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Nickel-catalyzed oxidative dehydrogenative coupling of alkane with thiol for C(sp³)-S bond formation



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Introduction

Alkyl thioethers have been broadly applied into the fields of pharmaceuticals [1], agrochemicals [2], natural products [3], and polymeric material [4]. As a result, a large number of methods, particularly catalytic approaches to alkyl thioethers production have been extensively developed [5]. Among them, the transition-metal catalyzed directed sulfuration of sp³ C-H bond is an atom and step economical process for the C(sp³)-S bond formation [6]. However, the introduction of directing group into hydrocarbon substrate is indispensable to low the bond dissociation energy of unactivated sp³ C–H bond [7], leading to the restricted scope of hydrocarbons. Oxidative dehydrogenative coupling reaction of alkane with sulfur reagent via radical pathway is capable of construction of C-S bond in absence of any directed group [8]. But in this field, the issues of the use of large stoichiometric amount of oxidant, the intrinsic over oxidation, and tolerates a broad range of functional groups remains highly sought. Therefore, we envisioned that transitionmetal catalysis might be the vital factor in the oxidative dehydrogenative coupling transformation of alkane with thiol. Nickel serves as a non-noble metal catalyst have been well applied in the dehydrogenation of sp³ C-H bond or N-H bond, such as nickel-catalyzed C- or N-alkylation/olefination reactions [9]. Nevertheless, nickel has not been used as a catalyst in the oxidative

ABSTRACT

A nickel-catalyzed oxidative dehydrogenative coupling reaction of alkane with thiol for the construction of C(sp³)-S bond has been established, affording more than 50 alkyl thioethers. Notably, pharmaceutical and agrochemicals, such as Provigil, Chlorbenside and Pyridaben, were readily synthesized by this approach. The sterically hindered ligand BC and disulfide which was formed in situ oxidation of thiol, efficiently avoiding nickel-catalyst poisoning. A set of mechanistic experiments disclose both Ni-catalyzed and Ni-free HAA processes.

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dehydrogenative coupling reaction of sp³ C–H bond with S–H bond for C(sp³)-S bond construction, probably due to the strong coordination ability of thiol would significantly deactivate nickel-catalyst [5]. Considering this point, on the one hand, we planned to use sterically hindered bathocuproine (BC) as ligand to stabilize the nickel-center and avoid catalyst poisoning. BC could not only increase the nucleophilicity of nickel complex which will easily reacts with alkyl radical, but also is in favor of C–S reductive elimination. On another hand, we postulated that the steric-demand disulfide, which could be in situ produced by the oxidation of thiol, possessing weak coordination ability to suppress the catalyst poisoning.

To the best of our knowledge, di-*tert*-butyl peroxide (DTBP) is able to severally oxidize thiol and alkane to provide disulfide and alkyl radical by metathesis reaction (Scheme 1a, Eq. (1) & (2)). Moreover, according to the seminal work by Yamaguchi and coworkers on rhodium-catalytic C(sp)-H/S–S bond metathesis reaction, C-M and S-M intermediates could be generated via the treatment of transition-metals with alkyne and disulphide [10]. Simultaneously, Zhang [11], Liu [12], Stahl [13], and our group [14] work for transition-metal catalyzed oxidative reactions of benzylic sp³ C–H bond inspired us that alkyl radical could treat with metal-complex via single-electron transfer (SET), thereby availably inhibiting the homocoupling of alkyl radicals. Herein a nickel-catalyzed oxidative dehydrogenative coupling reactions of alkanes with thiols employing DTBP as an oxidant has been first



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Scheme 1. Our strategy for Ni-catalyzed oxidative dehydrogenative coupling reaction.

demonstrated. The intermediates S-Ni or S-Ni-C might be produced under nickel-catalysis, which would further transform to alkyl thioether compounds (Scheme 1a, Eq. (3)). It is worthy to note that, more than fifty alkyl thioethers, containing pharmaceutical and agrochemicals such as Provigil, Chlorbenside and Pyridaben, can be facilely synthesized by this new C(sp³)-S bonding strategy (Scheme 1b).

Results and discussion

To investigate the optimal reaction conditions, the transformation of **A1** with **B1** was occurred in the present of 1 equivalent of DTBP with Ni(OAc)₂·4H₂O/BC, smoothly providing alkyl thioether **1** in 79% yield (Table 1, entry 1). Among a number of inexpensive metal-catalysts, Ni(OAc)₂·4H₂O exhibited better reactivity (Table 1, entries 1–6 & Table S1). To our delight, prolong the time from 12 to 24 h, slight improvement of efficiency could be achieved (Table 1, entry 7). When Ni(OAc)₂·4H₂O or BC independently was participated in the reaction, only disappointed efficiencies of product **1** could be attained, respectively (Table 1, entries 8 & 9). Additionally, BC presented higher reactivity than other ligands through the screening of ligands (Table S2), which illustrates that the ligand

