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Alkyl Carbazates for Electrochemical Deoxygenative Functionalization of Heteroarenes

Yongyuan Gao, Zhengguang Wu, Lei Yu, Yi Wang*, and Yi Pan

Dedicated to the 100th anniversary of the School of Chemistry and Chemical Engineering, Nanjing University

Abstract: The C-O bond cleavage for activation of alcohols is synthetically useful and practically challenging. This work describes carbazate as a new type of electrochemically activated alkylating agent derived from ubiquitous alcohols for direct functionalization of heteroarenes under mild electrolytic conditions. The simple undivided cell at low oxidative potentials with carbon/platinum electrode set-ups offers excellent substrate tolerance, affording a variety of primary, secondary and tertiary alkyl-decorated heterocycles in good chemical yields. Furthermore, the mechanism for this electrochemical deoxyalkylation reaction has been investigated.

Radical based concise synthesis of C-C bonds has emerged as a powerful transformation to rapidly increase molecular complexity for the utility of biomedicine and materials science.[1] In recent years, a myriad of alkyl radical precursors have been developed, such as pyridinium salts,[2] Hantzsch esters,[3] haloalkanes,[4] organoborons[5] and sulfides.[6] Along this line, the effort in search of readily accessible radical precursors is still highly appreciated. Alcohols are among the most available feedstock in food and chemical industry. The delivery of alkyl radicals through dehydroxylation of alcohols under mild conditions is strategically appealing.[7] However, due to the strong C-O bonding energy (BDE~95 kcal/mol) and high redox potentials of unactivated alcohols, radical cleavage of hydroxyl functionality requires harsh conditions and represent tremendous difficulties[8-9]. In the classic Barton-McCombie framework, tertiary alcohols undergo radical deoxygenation via the activation of thiocarbonyl moiety. However, inevitable high temperatures and toxic tin reagents limited the application.[10] In this decade, alkyl oxalates have been developed as an alternative for Barton deoxygenation. Overman and MacMillan have reported the photocatalyzed deoxygenative alkylation of conjugated alkenes.[11-12]. Gong has described an alkylation of unactivated olefins using dialkyl oxalates and zinc as reducing agent.[13] Nevertheless, primary and secondary alcohols are generally inapplicable to such fragmentation process and often require metal catalysts or chemical oxidants.[11-15] Therefore, a more compatible and sustainable protocol for deoxygenative alkylation represents unmet challenge and urgent demand.

Electrochemically initiated radical reaction has drawn much attention for the redox-efficiency, innate scalability and sustainability of electrolytic process.[16] Anodic oxidation methods have been established for C-C,[17] C-O,[18] C-N[19] and C-S[20] bond formations and display pronounced advances in the kinetic control of radical reactivity and compatibility. However, no electrochemical deoxygenative functionalization have been reported up-to-date, mainly since alkyl radicals are prone to over-oxidize to their carbocations at high potentials.[5f,9,21] Whereas the documented oxalate salts are not compatible under cell conditions, it is important to design a radical precursor derived from alcohol that can be readily initiated at lower oxidative potentials. In light of previous reports,[20g,20h,22] we speculate that by installing a hydrazine leaving group to the carboxylic ester of alcohols, improved solubility and reactivity could be realized through the employment of hydrazinecarboxylates (carbazates) (Figure 1). Alkyl carbazates have previously been recognized as a type of acyl radical precursor. Under iron-catalyzed oxidative conditions, carbazates undergo dehydrazinative acylation and release molecular nitrogen.[23] It is envisioned that under suitable cell conditions, further anodic oxidative decarboxylation could occur to furnish alkyl radical. Herein, we describe carbazate as a new electrochemically activated alkylating agent for direct functionalization of heteroarenes with an oxidative dehydrazination/decarboxylation sequence.

