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Electrochemical trifluoromethylation/semipinacol rearrangement sequences of alkenyl alcohols: synthesis of β-CF_3-substituted ketones†

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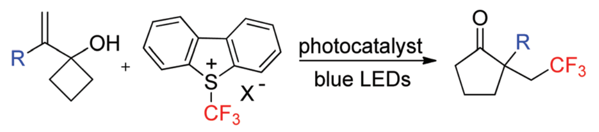
Electrochemical oxidative radical trifluoromethylation/semipinacol rearrangement sequences of alkenyl alcohols were developed in this study. This approach is environmentally benign and uses the shelf-stable Langlois reagent as a trifluoromethyl radical precursor and electrons as the oxidizing reagents. The present protocol offers a facile route to prepare β-trifluoromethylated ketone derivatives.

Organofluorine compounds have attracted considerable attention in organic and medicinal chemistry and materials science because of their chemical, biological, and physical properties.[1] The introduction of a trifluoromethyl moiety into biologically active compounds usually leads to improvement of their physical properties and biological activities.[2] Due to the wide applications of these compounds, intensive efforts have been made to developing novel and practical synthetic methods and new organofluorine compounds.[3] The radical trifluoromethylation to alkenes is among the most direct approaches for the construction of C–CF_3 bonds, which uses electrophilic and nucleophilic trifluoromethylation reagents in the presence of various types of reductants or oxidants.[4] The Langlois reagent (CF_3SO_2Na) is readily available and shelf-stable. It has emerged as a valuable nucleophilic trifluoromethylation agent for the synthesis of organofluorine compounds. The reaction of the Langlois reagent with various substrates has been used to furnish diverse trifluoromethyl-containing organic compounds.[5]

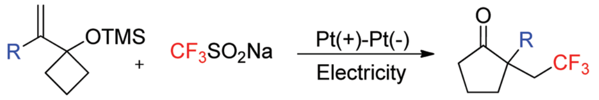
The radical-mediated difunctionalization of alkenes provided a practical approach for the difunctionalization of unactivated alkenes with high chemo- and regioselectivity.[6,7] Recently, several groups have reported radical addition and the 1,2-carbon rearrangement cascade process of alkenyl alcohols with various radicals including alkyl, aryl, acyl, azido, amine, difluoromethyl, and phenylsulfonyl radicals for the synthesis of β-functionalized ketones.[8] Recently, Glorius and our groups have independently reported the preparation of trifluoromethyl-substituted cyclopentanones from 1-(1-arylvinyl)cyclobutanols *via* visible-light photoredox catalyzed trifluoromethylation and ring expansion using Umemoto's reagents in the presence of the Ru-complex as a photoredox catalyst (Scheme 1a).[9]

Over the past few years, electrochemistry has emerged as an attractive approach for organic chemists to introduce a chemical functionality into organic molecules due to its environmentally benign and practical nature. Synthetic electrochemistry could achieve redox reactions without requiring transition-metal catalysts or toxic reagents due to the use of electrons as oxidizing or reducing reagents.[10] Recently, electrochemical trifluoromethylation of alkene derivatives to trifluoromethylated ones has been achieved through the anodic oxidation of the Langlois reagent.[11] To the best of our knowledge, electrochemical oxidative trifluoromethylation and ring expansion sequences of alkenyl alcohols have not been reported yet. We envisioned the transformation of alkenyl alcohols into trifluoromethyl-substituted ketones by the electrochemical oxidative trifluoromethylation/semipinacol rearrangement sequence

a) Previous work (ref. 11)



b) This work



Scheme 1 Strategy for the radical trifluoromethylation/semipinacol rearrangement sequence.

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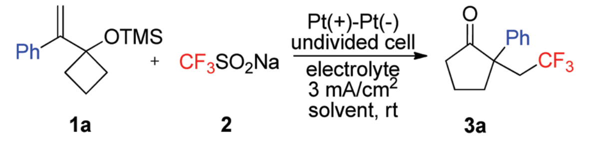
with the Langlois reagent as the trifluoromethyl radical precursor (Scheme 1b).

As part of the research program related to redox reactions and cyclization sequences, we recently reported intramolecular redox reactions[12] and radical addition and ring expansion reactions of alkenes with several radical sources under redox conditions.[8c–h] Herein, we report electrochemical oxidative trifluoromethylation and semipinacol rearrangement sequences *via* 1,2-carbon migration of alkenyl alcohol derivatives.

