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Redox active sodium iodide / recyclable heterogeneous solid acid: An efficient dual catalytic system for electrochemically oxidative α-C-H thiocyanation and sulfenylation of ketones

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Abstract. An efficient electrochemically oxidative α-C-H thiocyanation and sulfenylation of ketones has been developed in a simple undivided cell under constant current condition. The electrochemistry performs using NaI as the redox catalyst and heterogeneous solid salt Amberlyst-15(H)® (A-15(H)) as proton catalyst without the addition of external conductive salts. The protocol proved to be practical since the solid salt could be reused in up to five consecutive gram-scale runs without significant decrease in efficiency. Control experiments and cyclic voltammetry analysis disclose that the reaction proceeds likely via a cascade α-halogenation and subsequent thiocyanation or sulfenylation.

Keywords: electrochemistry, redox chemistry, C-H functionalization, C-S bond formation, indirect electrolysis, halide ion as redox catalyst

Introduction

The efficient synthesis of sulfur-containing compounds is significant in organic chemistry, pharmaceutical industry and materials science.[1] Among various sulfur-containing organic compounds, α-thiocyanato and sulfenyl ketones have been paid much attention due to their widespread existing as core structural scaffolds in various natural products and pharmaceuticals.[2] In addition, as versatile building blocks and pivotal intermediates, α-thiocyanato and sulfenyl ketones have also been employed in preparing sulfur-containing heterocycles such as thiazoles,[3a-3b] in oxidative generation of sulfoxides or sulfones,[3c-3d] in ring cleavage forming 1,2-diketones,[3e] in 1,2-carbonyl transposition,[3f] and in preparation of α,β-unsaturated ketones via the dehydrosulfenylation.[3g]

Although the substitution reaction of a α-halo ketone with a S-centered nucleophilic agent is typically used for the preparation of α-thiocyanato and sulfenyl ketones, [4] the oxidative cross coupling of ketones with S-centered agents has recently emerged as a dominant and popular strategy due to its step- and atom economic characteristics as well as avoiding the prefunctionlization of substrates. For example, Kumar and co-workers reported a direct α-thiocyanation of carbonyl compounds with ammonium thiocyanate using $K_2S_2O_8$ as an oxidant in the presence of catalytic amounts of copper (II) sulfate (Scheme 1a).[5a] The oxidative cross dehydrogenative coupling of ketones with heteroaromatic thiols was also achieved in the presence of aqueous $HClO_4$ (Scheme 1b).[5b] Very recently, a one-pot synthesis of α-sulfenyl ketones has also been developed by Barman and co-workers using I_2 as the catalyst and DMSO as the oxidant in *t*-BuOH/DMI(1,3-Dimethyl-2-imidazolidinone) solvent (Scheme 1c).[5c] Although much progress has been made in the oxidative cross coupling for the formation of C-S bonds, there is still great challenge due to the instability of most of sulfur reagents under oxidative conditions.[6] In addition, most of these methods suffer from certain limitations, including the use of toxic transition metal catalysts and excess of external oxidants, which deter the development of green and sustainable chemistry (Scheme 1).[7] Consequently, to develop more efficient, economical and practical synthetic methods for synthesizing α-

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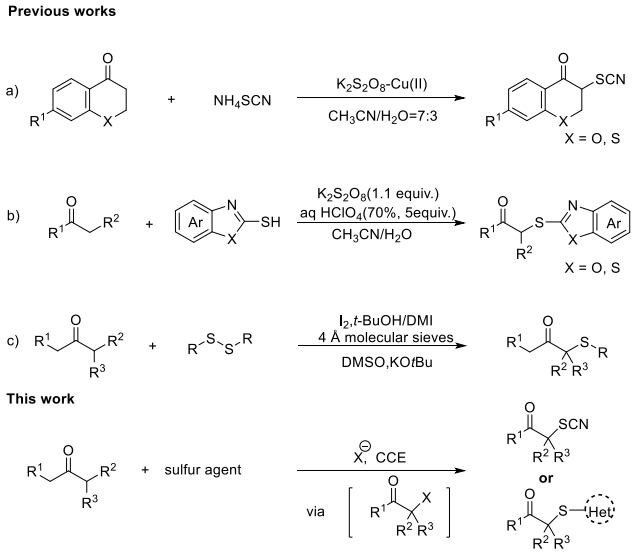
thiocyanato and sulfenyl ketones remains a challenging task.

Scheme 1. Methods for the synthesis of α-thiocyanato and sulfenyl ketones



Electrochemistry provides an alternative method to achieve the formation of a new chemical bond by heterogeneous electron transfer between an electrode and a substrate (direct electrolysis) or by using a redox catalyst (indirect electrolysis).[8] In the context, we have achieved electrochemical C-H bond functionalization, leading to the formation of new C-C, C-N, C-O and C-S bonds using simple halide ions as redox catalysts.[9] Based on our experience, we hypothesized that a constant current electrolysis (CCE) of ketone in the presence of a halide ion might initially form active α-halogenated ketone, which then undergoes substitution reaction with nucleophilic sulfur agents to fulfill the desired α-thiocyanato or sulfenyl ketones (Scheme 1).

Herein we reported an efficient electrochemical protocol for the one-pot α-C-H thiocyanation and sulfenylation of ketones employing redox active NaI / heterogeneous solid acid Amberlyst-15(H)® dual catalysts system in a simple undivided cell. In this protocol, the solid acid plays two-fold roles: to suppress the polymerization of sulfur-containing agents and to promote the enolization of the carbonyl group for an easier α-halogenation. This protocol features step- and atom economy, avoiding pre-functionalization of the starting ketone compounds and tedious isolation of intermediates. Moreover, the solid acid Amberlyst-15(H)® could be reused without significant decrease in efficiency.