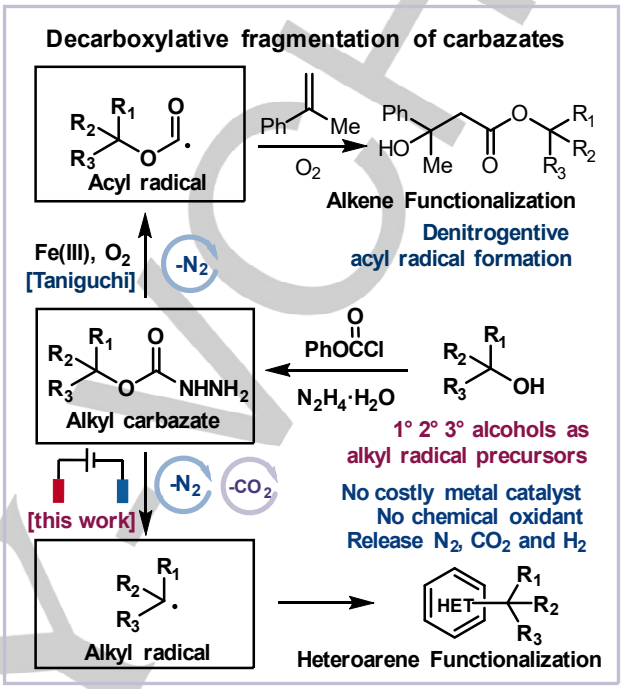

Figure 1. Fragmentation of carbazates for radical formations

We first employed quinoxalinone and *t*-butyl carbazate as model substrates for the initial electrolytic examination. Using platinum/graphite electrodes and n-$BuNClO_4$ electrolyte, the desired deoxygenative alkylation could take place at a constant current of 6 mA in acetonitrile. The t-butyl substituted quinoxalinone was afforded in 78% yield after 8 h (Table 1, entry 1). Next, several catalysts including CpFe, NH_4Br, TBAB and NH_4I were screened and only decreased yields were

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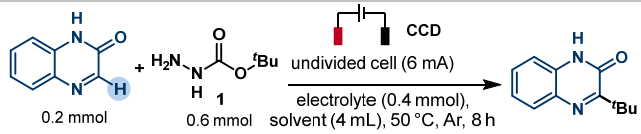