At the outset of this investigation, we examined the electrochemical oxidative trifluoromethylation/semipinacol rearrangement of trimethyl(1-(1-phenylvinyl)cyclobutoxy)silane (**1a**) with Langlois reagent **2** as a trifluoromethyl radical source. The reaction was conducted in an undivided cell with platinum plates as electrodes under a constant current. Initially, $LiClO_4$ was employed as the electrolyte and DMSO as the solvent at a constant current of 3 mA. The radical addition and ring expansion product **3a** was obtained in 15% yield after the reaction proceeded at room temperature for 1 h (Table 1, entry 1). The choice of solvents affects the reaction efficiency. We then surveyed different kinds of common solvents, such as DMSO, DMF, methanol, THF, and acetonitrile (Table 1, entries 1–5). Of them, acetonitrile was found to be the best medium. Protic solvents such as water and hexafluoroisopropyl alcohol (HFIP) could promote this reaction (Table 1, entries 6–10). Pleasingly, we found that the addition of 1.0 equiv. of water led to an improvement in the yield of the desired product **3a** (83%, Table 1, entry 9). Various supporting electrolytes such as $LiClO_4$, Bu_4NClO_4, Bu_4NBF_4, Bu_4NPF_6, KBr, KI, and Bu_4NI were screened (Table 1, entries 9 and 11–16). $LiClO_4$ was found to be the most efficient electrolyte for this transformation (Table 1, entry 9). Using glassy carbon and nickel plates to replace platinum plates led to a decrease in reaction yields (Table 1, entries 17–19). The reaction with 1-(1-phenylvinyl)cyclobutanol instead of trimethyl(1-(1-phenylvinyl)cyclobutoxy)silane (**1a**) affords the desired product **3a** with 75% yield (Table 1, entry 20). Finally, no desired product was obtained without an electric current (Table 1, entry 21).

With the optimal reaction conditions in hand, we investigated the scope of substrates for the electrochemical radical trifluoromethylation/semipinacol rearrangement sequences of alkenylcyclobutanol derivatives **1** with Langlois reagent **2**. As shown in Table 2, various alkenylcyclobutanols **1** with the substituted-aryl group (**1b–1j**) and the naphthyl group (**1k**) furnished the corresponding migration products with moderate to high yields (59–87%, Table 2, **3a–3k**). The steric effect of aryl substituents had an appreciable influence on this reaction, and the reactivity of aryl substituents was *para* > *meta* > *ortho* (**3b**, **3g**, and **3j**). The electronic effect also affected the trifluoromethylation/semipinacol rearrangement cascade reaction, and

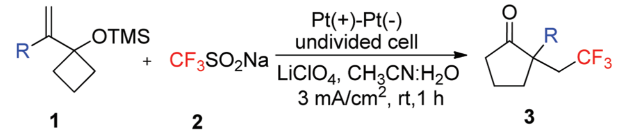
Table 1 Optimization of the reaction conditions[a]

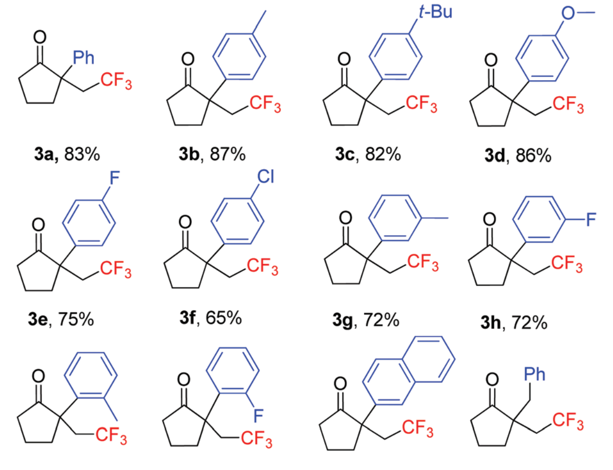


Entry	Solvent	Electrolyte	Time (h)	Yield[b] (%)
1	DMSO	$LiClO_4$	1	15
2	DMF	$LiClO_4$	1	Trace
3	MeOH	$LiClO_4$	1	41
4	THF	$LiClO_4$	1	Trace
5	MeCN	$LiClO_4$	1	50
6	MeCN : H_2O (9 : 1)	$LiClO_4$	1	28
7[c]	MeCN : H_2O	$LiClO_4$	1	55
8[d]	MeCN : H_2O	$LiClO_4$	1	64
9[e]	MeCN : H_2O	$LiClO_4$	1	83
10[f]	MeCN : HFIP	$LiClO_4$	1	64
11[e]	MeCN : H_2O	$BuNClO_4$	1	44
12[e]	MeCN : H_2O	Bu_4NBF_4	1	78
13[e]	MeCN : H_2O	Bu_4NPF_6	1	79
14[e]	MeCN : H_2O	KBr	1	70
15[e]	MeCN : H_2O	KI	1	Trace
16[e]	MeCN : H_2O	Bu_4NI	1	Trace
17[e,g]	MeCN : H_2O	$LiClO_4$	2	50
18[e,h]	MeCN : H_2O	$LiClO_4$	2	46
19[e,i]	MeCN : H_2O	$LiClO_4$	1	49
20[e,j]	MeCN : H_2O	$LiClO_4$	1	75
21[e,k]	MeCN : H_2O	$LiClO_4$	1	0