Results and Discussion

At the outset, to demonstrate the feasibility of the one-pot electrochemical α-thiocyanation of ketones via the cascade α-halogenation and thiocyanation sequence, we chose propiophenone (**1a**) and NaSCN (**2a**) as model substrates to optimize the reaction conditions. Based on our previous successful use of the graphite working electrode in halide ion-induced C-H bonds functionalization, [8] we decided to use it rather than to explore other options. The initial constant current electrolysis of a mixture of **1a** and **2a** was carried out using NaI as a redox catalyst in aqueous EtOH at 50 °C and the desired product **3a** was not detected (entry 1, Table 1). Considering that the keto-enol tautomerization of a carbonyl compound can be catalyzed via either a base or an acid, we initially tested the effects of bases on the electrochemical reaction. However, our attempt failed and no desired **3a** was detected in the presence of bases tested (entries 2-5). Then, we turned to examine the role of acids. As shown in Table 1, the reaction did work and gave the desired **3a** in 20% and 30% yields when H_2SO_4 and *p*-toluenesulfonic acid (PTSA) were employed, respectively (entries 6-7). Since usage of H_2SO_4 or PTSA results in tedious workup and isolation process as well as producing large amounts of waste, we envisioned that heterogeneous solid acid (such as Amberlyst-15(H)®), which is recyclable and easily to workup by simple filter, might overcome these limitations. To our delight, the desired product **3a** was obtained in 44% yields when Amberlyst-15(H)® was employed (entry 8). Increasing temperature to 70 °C improved the yield of **3a** to 60% (entry 9). Notably, chloride and bromide are inefficient for the reaction; only trace **3a** was detected (entries 10-11).[10]

Subsequent solvent screening disclosed that DMSO as a solvent benefited the electrochemically oxidative thiocyanation of ketone since the desired product **3a** was obtained in lower yields when the electrochemical reactions were performed in aqueous MeCN or aqueous 1,2-dimethoxyethane (DME) (entries 12-13), [11] whereas, it increased to 70% yield in aqueous DMSO (entry 14). Owing to the tedious workup process in using large amount of DMSO as solvent, we decided to perform the reaction in a mixed solution comprising EtOH (10 mL), DMSO (3 mL) and H_2O (2 mL), and more than 75% yield of **3a** was afforded (entry 15). The addition of water is necessary; it improves the solubility of NaSCN and enhances the conductivity of the reaction system.

Table 1. Optimization of the reaction conditions [a]

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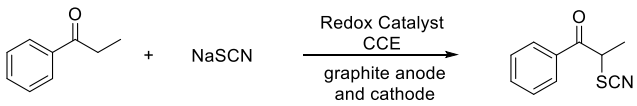

1 a (1 mmol) **2 a** **3 a**

Entry	J /mA·cm^{-2}	T/ ^{o}C	Redox catalyst	Additive	Solvent [e]	Yield [b]
1	4	50	NaI	-	EtOH/H_2O	0
2	4	50	NaI	Na_2CO_3[c]	EtOH/H_2O	0
3	4	50	NaI	NaOH[c]	EtOH/H_2O	0
4	4	50	NaI	DBU[c]	EtOH/H_2O	0
5	4	50	NaI	2,6-lutidine[c]	EtOH/H_2O	0
6	4	50	NaI	H_2SO_4[c]	EtOH/H_2O	15
7	4	50	NaI	PTSA[c]	EtOH/H_2O	30
8	4	50	NaI	A-15(H)®	EtOH/H_2O	44
9	4	70	NaI	A-15(H)®	EtOH/H_2O	60
10	4	70	NaCl	A-15(H)®	EtOH/H_2O	Trace
11	4	70	NaBr	A-15(H)®	EtOH/H_2O	6
12	4	70	NaI	A-15(H)®	MeCN/H_2O	6
13	4	70	NaI	A-15(H)®	DME/ H_2O	23
14	4	70	NaI	A-15(H)®	DMSO/H_2O	70
15	4	70	NaI	A-15(H)®	EtOH/DMSO/H_2O	75
16	2	70	NaI	A-15(H)®	EtOH/DMSO/H_2O	68
17	6	70	NaI	A-15(H)®	EtOH/DMSO/H_2O	74
18	4	70	NH_4I	A-15(H)®	EtOH/DMSO/H_2O	73
19	4	70	Et_4NI	A-15(H)®	EtOH/DMSO/H_2O	75
20	4	70	Bu_4NI	A-15(H)®	EtOH/DMSO/H_2O	72
21[d]	4	70	NaI	A-15(H)®	EtOH/DMSO/H_2O	52
22	4	50	-	A-15(H)®	EtOH/DMSO/H_2O	trace

[a] Reaction conditions: propiophenone **1a** (1 mmol), NaSCN **2a** in 15 mL of solvent, undivided cell, graphite plate anode and cathode, CCE. [b] ^{1}H NMR yields using 1,3,5-trimethoxybenzene as an internal standard. [c] 5 equiv. additives were used. [d] 0.2 equiv. NaI was added. [e] EtOH (13 mL) / H_2O (2 mL); MeCN (13 mL) / H_2O (13 mL); DME (13 mL) / H_2O (13 mL); DMSO (13 mL) / H_2O (13 mL); EtOH (10 mL) / DMSO (3 mL) / H_2O (2 mL)

The evaluation of current density indicated that comparative yields of **3a** was produced when a density of 2 mA/cm^2 (entry 16) and 6 mA/cm^2 (entry 17) were employed instead of the optimal 4 mA/cm^2. Interestingly, almost same yields of **3a** was isolated when NH_4I, Et_4NI, *n*-Bu_4NI was used as a mediator (entries 18-20). In addition, lowering the amount of NaI to 0.2 equiv resulted in a decrease of the yield of **3a** to 52 % (entry 21). The reactions did not proceed in the absence of NaI (entry 22). These observations indicate that iodide ion plays the essential role.

From the results described above, we concluded that the optimal reaction conditions call for the constant current electrolysis at a current density of 4 mA/cm^2 at 70 ^{o}C, using 0.5 equiv of NaI as the redox catalyst in the presence of Amberlyst-15(H)®. The reaction prefers proceeding in an undivided cell equipped with graphite plate anode and cathode using aqueous EtOH and DMSO solvent (entry 15).