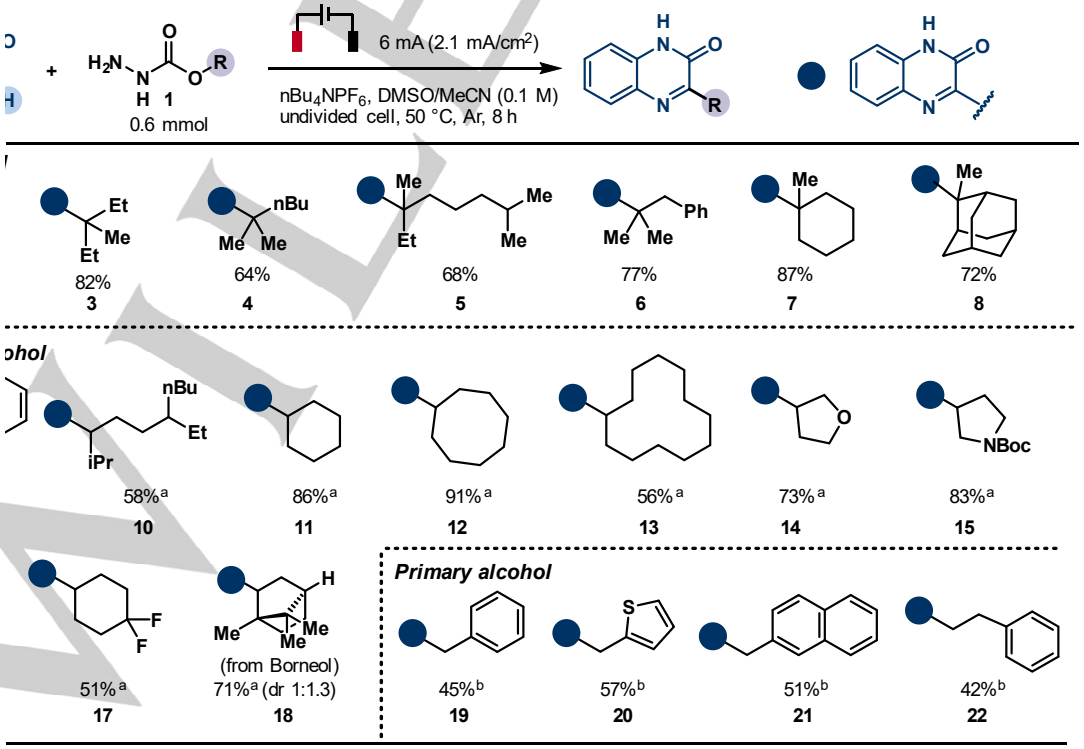
entry	electrode	catalyst	solvent	electrolyte	yield[a]
1	C/Pt	-	MeCN	nBu_4NClO_4	78
2	C/Pt	CpFe	MeCN	nBu_4NClO_4	62
3	C/Pt	NH_4Br	MeCN	nBu_4NClO_4	41
4	C/Pt	TBAB	MeCN	nBu_4NClO_4	43
5	C/Pt	NH_4I	MeCN	nBu_4NClO_4	38
6	Pt/Pt	-	MeCN	nBu_4NClO_4	58
7	C/C	-	MeCN	nBu_4NClO_4	52
8	C/ Ni	-	MeCN	nBu_4NClO_4	66
9	C/Fe	-	MeCN	nBu_4NClO_4	72
10	C/Pt	-	MeCN	nBu_4NPF_6	82
11	C/Pt	-	MeCN	$LiClO_4$	72
12	C/Pt	-	MeCN	nBu_4NPF_6	67
13	C/Pt	-	MeOH	nBu_4NPF_6	43
14	C/Pt	-	THF	nBu_4NPF_6	28
15[c]	C/Pt	-	DMSO	nBu_4NPF_6	88
16[d]	C/Pt	-	DMSO	nBu_4NPF_6	94[b]
17[e]	C/Pt	-	DMSO	nBu_4NPF_6	84
18[f]	C/Pt	-	DMSO	nBu_4NPF_6	76

Table 1. Optimization of the reaction conditions. [a] Yields determined by ^1H NMR spectroscopy using 1,3,5- trimethoxybenzene as internal standard; [b] 87% isolated yield; [c] 1:1 DMSO/MeCN; [d] 3:1 DMSO/MeCN; [e] 3 mA for 16 h. [f] 12 mA for 4 h.

obtained (entries 2-5). For the screening of electrode materials, platinum/graphite electrodes were found superior to iron and nickel (entries 6-9). Using different electrolytes for the undivided cell, n-Bu_4NBF_4 was able to afford the product in a higher yield (82%, entry 10). The choice of solvent was also proven crucial for this reaction. With a 1:1 mixutre of DMSO and MeCN, the reaction yield was significantly enhanced (88%, entry 15). Altering the ratio of DMSO/MeCN to 3:1 afforded the product in a satisfactory 94% yield (entry 16). Thus, the optimized conditions were determined for the following investigations.

To explore the scope of this deoxygenative alkylation reaction, a range of primary, secondary and tertiary alcohol-derived carbazates have been treated with the electrochemical conditions (Scheme 1). Tertiary alkylated carbazates bearing branched (**2**-**6**) and cyclic hydrocarbons (**7**-**8**) were tolerated in this process. In addition, linear and cyclic secondary alcohol-derived carbazates were also applied to the reaction (**9**-**13**). Tetrahydrofuran (**14**), pyrrolidine (**15**), indane (**16**), and difluorocyclohexane (**17**) substituted carbazates could furnish the corresponding alkylated quinoxalinones in good yields. Restrained natural product borneol was also compatible under the oxidative radical coupling conditions (**18**). Moderate conversions were observed for primary alcohcol-derived carbazates such as benzyl alcohol (**19**), thiophenylmethanol (**20**), naphthalenylmethanol (**21**) and 2-phenylethanol (**22**). This could due to the relative inertness of primary acyl and benzyl radicals.