[a] Reaction conditions: Pt anode, Pt cathode, trimethyl(1-(1-phenylvinyl)cyclobutoxy)silane (**1a**, 0.1 mmol), Langlois reagent (**2**, 0.2 mmol), electrolyte (0.5 mmol), solvent (2.5 mL), 3 mA cm^{-2} at room temperature. [b] Isolated yields. [c] H_2O (5 equiv.) was added. [d] H_2O (3 equiv.) was added. [e] H_2O (1 equiv.) was added. [f] HFIP (1 equiv.) was added. [g] C(+)–C(−) instead of Pt(+)–Pt(−). [h] C(+)–Pt(−) instead of Pt(+)–Pt(−). [i] C(+)–Ni(−) instead of Pt(+)–Pt(−). [j] 1-(1-Phenylvinyl)cyclobutanol instead of trimethyl(1-(1-phenylvinyl)cyclobutoxy)silane (**1a**). [k] No electricity.

Table 2 Variation of substrates[a,b]

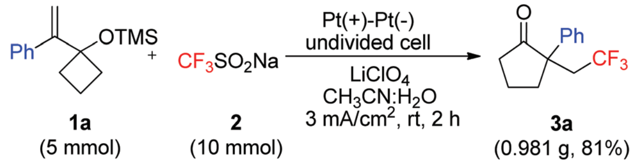




3a, 83% **3b**, 87% **3c**, 82% **3d**, 86%
3e, 75% **3f**, 65% **3g**, 72% **3h**, 72%
3i, 59% **3j**, 66% **3k**, 66% **3l**, 68%

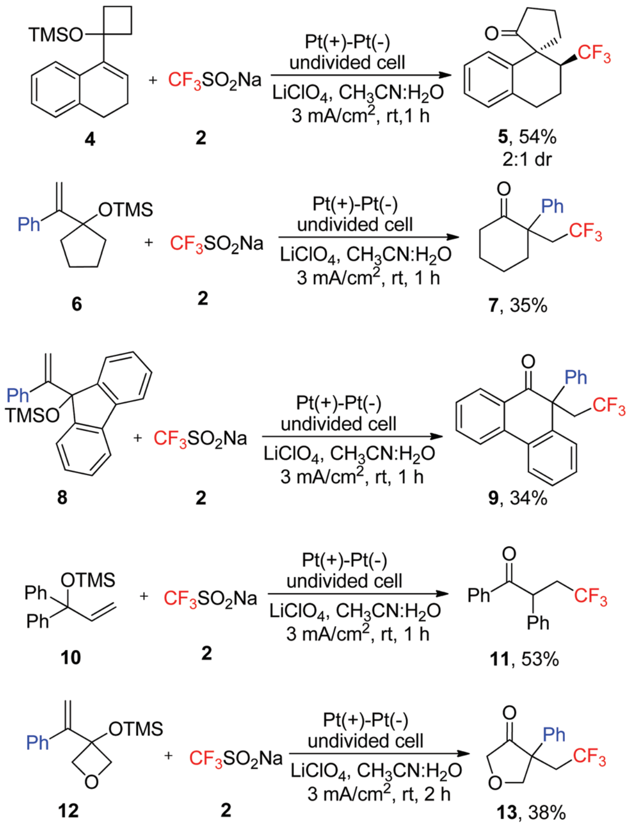
[a] Reaction conditions: Pt anode, Pt cathode, trimethyl(1-(1-arylvinyl)cyclo-butoxy)silane **1** (0.1 mmol), Langlois reagent (**2**, 0.2 mmol), $LiClO_4$ (0.5 mmol), CH_3CN (2.5 mL), water (1.8 μL), 3 mA cm^{-2}, 1.12 F mol^{-1}, at room temperature. [b] Isolated yields.