With the optimized conditions in hand, we turned to explore the scope and limitation of the α-thiocyanation of ketones (Table 2). First, the reactions of NaSCN with different aromatic and aliphatic ketones were investigated. It was observed that the α-thiocyanation of aromatic ketones proceeded smoothly. For example, propiophenone and acetophenone afforded the corresponding α-thiocyanated products **3a** and **3b** in 70% and 60% isolated yield under the standard conditions. The α-thiocyanation of α-methyl propiophenone (**1c**) also proceeded but the corresponding product **3c** was obtained in only 15% yields due to the steric hindrance and most of the starting **1c** was recovered. Notably, the α-thiocyanation of 2-cyclopropyl-1-phenylethanone, **1d**, proceeded smoothly to afford the corresponding **3d** in 50% yield. This observation implies that the electrochemical α-thiocyanation of ketones may not involve a radical pathway (*Detailed discussion see mechanism discussion and Scheme 5*). It was observed the electrochemical α-thiocyanation was more efficient when an electron-donating substituent was appended on the benzene ring of propiophenone. For example, the methyl- and methoxyl substituted propiophenones afforded the corresponding adducts **3e** and **3g** in 71% and 72% yields, respectively, whereas, the corresponding **3h** and **3j** was isolated in a slightly lower yield when chloro- or fluoro- were installed in the phenyl ring. Cyclic aromatic ketones were also amenable to the reaction. For example, **3k** was afforded in a 45% yield.

Owing to less prone to enolization, simple aliphatic ketones are generally not suitable substrates for the oxidative α-functionalization. To our delight, our protocol could also be applied to aliphatic ketones, although in a bit lower yield compared with that of aromatic ketones. For example, when symmetric aliphatic ketone, such as **1l,** was subjected to reaction with NaSCN under the standard electrochemical conditions, the corresponding product **3l** was isolated in 35% yields. In the case of an unsymmetrical aliphatic ketone, such as 4-oxopentyl-4-chlorobenzoate (**1m**), a mixture of regioisomers of **3m** and **3m'** was obtained in 28% total yield and most of **1m** was recovered. 1,3-Dicarbonyl compounds were also suitable substrates for the α-thiocyanation reaction due to their easier keto-enol tautomerism. [12] As expected, **3n** and **3o** were afforded in good yields.

Table 2. Electrochemical oxidative α-thiocyanation of different ketones [a,b]

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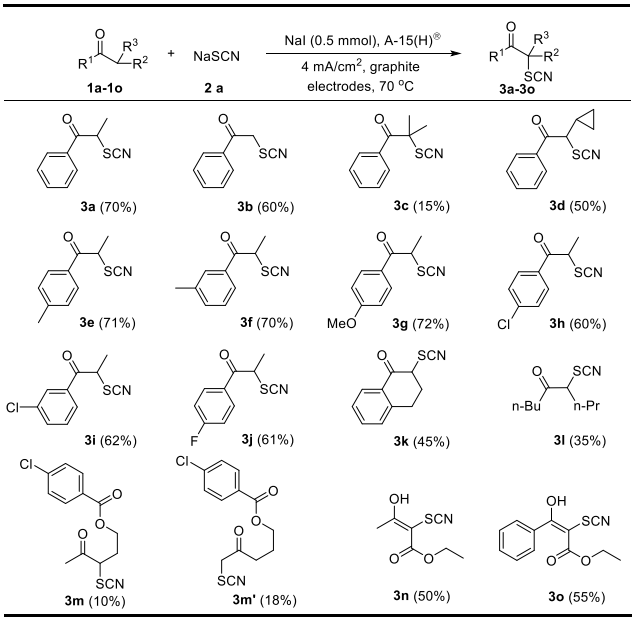
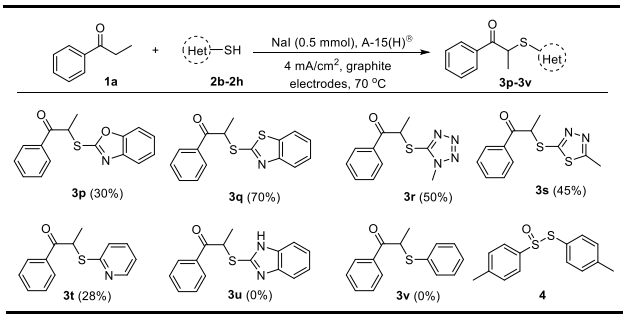


[a] Reaction conditions: ketones **1** (1 mmol), NaSCN **2a** (3 mmol) and in EtOH 10 mL / DMSO 3 mL / H_2O 2 mL of solvent, undivided cell, graphite plate anode and cathode, CCE.[b] Isolated yield

This protocol proved to be general and could also be applied in α-sulfenylation of ketones. As shown in Table 3, the reactions of propiophenone with various aromatic thiols, such as 2-mercaptobenzoxazole, 2-mercaptobenzothiazole, 5-mercapto-1-methyltetrazole, 2-mercapto-5-methyl-1,3,4-thiadiazole, and 2-mercaptopyridine proceeded smoothly to furnish the desired products **3p**-**3t** in moderate yields. For 2-mercapto-benzimidazole, **1u**, it failed to give the corresponding **3u**. Moreover, when *p*-toluenethiol was subjected to reaction with propiophenone under the standard conditions, the desired **3v** was not afforded, instead, *p*-tolyl-*p*-toluenesulfinate, **4**, was isolated due to the over-oxidation of homocoupling product of starting *p*-toluenethiol. [5]

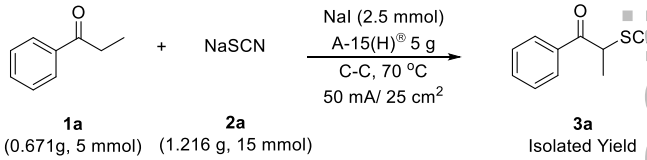
Table 3. Electrochemical oxidative sulfenylation of ketone with different thiols a,b