Next, the reaction scope of heteroarenes was explored (Scheme 2). The reactions of electron-donating (**23**, **29**) and electron-withdrawing group (**24**-**28**) substituted quinoxalinones proceeded smoothly to furnish the corresponding alkylated products. Different *N*-protected quinoxalinones were also tolerated under the cell conditions (**31**-**36**). Furthermore, a variety of heterocycles including benzoquinoxalinone (**37**), pyrazinone (**38**), quinazolinone (**39**), isoquinoline (**40**), phthalazine (**41**), quinazoline (**42**), and phenanthridine (**43**) were susceptible to the reaction conditions to acheive the corresponding alkylated products. Benzofuran (**44**) and benzothiophene (**45**) were not compatible for the reaction. Notably, bioactive caffeine (**46**) and prothioconazole (Provost, **47**) are also compatible with this reaction.



Scheme 1. Substrate scope of carbazates. [a] Reactions were performed at 80 °C for 8 h. [b] Reactions were performed at 85 °C for 14h.

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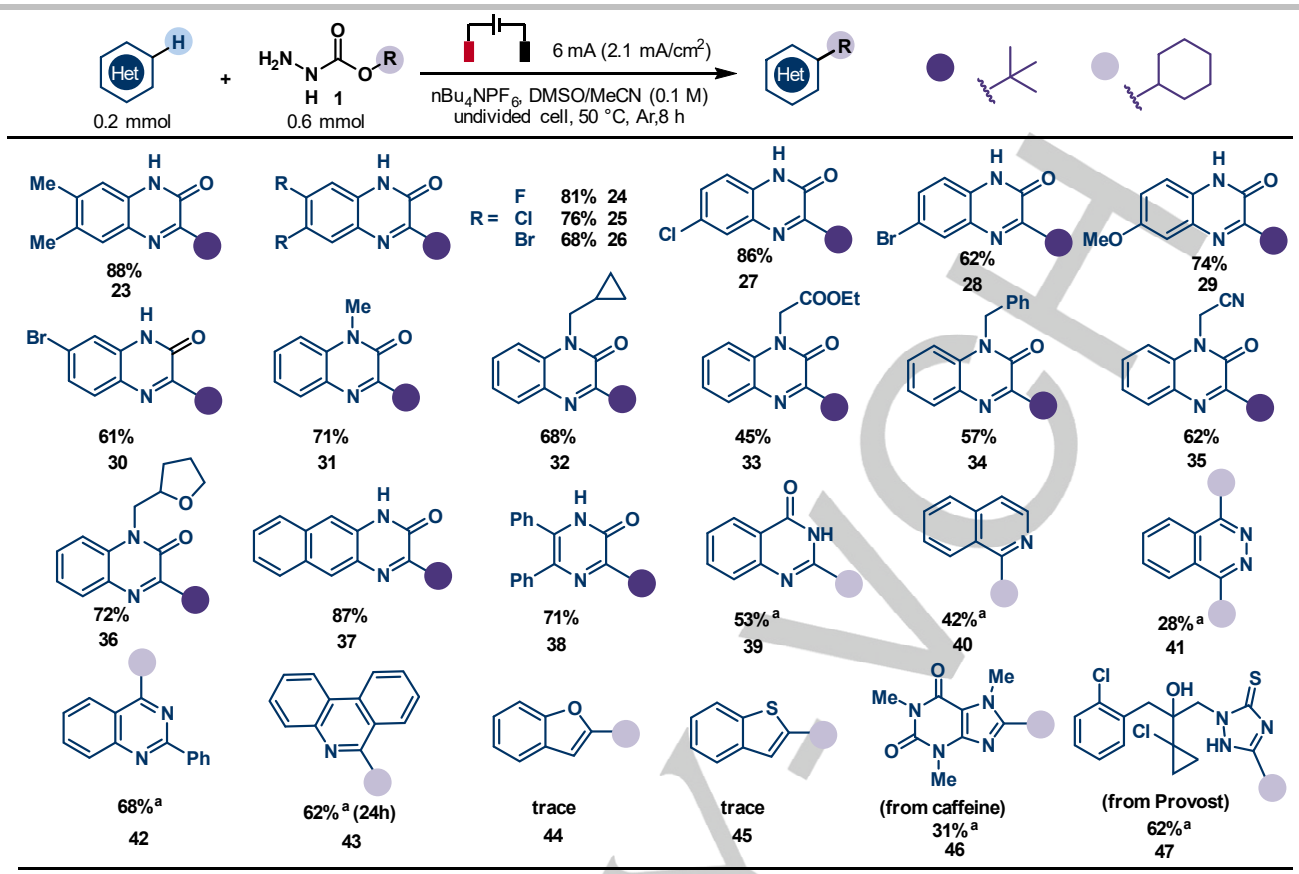
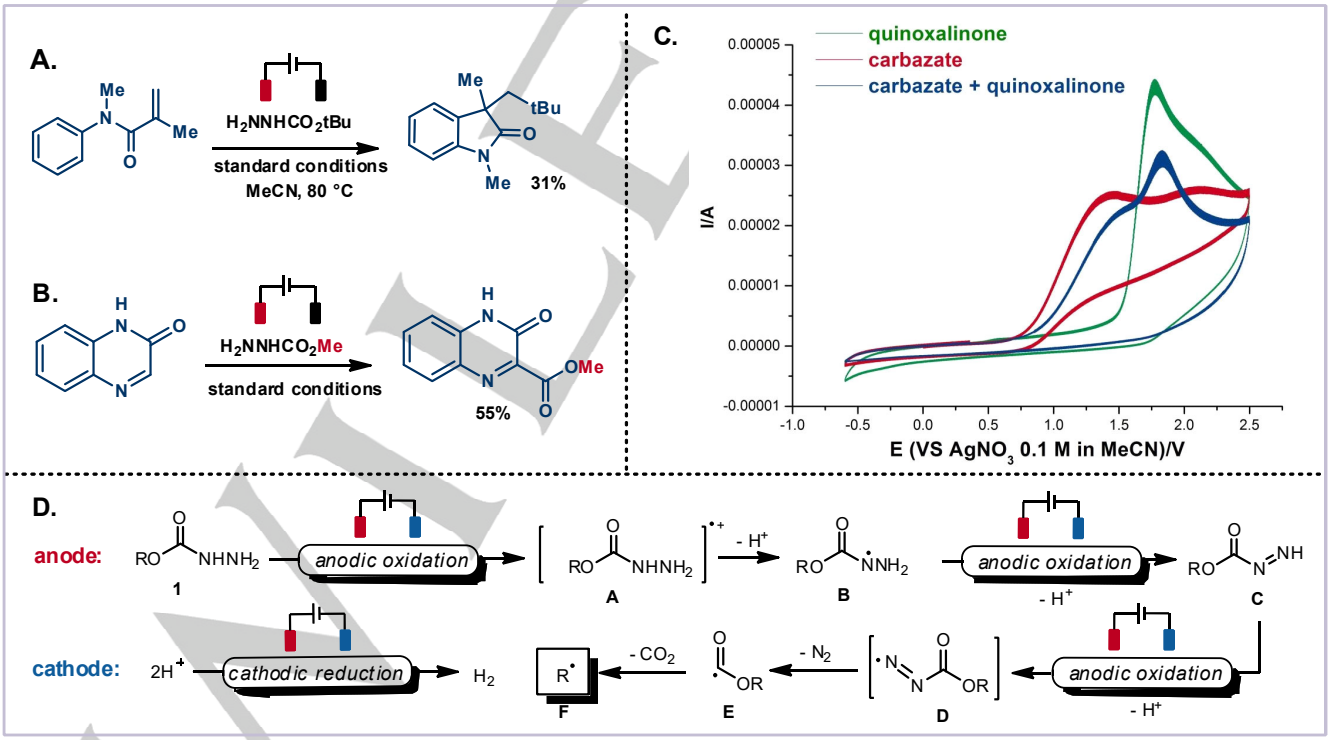


