
5	CH_2Br_2 instead of **2**	56
6	CBr_4 instead of **2**	39
7	$CHBr(COOEt)_2$ instead of **2**	26
8	**2** (2.0 equiv.)	64
9	$LiClO_4$ (0.5 equiv.) as electrolyte	58
10	Me_4NBF_4 (0.5 equiv.) as electrolyte	39
11	$^nBu_4NBF_4$ (0.5 equiv.) as electrolyte	68
12	$^nBu_4NClO_4$ (0.5 equiv.) as electrolyte	48
13	$MeCN/H_2O$ (13 : 1)	65
14	$MeCN/H_2O$ (5 : 2)	17
15	No electricity	0
16	With N_2	70

[a] Reaction conditions: RVC anode, Pt cathode, undivided cell, **1** (0.20 mmol), 2-bromoethan-1-ol (**2**, 0.60 mmol), KPF_6 (0.10 mmol), $MeCN/H_2O$ (6.0 mL/1.0 mL), rt, 10 mA, 2.5 h (4.6 F mol^{-1}). [b] Yield determined by the ^1H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [c] Isolated yield.

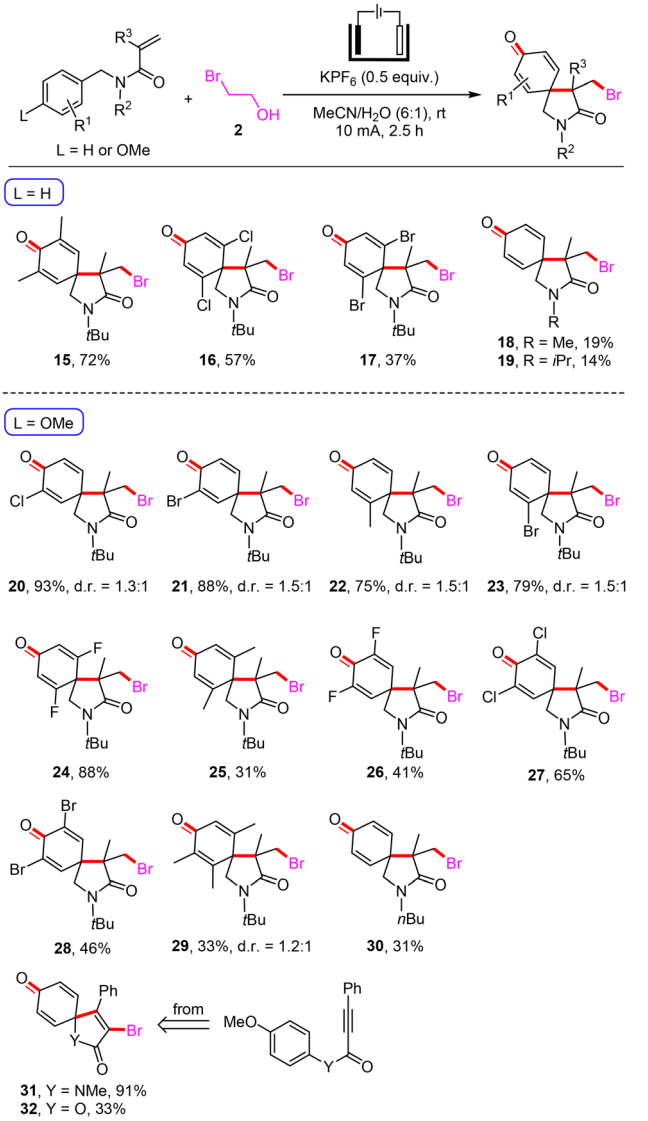
At the beginning of the study, the electrolysis reaction conditions of *N*-benzyl-*N*-(*tert*-butyl)methacrylamide (**1**) with 2-bromoethan-1-ol (**2**) were screened. The electrochemical electrophilic bromination/spirocyclization was performed in a simple undivided cell with reticulated vitreous carbon (RVC) as the anode and a platinum plate as the cathode (Table 1). 4-(Bromomethyl)-2-(*tert*-butyl)-4-methyl-2-azaspiro[4.5]deca-6,9-diene-3,8-dione (**3**) was obtained in 71% isolated yield in a solution of KPF_6 in $MeCN/H_2O$ (6 : 1) at 10 mA and room temperature for 2.5 h (Table 1, entry 1). The structure of **3** was determined by X-ray single crystal diffraction analysis (see the ESI for details†). Various bromides, such as BnBr (entry 2), CH_2BrCN (entry 3), CH_2BrNO_2 (entry 4), CH_2Br_2 (entry 5), CBr_4 (entry 6) and $CHBr(COOEt)_2$ (entry 7), were investigated as the source of bromide under simple conditions, and 26–66% yields of **3** were obtained. On reducing the amount of 2-bromoethan-1-ol (**2**) to 2.0 equivalents, brominated 2-azaspiro[4.5]decane (**3**) was generated in 64% yield (entry 8). Applying other supporting electrolytes including $LiClO_4$ (entry 9), Me_4NBF_4 (entry 10), $^nBu_4NBF_4$ (entry 11) and $^nBu_4NClO_4$ (entry 12) did not afford better results. The proportion of water in the mixed solvent has a great influence on the reaction efficiency (entries 13 and 14). We did not find the generation of product **3** under electricity-free conditions (entry 15). The electrochemical electrophilic bromination/spirocyclization occurred smoothly under a nitrogen atmosphere, providing the desired product **3** in 70% yield (entry 16).