[a] Reaction conditions: propiophenone **1a** (1 mmol), thiols **2** (3 mmol) in a mixed solvent of EtOH (10 mL) / DMSO (3 mL) / H2O (2 mL), undivided cell, graphite plate anode and cathode, CCE. [b] isolated yield

Gram scale experiments of the one-pot electrochemical α-thiocyanation proved our protocol to be practicable. For example, when 5 mmol of **1a** (0.671 g) was subjected to electrolysis with NaSCN under the standard reaction conditions, the desired product **3a** was isolated in a 60% yield without significant loss in reaction efficiency (Scheme 2). Moreover, the recovered solid acid Amberlyst-15(H)® could be reused after prior treatment with 0.1 N HCl for 5 h. As shown in Scheme 2, the desired product **3a** was afforded in the range of 55 to 60% yields when the pre-activated solid acid was reused in five successive gram-scale reactions, without significant decrease of catalytic efficiency.

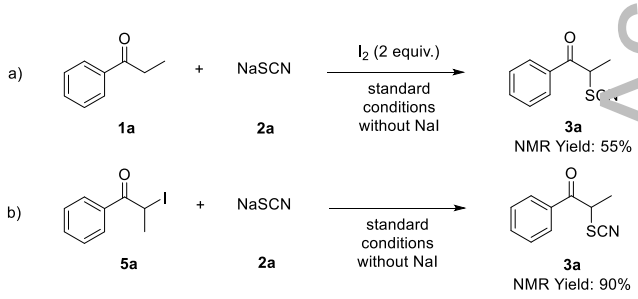
Scheme 2. Gram scale electrochemically oxidative α-C-H thiocyanation of propiophenone (**1a**) and recyclability of Amberlyst-15(H)®



Run	first	second	third	fourth	firth
Yield (%)	60	60	58	57	55

In order to better understand the reaction mechanism, several control experiments were conducted. As shown in Scheme 3, when molecular iodine was employed as oxidant, the desired product was obtained in a 55% yield (Scheme 3a). Therefore, the in situ generated molecular iodine (I_2) is likely one of the active species. Moreover, the reaction of separated synthesized 2-iodo-1-phenylpropan-1-one, **5a**, with NaSCN afforded excellent yield of **3a** (Scheme 3b), which suggests that **5a** is a possible intermediate in this transformation and that a nucleophilic substitution might be involved in the reaction process.

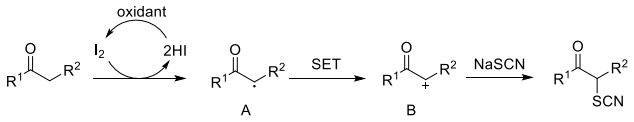
Scheme 3. Control experiments



It is worth noting that oxidative α-thiocyanation of ketone may also proceed via a radical pathway. For example, iodine radical from homolytic dissociation of molecular iodine abstracts one of the α-H of propiophenone, generating the carbon-centered

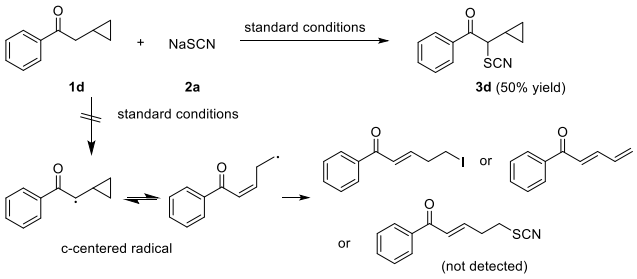
radical intermediate A. Followed by single electron transfer (oxidation), carbonic cation B afforded. Finally, the nucleophilic substitution of NaSCN to B gives the desired α-sulfenyl products (Scheme 4). Such a radical mechanism was previously proposed in the cases of α-C−H amination [13] and α-nitrotion of ketones [14].

Scheme 4. A possible radical pathway for the α-thiocyanation of ketones



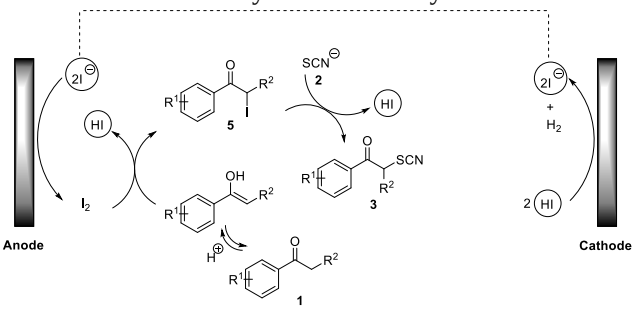
To clarify whether our electrochemical α-thiocyanation of ketones involves the formation of carbon-centered radical A, a radical clock experiment was performed (Scheme 5). As mentioned in Table 2, when substrate **1d** was subjected to electrolysis in the presence of **2a** under the standard electrochemical conditions, adduct **3d** was obtained in a 50% yield, whereas possible products, such as 5-iodo-1-phenyl-2-penten-1-one, 1-phenylpenta-2,4-dienone or 5-thiocyanato-1-phenyl- 2-penten-1-one, were not detected from ^{1}H NMR experiment, therefore we can rule out the radical pathway in our electrochemical α-thiocyanation of ketones.

Scheme 5. A radical clock experiment.



Based on these control experiments and radical clock experiment, a possible reaction mechanism for the electrochemical α-thiocyanation / sulfenylation of ketones with NaSCN or heterocyclic thiols is proposed. As illustrated in Scheme 6, the reaction begins with the anodic oxidation of iodide ion to generate molecular iodine, which undergoes reaction with enol isomer of ketone **1** to form α-iodo ketone **5**, along with one molecule of HI. Once the key intermediate **5** is formed, it soon undergoes a nucleophilic substitution reaction with NaSCN or heterocyclic thiols, leading to the final α-thiocyanation / sulfenylation product **3**, accompanying the generation of a second molecule of HI. Simultaneously, the in situ generated HI is reduced to evolve H_2 on the surface of cathode. In the course of the reaction, iodide ion is regenerated from steps of the α-iodination of ketone **1**, leading to **5** and following nucleophilic substitution of **5** to **3**, and re-enters the redox catalyst cycle, thereby only sub-stoichiometric or catalytic amount of iodide ion is required.