Scheme 2. Substrate scope of heteroarene. [a] The reactions were performed in MeCN (4 mL) with n-Bu_4NClO_4 (0.4 mmol) at a constant current (3 mA) and 80 °C for 14 h.



Scheme 3. Control experiments and reaction mechanism. A) Cyclic voltammetry of related compounds in 0.1 M nBu_4NPF_6/MeCN using glass carbon working electrode, Pt wire, and $Ag/AgNO_3$ (0.1 M in MeCN) as counter and reference electrode: 2-quinoxalinone (5 mM, green); t-butyl carbazate (5 mM, red); 2-quinoxalinone and t-butyl carbazate (5 mM, blue).

To elucidate the reaction mechanism, control reactions have been carried out (Scheme 3). The radical relay reaction of *N*-phenylmethacrylamide proceeded to deliver the alkylated oxindole in 31% yield (Scheme 3A). When subjecting methyl carbazate to the standard conditions, no alkylation was observed. Instead, the isolated product was the corresponding methyl ester (Scheme 3B). This indicates that a stepwise dehydrazination-decarboxylation sequence was involved in the electrochemical fragmentation of carbazate. Furthermore, the cyclic voltammetry results demonstrated that carbazate can be easily oxidized under electrochemical conditions ($E^{1/2}_{ox}$ = 1.44 V vs $AgNO_3$) for deoxyalkylation of quinoxalinone (Scheme 3C). Based on the above experimental facts, a plausible reaction mechanism is proposed. The first stage is consecutive anodic oxidation of carbazate and deprotonation to generate hydrazinecarboxylate radical **B** and diazenecarboxylate **C**.[24] Further anodic oxidation cleaves diazene to form acyl radical **E** and releases molecular nitrogen. The second step is decarboxylation of acyl radical **E** to furnish alkyl radical **F** (Scheme 3D).

In summary, we have reported carbazate as an alkyl source under electrochemical conditions. Primary, secondary and tertiary alkyl radicals can be readily accessed via the sequential anodic oxidative fragmentation for the direct functionalization of *N*-heteroarenes. This sustainable method avoids the use of chemical oxidants and only releases nitrogen, carbon dioxide and hydrogen. Further study of carbazate is underway in the laboratory.

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Keywords: carbazate • electrochemistry • deoxgenative alkylation • radical fragmentation

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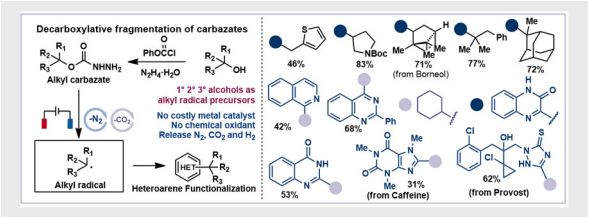

Carbazates as a new type of electrochemically activated alkylating agent for direct functionalization of heteroarenes under mild cell conditions.

Yongyuan Gao, Zhengguang Wu, Lei Yu, Yi Wang, and Yi Pan*

Page No. – Page No.

Alkyl Carbazates for Electrochemical Deoxygenative Functionalization of Heteroarenes