After determining the conditions, we first explored the scope of *para*-substituents on the benzyl moiety for the electrochemical bromination/spirocyclization (Scheme 2). *N*-Benzyl- (**1**, 71% yield), *N*-(4-alkoxybenzyl)- (**4–8**, 40–80% yields) and *N*-(4-((*tert*-butyldimethylsilyl)oxy)benzyl)-acrylamide (**9**, 52% yield) all could successfully react with 2-bromoethan-1-ol (**2**) to give brominated 2-azaspiro[4.5]decane (**3**) in accepted yields. The formation of **3** was inhibited when using *N*-(4-(methylthio) benzyl)acrylamide (**10**, 16% yield) as the substrate. *N*-(4-Fluorobenzyl)acrylamide (**11**) could also be applied to this paired electrolysis reaction, providing the corresponding product **3** in 60% isolated yield. Regrettably, the electrochemical electrophilic bromination/spirocyclization was unsuccessful when employing *N*-(4-chlorobenzyl)acrylamide (**12**), benzyl methacrylate (**13**) and *N*-benzyl-*N*-(2-methylallyl) acetamide (**14**) as substrates.

We then investigated the compatibility of the electrochemical electrophilic bromination/spirocyclization by electrolyzing *N*-(4-unsubstituted-benzyl)-acrylamides and **2** with H_2O as the oxygen source under metal-free and oxidant-free conditions (Scheme 3). Substrates with 3,5-dimethyl, 2,6-dichloro and 2,6-dibromo groups on the benzene rings were well toler-