Scheme 6. A proposed reaction mechanism for the electrochemical α-thiocyanation / sulfenylation of ketones



This proposed mechanism is consistent with cyclic voltammetry analysis. As shown in Figure 1, CV of NaI exhibits two typical oxidative waves at 0.62 V and 0.86V vs Ag/AgCl (3M KCl) (curve b). When 1.0 equiv of propiophenone was added to the solution of NaI, a dramatic increase of the oxidation peak current was observed, along with a decrease of reduction peak current (curve c). Since propiophenone is not oxidized in the potential range from 0.0 V to 1.4 V vs Ag/AgCl that was used (curve d), the increase in the oxidative peak current is attributed to a catalytic current, resulting from the reaction of the in situ electrochemically generated I_2 and propiophenone, affording α-iodopropiophenone **5** and regenerated iodine ion that leads to the appearance of catalytic current and decrease of reduction current (the conversion of **1** to **5** in Scheme 6). Although a slight increase of catalytic current was observed in the presence of solid acid Amberlyst-15(H)® (curve e), subsequent addition of NaSCN to the system led to an additional increase of catalytic current, simultaneously, the reduction peak disappeared completely (curve f). This is due to the nucleophilic substitution of **5** and SCN^- under the acidic medium, generating desired product **3** and regenerating iodide ion (the conversion of **5** to **3** in Scheme 6).

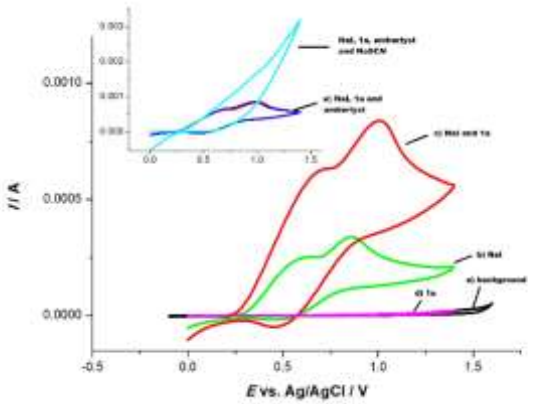


Figure 1. Cyclic voltammogram NaI, propiophenone and NaSCN in 0.1 M $LiClO_4$ in a mixed solvent of EtOH (10

mL), DMSO (3 mL) and H_2O (2 mL) using GC disk working electrode, Pt wire and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate. a) background, b) NaI (0.1 M), c) NaI (0.1 M) and **1a** (0.1 M), d) **1a** (0.1 M), e) NaI (0.1 M), **1a** (0.1 M), Amberlyst-15(H)® (0.5 g), f) NaI (0.1 M), **1a** (0.1 M), Amberlyst-15(H)® (0.5 g) and NaSCN (0.3 M).

It is well known that an acid (Brønsted acid or Lewis acid) can promote the keto-enol tautomization of a ketone. In addition, it is well documented by Becker and coworkers in their electrochemical thiocyanation of alkenes and aromatics that polymerization of thiocyanate or thiol is diminished considerably in the presence of acid recourse. [15] In our electrochemical α-thiocyanation / sulfenylation of ketones, Amberlyst-15(H)® not only promotes the enolization of the carbonyl group for the easier α-halogenation, but also suppress the polymerization of sulfur-containing reagents.

Conclusion

In conclusion, we have developed an efficient electrochemical protocol for the α-thiocyanation / sulfenation of ketones via the cascade oxidative α-C-H halogenation of ketones and subsequent nucleophilic substitution with NaSCN or heterocyclic thiols. The electrochemistry was performed under constant current conditions in a simple undivided cell equipped with simple graphite plate electrodes using NaI as the redox catalyst in the presence of Amberlyst-15(H)® without the assistance of additional conductive salts. A wide range of functional groups are proved to be compatible with the standard conditions. Gram scale reaction of **1a** and **2a** demonstrates the practicality of the protocol. The heterogeneous catalyst, Amberlyst-15(H)®, can be reused in up to five consecutive runs without significant loss in reaction efficiency. Mechanistic studies reveal that the electrochemical α-thiocyanation / sulfenation of ketones likely undergoes initial α-iodination, followed by a nucleophilic substitution of NaSCN or heterocyclic thiols. In this way, the iodide ion can be used catalytically, thereby avoiding the utilization of stoichiometrical amount of molecular iodine or a combination of iodide and co-oxidant and thereby represents an environmentally benign means by which to achieve the transformation. Application of these ideas and results to other types of reactions is underway in our laboratory.

Experimental Section

Instruments and reagents

NMR spectra were recorded with a spectrometer (300 MHz or 600 MHz ^{1}H frequency, 75 MHz or 150 MHz ^{13}C frequency). Chemical shifts are given as δ values (internal standard: TMS). Coupling constants are reported in Hz. Cyclic voltammograms were obtained using Metrohm Autolab. Starting materials and solvents were obtained from commercial sources and used without further purification. Products were purified by chromatography on silica gel (Petroleum ether/EtOAc).

General procedure for the electrochemical oxidation sulfenylation of ketones

A 50 mL undivided cell was equipped with a graphite plate cathode and a graphite plate anode (each about 2 × 3 cm^2 and the inter electrode distance is about 0.5 cm) which were connected to a DC regulated power supply. To the cell was added ketone **1** (1 mmol), NaSCN **2** (3 mmol), NaI (0.5 mmol), Amberlyst-15(H)® (1 g) and dissolved in EtOH 10 mL + DMSO 3 mL + H_2O 2 mL. The mixture was electrolyzed under constant current conditions at 4 mA/cm^2 at 70 °C while stirring. The electrolysis was terminated when 15 F/mol of charge had been consumed. After the electrolysis, the solvent was removed under reduced pressure. The residue was poured into a saturated aqueous $Na_2S_2O_3$ and the product was then extracted with EtOAc (3×10 mL), dried over $MgSO_4$, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc as eluent.