the alkenyl cyclobutanols **1** with electron-donating substituted-aryl groups showed higher reactivity than those with electron-withdrawing substituted-aryl groups. Notably, this radical trifluoromethylation/semipinacol rearrangement reaction with alkyl-substituted vinylcyclobutanol, 1-(3-phenylprop-1-en-2-yl) cyclobutanol, gave 68% yield of the desired product **3l** under the optimal reaction conditions. Furthermore, (1-(3,4-dihydronaphthalen-1-yl)cyclobutoxy)trimethylsilane (**4**), trimethyl((1-(1-phenylvinyl)cyclopentyl)oxy)silane (**6**), trimethyl((9-(1-phenylvinyl)-9*H*-fluoren-9-yl)oxy)silane (**8**), ((1,1-diphenylallyl)oxy) trimethylsilane (**10**), and trimethyl((3-(1-arylvinyl)oxetan-3-yl) oxy)silane (**12**) derivatives were also used as substrates in these electrochemical radical trifluoromethylation/semipinacol rearrangement sequences. The corresponding products **5**, **7**, **9**, **11**, and **13** were obtained in 54% (2 : 1 dr), 35%, 34%, 53%, and 38% yields (Scheme 2). In order to demonstrate the practical feasibility of this electrochemical trifluoromethylation and ring expansion, the gram-scale reaction was explored. As shown in Scheme 2, when 1-(1-phenylvinyl)cyclobutanol (**1a**) with Langlois reagent **2** was used under the optimum reaction conditions, the reaction proceeded to afford the desired trifluoromethyl-substituted cyclopentanone **3a** on a gram scale with 81% yield (Scheme 3).

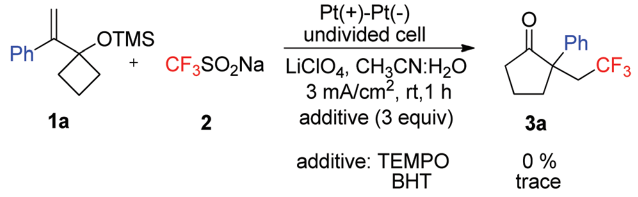


Scheme 3 Gram-scale synthesis of **3a**.

To gain mechanistic insights into this transformation, some preliminary experiments were performed. The reaction did not proceed without an electric current (Table 1, entry 21). A trace or reduced yield of the product was detected in the presence of radical scavengers, 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) (Scheme 4). We also carried out cyclic voltammetry (CV) experiments to study the redox potential of substrates. Oxidation peaks of trimethyl(1-(1-phenylvinyl)cyclobutoxy)silane (**1a**) and Langlois reagent **2** in acetonitrile were observed at 1.71 and 1.39 V, respectively (see the ESI†). We proposed the reaction mechanism as shown in Fig. 1 based on our results and previously reported work.[11] Langlois reagent **2** is oxidized to generate a trifluoromethyl radical (**I**). This trifluoromethyl radical **I** then reacts with 1-(1-arylvinyl)cyclobutanol derivatives **1**, yielding intermediate **II** which is oxidized on the anode to afford cation **III**. 1,2-Carbon migration of cation **III** then leads to ring



Scheme 2 Electrochemical radical trifluoromethylation/semipinacol rearrangement sequences of **4**, **6**, **8**, **10**, and **12**.



Scheme 4 Control experiments.

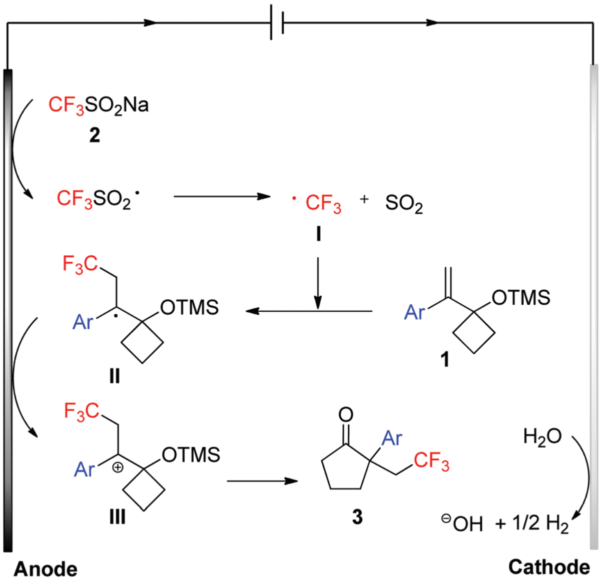


Fig. 1 Proposed reaction mechanism.

expansion that yields products **3**. The water is reduced on the cathode, releasing hydrogen and hydroxide ion which can be accelerated by the removal of the trimethylsilyl group of cation intermediate **III** to obtain the desired products **3**.[11f–h]

Compared to the previously reported work on visible-light photoredox catalysis (Scheme 1a), this electrochemical method has some advantages in terms of good yields, broad substrate scope, and the use of an inexpensive and stable trifluoromethylation reagent under metal-free conditions.

Conclusions

In conclusion, we have developed a new and efficient strategy for the synthesis of β-trifluoromethylated ketone derivatives *via* electrochemically oxidative trifluoromethylation/1,2-carbon migration sequences of alkenyl alcohol derivatives with the Langlois reagent. This approach is environmentally benign as it uses the shelf-stable Langlois reagent as a trifluoromethyl radical precursor and electrons as oxidizing reagents. The present protocol is an efficient option for synthesizing trifluoromethyl-substituted ketone derivatives.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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