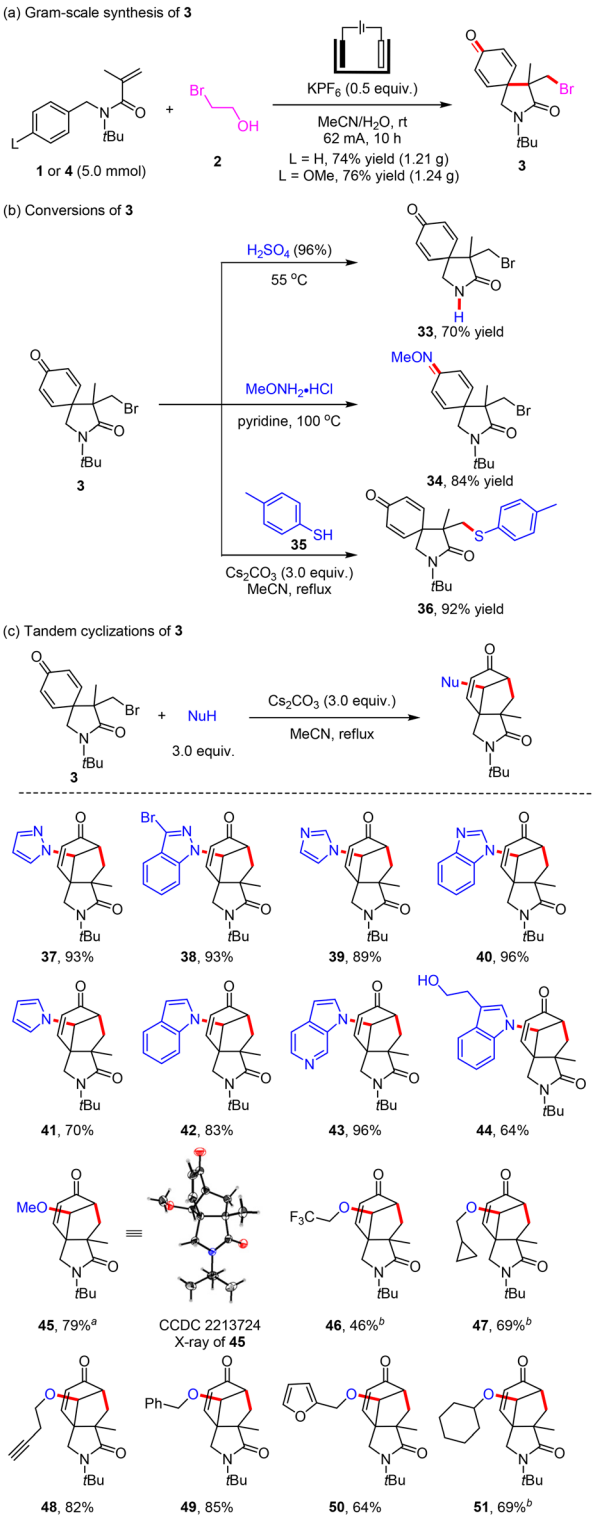
Scheme 2 Scope of substituent L [Reaction conditions: RVC anode, Pt cathode, undivided cell, acrylamide (0.20 mmol), 2-bromoethan-1-ol (**2**, 0.60 mmol), KPF_6 (0.10 mmol), $MeCN/H_2O$ (6.0 mL/1.0 mL), rt, 10 mA, 2.5 h (4.6 F mol^{-1}); isolated yields; n.d. = not detected].



Scheme 3 Scope of the electrochemical bromination/spirocyclization [Reaction conditions: RVC anode, Pt cathode, undivided cell, acrylamide (0.20 mmol), 2-bromoethan-1-ol (**2**, 0.60 mmol), KPF_6 (0.10 mmol), $MeCN/H_2O$ (6.0 mL/1.0 mL), rt, 10 mA, 2.5 h (4.6 F mol^{-1}); isolated yields; d.r. = diastereomeric ratio].

ated, and the corresponding brominated 2-azaspiro[4.5] decanes (**15–17**) were obtained in 37–72% yields. When the *tert*-butyl group on the nitrogen-atom was replaced with the methyl (**18**, 19% yield) or iso-propyl (**19**, 14% yield) group, the reaction efficiency greatly reduced. The linking group on the nitrogen atom has a great influence on this electrophilic spirocyclization reaction, which may be due to the obvious steric hindrance effect. Despite our many attempts, the electrochemical electrophilic bromination/spirocyclization of *N*-(4-unsubstituted-benzyl)-acrylamides was not as good as expected. In addition, the reactions showed good compatibility with *N*-(4-methoxybenzyl)-acrylamides, including mono-substituted groups (**20–23**, 75–93% yields), di-substituted groups (**24–28**, 31–88% yields), and a tri-substituted group (**29**, 33% yield) in the benzyl moiety. A series of highly functionalized brominated 2-azaspiro[4.5]decanes were also synthesized with satisfactory efficiency under simple and mild conditions. When the nitrogen atom of the substrate was attached with one *n*-butyl group, the spiro product **30** was obtained in 31% yield. Furthermore, this approach was also applicable to the electrochemical electrophilic bromination/spirocyclization of *N*-(4-methoxyphenyl)-*N*-methyl-3-phenylpropiolamide and 4-methoxyphenyl 3-phenylpropiolate with **2** to construct brominated 1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**31**) in 91% yield and 1-oxaspiro[4.5]deca-3,6,9-triene-2,8-dione (**32**) in 33% yield. Some unsuccessful substrates such as *N*-benzyl-acrylamides containing a thiophene or indole structure in the benzyl moiety are listed in the ESI.†