1-Phenyl-2-thiocyanatopropan-1-one (**3a**) [16] Yield: 134 mg, 70%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 15 / 1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.87 (d, *J* = 7.2 Hz, 3H), 5.09 (q, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.9, 50.0, 111.5, 128.8, 129.2, 133.1, 134.6, 194.8.

1-Phenyl-2-thiocyanatoethanone (**3b**) [15] Yield: 106 mg, 60%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 10 / 1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.75 (s, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.0, 111.8, 128.4, 129.2, 133.9, 134.8, 190.8.

2-Methyl-1-phenyl-2-thiocyanatopropan-1-one (**3c**) Yield: 31 mg, 15%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 20 / 1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01 (s, 6H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.8, 64.1, 111.9, 128.7, 129.1, 133.2, 133.9, 198.4; HRMS (ESI) m/z calcd for $C_{11}H_{12}NOS$ $(M+H)^+$ 206.06341, found 206.06356; HRMS (ESI) m/z calcd for $C_{11}H_{15}N_2OS$ $(M+NH_4)^+$ 223.08996, found 223.09019; HRMS (ESI) m/z calcd for $C_{11}H_{11}NNaOS$ $(M+Na)^+$ 228.04536, found 228.04560.

2-Cyclopropyl-1-phenyl-2-thiocyanatoethanone (**3d**) Yield: 108 mg, 50%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 15 / 1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.53-0.57 (m, 1H), 0.70-0.75 (m, 1H), 0.77-0.81 (m, 1H), 0.88-0.94 (m, 1H), 1.53-1.59 (m, 1H), 4.49 (d, *J* = 9.0 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 5.8, 6.7, 14.6, 58.1, 111.7, 128.9, 129.1, 134.4, 134.5, 194.0; HRMS (ESI) m/z calcd for $C_{12}H_{12}NOS$ $(M+H)^+$ 218.06341, found 218.06286; HRMS (ESI) m/z calcd for $C_{12}H_{15}N_2OS$ $(M+NH_4)^+$ 235.08996, found 235.08944; HRMS (ESI) m/z calcd for $C_{12}H_{11}NNaOS$ $(M+Na)^+$ 240.04536, found 240.04487.

2-Thiocyanato-1-(*p*-tolyl) propan-1-one (**3e**) Yield: 145 mg, 71%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 15 / 1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.85 (d, *J* = 7.2 Hz, 3H), 2.44 (s, 3H), 5.07 (q, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.0, 21.8, 50.2, 111.7, 128.9, 129.8, 130.5, 145.8, 194.4; HRMS (ESI) m/z calcd for $C_{11}H_{12}NOS$ $(M+H)^+$ 206.06341, found 206.06286; HRMS (ESI) m/z calcd for $C_{11}H_{15}N_2OS$ $(M+NH_4)^+$ 223.08996,

found 223.08948; HRMS (ESI) m/z calcd for $C_{11}H_{11}NNaOS$ $(M+Na)^+$ 228.04536, found 228.04491.

2-Thiocyanato-1-(m-tolyl) propan-1-one (**3f**) Yield: 144 mg, 70%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 15 / 1). ^1H NMR (300 MHz, $CDCl_3$) δ 1.85 (d, *J* = 7.1 Hz, 3H), 2.43 (s, 3H), 5.08 (q, *J* = 6.9 Hz, 1H), 7.38-7.48 (m, 2H), 7.70-7.74 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.9, 21.3, 50.1, 111.5, 126.0, 129.0, 129.3, 133.1, 135.3, 139.1, 195.0; HRMS (ESI) m/z calcd for $C_{11}H_{12}NOS$ $(M+H)^+$ 206.06341, found 206.06280; HRMS (ESI) m/z calcd for $C_{11}H_{15}N_2OS$ $(M+NH_4)^+$ 223.08996, found 223.08941; HRMS (ESI) m/z calcd for $C_{11}H_{11}NNaOS$ $(M+Na)^+$ 228.04536, found 228.04482.

1-(4-Methoxyphenyl)-2-thiocyanatopropan-1-one (**3g**) Yield: 159 mg, 72%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 10 / 1). ^1H NMR (300 MHz, $CDCl_3$) δ 1.85 (d, *J* = 7.2 Hz, 3H), 3.90 (s, 3H), 5.07 (q, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 9.0 Hz, 2H), 7.91 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.2, 50.3, 55.7, 111.9, 114.4, 125.9, 131.3, 164.7, 193.3; HRMS (ESI) m/z calcd for $C_{11}H_{12}NO_2S$ $(M+H)^+$ 222.05833, found 222.05851; HRMS (ESI) m/z calcd for $C_{11}H_{15}N_2O_2S$ $(M+NH_4)^+$ 239.084488, found 239.08500; HRMS (ESI) m/z calcd for $C_{11}H_{11}NNaO_2S$ $(M+Na)^+$ 244.04027, found 244.04077.

1-(4-Chlorophenyl)-2-thiocyanatopropan-1-one (**3h**) Yield: 135 mg, 60%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 12 / 1). ^1H NMR (300 MHz, $CDCl_3$) δ 1.85 (d, *J* = 7.2 Hz, 3H), 4.99 (q, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.6, 49.3, 111.0, 129.6, 130.2, 131.5, 141.3, 193.5; HRMS (ESI) m/z calcd for $C_{10}H_9ClNOS$ $(M+H)^+$ 226.00879, found 226.00869; HRMS (ESI) m/z calcd for $C_{10}H_{12}ClN_2OS$ $(M+NH_4)^+$ 243.03534, found 243.03511; HRMS (ESI) m/z calcd for $C_{10}H_8ClNNaOS$ $(M+Na)^+$ 247.99073, found 247.99064.