Table 1Optimization of reaction conditions.^a



^aReaction conditions: **A1** (15 mmol, 30 equiv), **B1** (0.5 mmol, 1 equiv), catalyst (5 mol %), BC (6 mol %), DTBP (1 equiv), 140 °C, 12 h, N₂ atmosphere. ^bYield was determined by GC using mesitylene as the internal standard. ^c24 h. ^disolated yield. ^eDTBP (4 equiv).

having large steric hindrance efficiently protect nickel center and avoid catalyst poisoning. Under catalyst-free conditions, poor yields of product **1** were got with using 1 and 4 equivalents of DTBP, respectively (Table 1, entries 10 & 11, 22% & 33% yields). Above control experiments illustrate that both Ni(OAc)₂.4H₂O and BC are beneficial to the C–S bond formation. We also attempted to perform this reaction when employing iodine as the catalyst, but only trace amount of corresponding product could be obtain (Table S1). Other reaction conditions, such as oxidants, temperatures, and amount of parameters, were also surveyed and none better efficiency could be got (Table S2–S5).

With the optimal reaction conditions in hand, the substrate tolerance of thiols was studied as shown in Table 2. Diversified electron-donating and electron-withdrawing substituents on aryl ring of thiols presented good to high efficiencies, providing desired alkyl thioethers **2–15**. Both 1- and 2-naphthalene substituted thiols could react with phenylethane **A1** to smoothly generate **16** and **17** with high yields, respectively. Heteroaryl substituted thiol was compatible with the catalytic oxidative dehydrogenative coupling reaction to give product **18**. In addition, alkyl thiols were also tolerated the transformation, facilely delivering alkyl thioethers **19–23**.

The sequential procedure concentrated on the Ni-catalyzed oxidative dehydrogenative coupling reaction for various alkane types (Table 3). Halogen atom substituted aryl ring of phenylethane were competent under the standard reaction conditions, forming **24–26** in moderate to high yields. *p*-Substituted benzyl (*p*-tolyl)sulfane **27–32** were easily isolated by the treatments of *p*-substituted toluenes with **B1**. Cumin readily transformed into the target product **33** with good efficiency. Alkyl thioethers **34** and **34**' stemming from isobutylbenzene were obtained with the ratio of 2:1. Cyclohexylbenzene and diphenylmethane were tolerated in this method, successfully affording products **35** and **36**, respectively. Additionally, both 2,3-dihydro-1*H*-indene and 1,2,3,4-tetrahydronaphthalene could separately reacted with **B1** to access to the desired products **37** and **38** with good to high yields. Furthermore, alkanes bearing pyridine groups also dis-

Table 2Substrate scope of thiols.⁴



^aReaction conditions: **A1** (15 mmol, 30 equiv), **B** (0.5 mmol, 1 equiv), Ni(OAc)₂·4H₂O (5 mol %), BC (6 mol %), DTBP (0.5 mmol, 1 equiv), 140 °C, 24 h, N₂, isolated yields. ^bNBS (5 mol %).

Substrate scope of alkanes.^a



^aReaction conditions: **A** (15 mmol, 30 equiv), **B1** (0.5 mmol, 1 equiv), Ni(OAc)₂·4H₂O (5 mol %), BC (6 mol %), DTBP (0.5 mmol, 1 equiv), 140 °C, 24 h, N₂, isolated yields. ^bNBS (5 mol %). ^c**A** (7.5 mmol, 15 equiv), fluorobenzene (7.5 mmol, 15 equiv).

played moderate to good reactivities to afford desired products 39-44. Gratifyingly, alkanes without aryl ring such as annular and heterocyclic alkanes demonstrated well tolerance in the oxidative dehydrogenative coupling reaction. Alkyl thioethers 45-48 arising from alkanes with six to twelve-member rings were facilely produced. Adamantyl thiol gave both the corresponding products 49 and 49' with the ratio of 2.4:1, and 49 was characterized by Xray single crystal diffraction (Figure S5 & Table S6). Heterocyclic alkanes such as tetrahydrofuran, tetrahydro-2H-pyran and 1,4dioxane captured *p*-methylphenylthiophenol at the orho-position of oxygen atom were successfully converted to products 50-52. We found that N-bromosuccinimide (NBS) can promoted the reactivities like 21, 23, 38, 49 and 49', and compared with the yields of this products under NBS free conditions. The results were displayed in the supporting information and probable NBS mediated reaction pathways were also presented.