Furthermore, gram-scale synthesis and a variety of further transformation reactions of **3** were performed (Scheme 4). The gram-scale brominated spiroproduct **3** was obtained in 74% yield or 76% yield, respectively, by the electrolysis of **1** or **4** with **2** at 62 mA and room temperature for 10 h (Scheme 4a). The *tert*-butyl moiety in **3** could be removed to obtain **33** in 70% yield under acidic conditions. The brominated spiroproduct **3** could undergo dehydration condensation with $MeONH_2{\cdot}HCl$ to give imine **34** in 84% yield, and could also

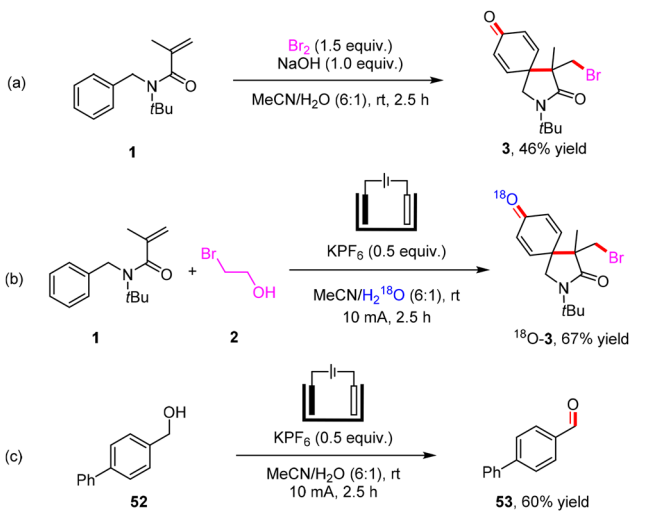


Scheme 4 Synthetic applications [Reaction conditions for the cyclization of **3**: **3** (0.10 mmol), NuH (0.30 mmol), Cs_2CO_3 (0.30 mmol), MeCN, reflux, 12–16 h; isolated yields]. [a]NaOMe (3.0 equiv.), MeOH, 16 h. [b]NaH (1.5 equiv.), ROH (5.0 equiv.), THF, rt to reflux, 16 h.

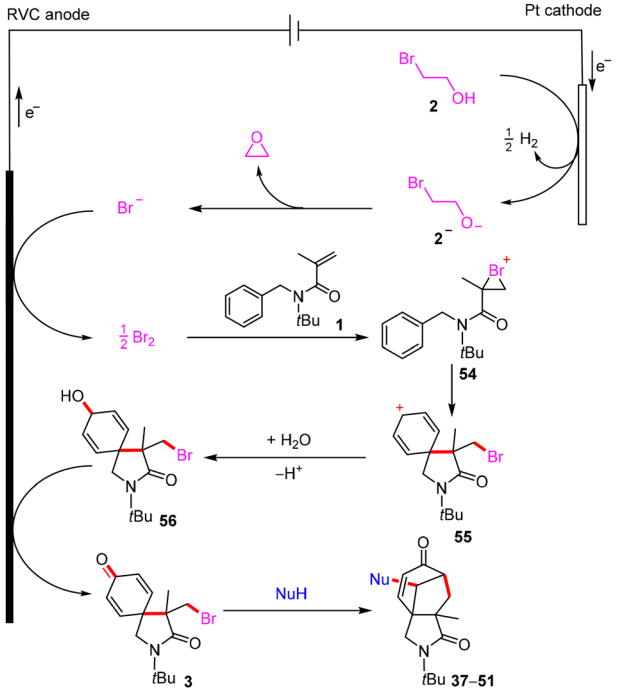
react with 4-methylbenzenethiol (**35**) to produce a nucleophilic substitution product **36** in 92% yield (Scheme 4b). In addition, when nitrogen-containing heterocycles, such as pyrazole (**37**, 93% yield), indazole (**38**, 93% yield), imidazole (**39**, 89% yield), benzoimidazole (**40**, 96% yield), pyrrole (**41**, 70% yield), indole (**42**, 83% yield), 1*H*-pyrrolo[2,3-*c*]pyridine (**43**, 96% yield) and tryptophol (**44**, 64% yield), were used as nucleophiles, the corresponding cyclohepta[*c*]pyrrole-1,6-diones were obtained in good yields *via* debromination tandem cyclization under simple basic conditions (Scheme 4c). Alkoxy cyclohepta[*c*]pyrrole-1,6-diones (**45–51**, 46–85% yields) could also be prepared efficiently by using sodium alkoxide and alcohols as nucleophiles. The structure of **45** was determined by X-ray single crystal diffraction analysis (see the ESI for details†). These results demonstrated the potential value of the obtained products in synthetic chemistry (Scheme 4).