1-(3-Chlorophenyl)-2-thiocyanatopropan-1-one (**3i**) Yield: 140 mg, 62%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 10 / 1). ^1H NMR (300 MHz, $CDCl_3$) δ 1.85 (d, *J* = 6.9 Hz, 3H), 4.97 (q, *J* = 6.9 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 6.9 Hz, 1H), 7.80 (d, *J* = 7.2 Hz, 1H), 7.91 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.4, 49.1, 110.8, 126.8, 128.8, 130.5, 134.4, 134.8, 135.6, 193.4; HRMS (ESI) m/z calcd for $C_{10}H_9ClNOS$ $(M+H)^+$ 226.00879, found 226.00882; HRMS (ESI) m/z calcd for $C_{10}H_{12}ClN_2OS$ $(M+NH_4)^+$ 243.03534, found 243.03525; HRMS (ESI) m/z calcd for $C_{10}H_8ClNNaOS$ $(M+Na)^+$ 247.99073, found 247.99075.

1-(4-Fluorophenyl)-2-thiocyanatopropan-1-one (**3j**) Yield: 127 mg, 61%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 12 / 1). ^1H NMR (300 MHz, $CDCl_3$) δ 1.85 (d, *J* = 7.2 Hz, 3H), 5.02 (q, *J* = 7.2 Hz, 1H), 7.18-7.23 (m, 2H), 7.95-8.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.7, 49.5, 111.2, 116.5 (d, *J* = 21.8 Hz), 129.6 (d, *J* = 3.1 Hz), 131.6 (d, *J* = 9.6 Hz), 166.5 (d, *J* = 256.5 Hz), 193.2; HRMS (ESI) m/z calcd for $C_{10}H_9FNOS$ $(M+H)^+$ 210.03834, found 210.03770; HRMS (ESI) m/z calcd for $C_{10}H_{12}FN_2OS$ $(M+NH_4)^+$ 227.06489, found 227.06428; HRMS (ESI) m/z calcd for $C_{10}H_8FNNaOS$ $(M+Na)^+$ 232.02028, found 232.01972.

2-Thiocyanato-3,4-dihydronaphthalen-1(2H)-one (**3k**) Yield: 91 mg, 45%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 10 / 1). ^1H NMR (300 MHz, $CDCl_3$) δ 2.36-2.50 (m, 1H), 2.82-2.90 (m, 1H), 3.17-3.21 (m, 2H), 4.56 (dd, *J* = 4.8, 13.2 Hz, 1H), 7.29-7.39 (m, 2H), 7.43 (dt, *J* = 3.0, 7.8 Hz, 1H), 8.02 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.0, 31.4, 55.7, 111.7, 127.4, 128.0, 130.6, 134.8, 143.4, 191.7; HRMS (ESI) m/z calcd for $C_{11}H_{10}NOS$ $(M+H)^+$ 204.04776, found 204.04736; HRMS (ESI) m/z calcd for $C_{11}H_{13}N_2OS$ $(M+NH_4)^+$ 221.07431, found 21.07393; HRMS (ESI) m/z calcd for $C_{11}H_9NNaOS$ $(M+Na)^+$ 226.02971, found 226.02938.

4-Thiocyanatononan-5-one (**3l**) Yield: 70 mg, 35%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 15 / 1). ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.5 Hz, 3H), 0.97 (t, *J* = 7.5 Hz, 3H), 1.24-1.52 (m, 4H), 1.56-1.66 (m, 2H), 1.85-2.11 (m, 2H), 2.51-2.70 (m, 2H), 3.94 (t, *J* = 6.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6, 13.8, 19.5, 22.2, 25.7, 33.0, 40.1, 56.6, 110.7, 204.3; HRMS (ESI) m/z calcd for $C_{10}H_{18}NOS$ $(M+H)^+$ 200.11036, found 200.11046; HRMS (ESI) m/z calcd for $C_{10}H_{21}N_2OS$ $(M+NH_4)^+$ 217.13691, found 217.13699; HRMS (ESI) m/z calcd for $C_{10}H_{17}NNaOS$ $(M+Na)^+$ 222.09231, found 222.09247.

4-Oxo-3-thiocyanatopentyl 4-chlorobenzoate (**3m**) Yield: 30 mg, 10%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 6 / 1). ^1H NMR (600 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.40-2.45 (m, 1H), 2.60-2.66 (m, 1H), 4.02 (t, *J* = 6.6 Hz, 1H), 4.48-4.55 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 27.7, 30.1, 53.6, 61.2, 109.3, 127.9, 129.0, 131.0, 140.0, 165.5, 200.3; HRMS (ESI) m/z calcd for $C_{13}H_{13}ClNO_3S$ $(M+H)^+$ 298.02992, found 298.02940; HRMS (ESI) m/z calcd for $C_{13}H_{16}ClN_2O_3S$ $(M+NH_4)^+$ 315.05647, found 315.05598; HRMS (ESI) m/z calcd for $C_{13}H_{12}ClNNaO_3S$ $(M+Na)^+$ 320.01186, found 320.01139.

4-Oxo-5-thiocyanatopentyl 4-chlorobenzoate (**3m'**) Yield: 53 mg, 18%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 6 / 1). ^1H NMR (600 MHz, $CDCl_3$) δ 2.12-2.16 (m, 2H), 2.76 (t, *J* = 6.6 Hz, 2H), 4.04 (s, 2H), 4.36 (t, *J* = 6.0 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 22.8, 37.9, 43.6, 63.8, 111.3, 128.3, 128.8, 128.8, 131.0, 139.7, 165.7, 200.2; HRMS (ESI) m/z calcd for $C_{13}H_{13}ClNO_3S$ $(M+H)^+$ 298.02992, found 298.02948; HRMS (ESI) m/z calcd for $C_{13}H_{16}ClN_2O_3S$ $(M+NH_4)^+$ 315.05647, found 315.05608; HRMS (ESI) m/z calcd for $C_{13}H_{12}ClNNaO_3S$ $(M+Na)^+$ 320.01186, found 320.01149.