For extending the utility of the Ni-catalyzed oxidative dehydrogenative coupling reaction in the area of drugs and agrochemicals preparation, a pharmaceutical and two pesticides were accessed with this method (Scheme 2). Initially, alkyl thioether **53** as a synthetic intermediate of Provigil was achieved with high yield via the reaction of diphenylmethane **A14** with thiol **B24**. Next, **53** was oxidized by *m*-chloroperoxybenzoic acid (*m*-CPBA) to afford sulfoxide **54** which easily converted to Provigil **55** with ammonia gas (Scheme 2a). An acaricide Chlorbenside **56** was also obtained by the treatment of **A2** with **B9** under the optimized reaction conditions (Scheme 2b). The reaction of thiol **A6** with **B25** gave the pesticide Pyridaben **57** without further optimizing reaction conditions (Scheme 2c). Besides, gram-scale coupling reaction of **A1** with **B1**



Scheme 2. Synthesis of Provigil, Pyridaben and Chlorbenside.

was worked under the standard conditions, generating **1** in 70% yield (1.6 g) (Scheme 2d).

In order to research the mechanism of the nickel-catalyzed oxidative dehydrogenative coupling transformation, a sequence of experiments were carried out under the standard reaction conditions (Scheme 3 and more details see SI). Radical scavengers 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) and 2,6-di-tertbutyl-4-methylphenol (BHT) were added into the reaction, affording only 14% and 19% GC yield of the desired products, respectively (Scheme 3a). The results suggest that radical pathway probably involved into this transformation. Then the reaction of A1 and B1 was run with only 30 min, detecting 50% yield of disulfide C which can further coupled with A1 to produce 1 (see SI). The data indicate that **C** may be an intermediate. The transformation of **C** with **A1** was also conducted under the catalysis of Ni-complex without DTBP, giving trace amount of 1 (see SI). This experiment declares that C only acts as an intermediate rather than an oxidant in the reaction. Furthermore, the reaction profiles have been used to separately monitor the reactions of A1 with B1 under the two conditions (with and without nickel-catalyst) over 12 h (Scheme 3b, Figure 2S and 3S). Alkyl thioether **1** is generated as the consumption of disulfide **C** which gets to peak during $2 \sim 3$ h and then decreases. These results are consistent with the perspective that C is an intermediate in the reaction. The formation rates of C almost the same in both nickel and nickel-free conditions, suggesting that DTBP plays as the pivotal factor instead of nickel for generating C. Significantly, as a catalyst, nickel obviously accelerates the consumption of **C** and generation of product **1**. In addition, kinetic isotope effect (KIE) experiments, including an intermolecular competition reaction and two parallel reactions were proceeded



Scheme 3. Preliminary mechanistic researches.

to give the value of $k_{\rm H}/k_{\rm D}$ = 5.7 and 4.6, respectively (Scheme 3c and SI). The results prove that the cleavage of C–H abstraction was possibly involved into the rate-determining step, and this reaction may be via a hydrogen atom abstraction (HAA) process [11,15].

The mechanism of nickel-catalyzed oxidative dehydrogenative coupling reaction was further studied by in situ HRMS (ESI) experiments (Scheme 4a and details see SI). The in situ HRMS detected peaks at *m*/*z* 837.2719, 901.2848 and 778.2597, which severally corresponded to the mass of I, II and IV (Figure S4). On the basis of above experimental evidences and previous works [7-17], three reaction pathways have been hypothesized in Scheme 4b. Path a and b are Ni-catalytic cycles. Ni-complex [II-OAc]⁺ is formed through the ligand exchange of [I-OAc]⁺ with thiol [17], which then reacts with alkyl raddical to afford complex [IV-OAc]⁺. Subsequently, the SET process of [IV-OAc]⁺ with disulfide C leads to the production of [I-OAc]⁺ (path a). Path b also cannot be expelled, that alkyl raddical adds to [II-OAc]⁺, following by the C-S reductive elimination of [III-OAc]⁺ to liberate the product **1** and [IV-OAc]⁺ which then reacts with disulfide **C** by SET process to regenerate [I-OAc]⁺. Path c involves a metal-free SET process. A hydrogen (a) In situ HRMS experiments



Scheme 4. Possible reaction mechanism.

atom in **A1** is trapped by *tert*-butyl oxygen radical, delivering alkyl radical and *tert*-butyl alcohol. The reaction of alkyl radical with **C** give the alkyl thioether **1**. In metal-free pathway, a large quantity of oxidative homocoupling product of **A1** can be detected by GC/MS. Thus, nickel-complex might in some extent restrain the homocoupling of alky radicals.

Conclusions

In conclusion, a novel nickel-complex-catalyzed oxidative dehydrogenative coupling reaction of alkane with thiol has been explored. Only one equivalent of DTBP was utilized into the reaction to readily access to a number of alkyl thioethers in moderate to high reactivities. The large steric hindrance of BC and the in situ production of disulfide from oxidation of thiol efficiently inhibited catalyst poisoning. A series of mechanistic experiments were carried out, suggesting plausible reaction pathways possessing both Ni-catalytic and Ni-free HAA processes. Besides, the synthesis of Provigil, Chlorbenside and Pyridaben has been easily realized, further proving the practicability of this methodology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Declaration of Competing Interest

We have issued Chinese patent (CN201910785627.5) relevant to this work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2021.152950.

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