In order to understand the reaction process, we further carried out control experiments (Scheme 5). When Br_2 was added to the solution of *N*-benzyl-*N*-(*tert*-butyl)methacrylamide (**1**) in MeCN/H_2O (6 : 1), the electrophilic bromination/spirocyclization could be achieved in 46% yield at room temperature for 2.5 h. ^{18}O-**3** was formed by electrolyzing **1** and **2** with MeCN/$H_2{}^{18}O$ (6 : 1) as the solvent, indicating that the oxygen atom in product **3** was derived from H_2O. Benzyl alcohol **52** was oxidized at the anode to form an aldehyde (**53**) under electrochemical conditions. In addition, electrochemical C–H bromination of (hetero)arenes with 2-bromoethan-1-ol as the brominating reagent through ethylene oxide and H_2 evolution has been reported by our group.[14]

Based on the above experimental results, mechanism studies, and previous reports,[14,15] a possible mechanism for the electrochemical electrophilic bromination/spirocyclization is outlined in Scheme 6 with the electrolysis of **1** and **2** as an example. Initially, 2-bromoethan-1-ol (**2**) is reduced to yield H_2 and an alkoxy anion [**2**]$^-$. The Br^- produced by the intramolecular cyclization of [**2**]$^-$ by releasing ethylene oxide is pre-



Scheme 5 Control experiments.



Scheme 6 Proposed mechanism.

ferentially oxidized at the anode to afford Br_2, because the oxidation potential of Br^- ($E_{p/2}$ = 1.05 V *vs.* Ag/AgCl) is significantly lower than that of **1** ($E_{p/2}$ = 1.99 V *vs.* Ag/AgCl) and **4** ($E_{p/2}$ = 1.72 V *vs.* Ag/AgCl). The electrophilic addition of **1** and Br_2 gives a bromonium ion intermediate **54**, followed by an H_2O-involved spirocyclization to produce **56**. Finally, **56** is further oxidized at the anode to give the final product **3**. The brominated 2-azaspiro[4.5]decanes can react with nucleophiles to construct cyclohepta[*c*]pyrrole-1,6-diones *via* debromination tandem cyclization.

Conclusions

In conclusion, we have developed an electrochemical electrophilic bromination/spirocyclization of *N*-benzyl-acrylamides with 2-bromoethan-1-ol as the brominating reagent. This method utilizes the bromine produced by cathodic reduction and anodic oxidation as an electrophile, avoids the need for metal and oxidizing reagents, and can be easily performed on a gram scale under mild conditions. A variety of late-stage transformations of brominated 2-azaspiro[4.5]decanes further confirm the applicability of this electrochemical bromination/spirocyclization.

Author contributions

Z. Zhang performed the experiments. Z. Zhang and Z.-W. Hou analyzed the data. H. Chen analyzed the X-ray crystallography data. Z.-W. Hou, P. Li and L. Wang designed and supervised the project. Z.-W. Hou and L. Wang wrote the manuscript. All of the authors discussed the results and contributed to the preparation of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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