Ethyl 3-hydroxy-2-thiocyanatobut-2-enoate (**3n**) Yield: 93 mg, 50%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 5 / 1). ^1H NMR (600 MHz, $CDCl_3$) δ 1.33 (t, *J* = 7.2 Hz, 3H), 2.49 (s, 3H), 4.27 (q, *J* = 7.2 Hz, 2H), 10.63 (br, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.7, 14.3, 61.2, 105.1, 141.9, 161.6, 174.0; HRMS (ESI) m/z calcd for $C_7H_{10}NO_3S$ $(M+H)^+$ 188.03759 found 188.03698; HRMS (ESI) m/z calcd for $C_7H_{13}N_2O_3S$ $(M+NH_4)^+$ 205.06414, found 205.06358; HRMS (ESI) m/z calcd for $C_7H_9NNaO_3S$ $(M+Na)^+$ 210.01953, found 210.01899.

Ethyl 3-hydroxy-3-phenyl-2-thiocyanatoacrylate (**3o**) Yield: 137 mg, 55%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 5 / 1). ^1H NMR (600 MHz, $CDCl_3$) δ 1.22 (t, *J* = 7.2 Hz, 3H), 4.18 (q, *J* = 7.2 Hz, 2H), 7.46-7.49 (m, 3H), 7.54-7.56 (m, 2H), 9.75 (br, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 61.4, 105.7, 128.4, 128.6, 129.0, 130.6, 142.3, 160.6, 172.1; HRMS (ESI) m/z calcd for $C_{12}H_{12}NO_3S$ $(M+H)^+$ 250.05324 found 250.05303; HRMS (ESI) m/z calcd for $C_{12}H_{15}N_2O_3S$ $(M+NH_4)^+$ 267.07979, found 267.07961; HRMS (ESI) m/z calcd for $C_{12}H_{11}NNaO_3S$ $(M+Na)^+$ 272.03518, found 272.03495.

2-(Benzo[d]oxazol-2-ylthio)-1-phenylpropan-1-one (**3p**)[16] Yield: 85 mg, 30%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 15 / 1). ^1H NMR (300 MHz, $CDCl_3$): δ 1.83 (d, *J* = 6.0 Hz, 3H), 5.72 (q, *J* = 6.0 Hz, 1H), 7.23-7.32 (m, 2H), 7.43 (d, *J* = 6.9 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 6.9 Hz, 2H), 8.09 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.2, 47.6, 110.0, 118.5, 124.1, 124.4, 128.9, 133.9, 134.4, 141.7, 152.0, 163.8, 197.0.

2-(Benzo[d]thiazol-2-ylthio)-1-phenylpropan-1-one (**3q**)[16] Yield: 209 mg, 70%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 15 / 1). ^1H NMR (300 MHz, $CDCl_3$): δ 1.76 (d, *J* = 7.2 Hz, 3H), 5.87 (q, *J* = 6.9 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.72 (d, *J*= 7.8

Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 8.09 (d, *J*=7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.3, 47.0, 121.0, 121.5, 124.4, 126.0, 128.7, 128.8, 133.5, 134.9, 135.6, 152.8, 164.6, 197.1.

2-((1-Methyl-1H-tetrazol-5-yl) thio)-1-phenylpropan-1-one (**3r**) Yield: 124 mg, 50%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 6 / 1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.78 (d, *J* = 7.2 Hz, 3H), 3.91 (s, 3H), 5.72 (q, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 8.01 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.4, 33.5, 49.5, 128.8, 129.0, 133.9, 134.2, 153.1, 196.8; HRMS (ESI) m/z calcd for $C_{11}H_{13}N_4OS$ $(M+H)^+$ 249.08046 found 249.08083; HRMS (ESI) m/z calcd for $C_{11}H_{12}N_4NaOS$ $(M+Na)^+$ 271.06240, found 271.06257.

2-((5-Methyl-1,3,4-thiadiazol-2-yl) thio)-1-phenylpropan-1-one (**3s**) Yield: 118 mg, 45%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 6 / 1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.73 (d, *J* = 6.9 Hz, 3H), 2.72 (s, 3H), 5.76 (q, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 8.04 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.6, 18.5, 47.6, 128.8, 128.8, 133.8, 134.6, 163.4, 165.9, 196.9; HRMS (ESI) m/z calcd for $C_{12}H_{13}N_2OS_2$ $(M+H)^+$ 265.04638 found 265.04667; HRMS (ESI) m/z calcd for $C_{12}H_{12}N_2NaOS_2$ $(M+Na)^+$ 287.02833, found 287.02895.

1-Phenyl-2-(pyridin-2-ylthio) propan-1-one (**3t**) Yield: 68 mg, 28%; Brown oil; Flash chromatography (Petroleum ether/EtOAc, 15 / 1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.64 (d, *J* = 7.2 Hz, 3H), 5.78 (q, *J* = 6.6 Hz, 1H), 7.00 (t, *J* = 6.0 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 8.39 (d, *J* = 4.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 17.6, 42.7, 119.9, 122.5, 128.5, 128.7, 133.1, 135.6, 136.2, 149.3, 156.8, 198.4; HRMS (ESI) m/z calcd for $C_{14}H_{14}NOS$ $(M+H)^+$ 244.07906 found 244.07833; HRMS (ESI) m/z calcd for $C_{14}H_{13}NNaOS$ $(M+Na)^+$ 266.06101, found 266.06029.

S-p-tolyl 4-methylbenzenesulfinothioat**e (4)** [18] white solid, m.p.: 54~56ºC; Flash chromatography (Petroleum ether/EtOAc, 15 / 1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.37 (s, 3H), 2.41 (s, 3H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.19-7.24 (m, 4H), 7.44 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (75MHz, $CDCl_3$): δ 21.4, 21.6, 124.5, 127.5, 129.3, 130.1, 136.4, 140.3, 142.0, 144.6.

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FULL PAPER

Redox active sodium iodide / recyclable heterogeneous solid acid: An efficient dual catalytic system for electrochemically oxidative α-C-H thiocyanation and sulfenylation of ketones

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