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Xanthate-Mediated Synthesis of (*E*)-Alkenes by Semi-Hydrogenation of Alkynes Using Water as the Hydrogen Donor

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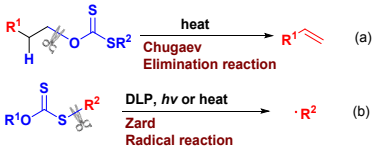
Semi-hydrogenation of alkynes is one of the most widely used methods for obtaining alkene in laboratory preparation and in industry. Transition metal catalysts have been extensively studied for this transformation, but the tolerance of functional groups, such as pyridine, -OH, -NH_2, -Bpin, and halides, and the toxicity of the trace amount of transition metal catalysts are still highly challenging. In this study, we report a general and robust strategy to achieve the semi-hydrogenation of alkynes using inexpensive and commercially available xanthate as the mediator. Mechanism studies support a non-radical process and H_2O act as the hydrogen donor.

The development of efficient, sustainable, and environmentally friendly procedures for the synthesis of organic molecules is an important task in modern organic chemistry. Xanthates are attractive starting materials in transition-metal-catalysed or transition-metal-free transformations due to their high reactivity and availability and are readily prepared from inexpensive alcohols and carbon disulphide on a large scale.[1-2] Xanthates are used in organic synthesis in several interesting and important ways. The Chugaev elimination reaction proceeds through the thermal decomposition of a xanthate to prepare alkenes without the rearrangement of the carbon skeleton that is frequently encountered in the dehydration of certain alcohols by other methods (Scheme 1a).[3] The Zard radical reaction provides a radical coupling strategy with DLP or Et_3B promoted cleavage of the weak C–S bonds of xanthates without tin or another heavy metal (Scheme 1b).[4] Xanthates can also be used as a sulphur source for the introduction of sulphur atoms in organic molecules and formation of sulphur-containing heterocycles, such as benzothiophene and thiazole.[5]



Scheme 1. Typical conversion of xanthates

The selective semi-hydrogenation of alkynes to the corresponding alkenes is an extensively used tool in organic synthesis for the preparation of alkenes. Alkenes are versatile building blocks for fine chemical synthesis, and the synthesis of pharmaceuticals and natural products. It is important to mention that alkenes are some of the most popular starting materials in the polymerization industry.[6] Thus, the semi-hydrogenation of alkynes is of significant importance. Heterogeneous[7] and homogeneous metal catalysts[8] have been explored for these chemoselective reduction reactions. In addition to the classical molecular hydrogen, a range of other hydrogen donors, such as tertiary amines[9], alcohols[10], HCOOH[11], H_3N-BH_3[12], DMF[13], $HSiEt_3$[14], and the Hantzsch ester 1,4-dihydropyridine[15] have also been shown to be efficient hydrogen donors. Unfortunately, these compounds often must be used in conjunction with transition metal catalysts. By contrast, transition metal-free semi-hydrogenation[16] of unactivated alkynes into trans-alkenes is still rare. Recently, Stephan and co-workers demonstrated an elegant alkyne semi-hydrogenation using hydrogen (H_2) as the reductant in the presence of a frustrated Lewis pair [p-(Mes_2P)C_6F_4($B(C_6F_5)_2$] as a catalyst.[17] In another recent work, Garcia and co-workers found that graphene could catalyse the hydrogenation of C–C multiple bonds.[18]

Inspired by our previous work on the construction of sulphur-containing heterocycles using $EtOCS_2K$ as a thiol surrogate [19] and the construction of various conjugated structures,[20] herein, we developed a transition-metal-free semi-hydrogenation system in which vinyl carbonodithioate is produced in situ from $EtOCS_2K$ and acts as an active intermediate. Comparing to the high price and sensitivity of the frustrated Lewis pair,[21] xanthates-mediated alkyne hydrogenation provides a general, robust and broad functional-group tolerated approach for obtaining *trans*-alkenes. To the best of our knowledge, the only report of an attempted sulphur reagent use for the hydrogenation of 1,2-diphenyl alkynes

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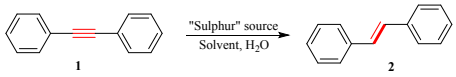
was by Liu and co-workers, who reported an approach for *trans*-selective alkene with $Na_2S{\cdot}9H_2O$.[22]

Initially, 1,2-diphenylethynes **1** were selected as model substrates for the optimization of the reaction conditions (Table 1). Without a sulphur source, no product was obtained and starting material recovered. Only a trace of the semi-hydrogenation product was obtained when thiourea was used as sulphur source (Table 1, entry 2). The continue screening of sulphur source indicated that the $EtOCS_2K$ was the superior sulphur source with a product yield of 98% (Table 1, entries 2-7). The screening of various solvents revealed that the solvent played a very important role in this semi-hydrogenation process. Compared to other solvents, DMF proves to be the best reaction solvent (Table 1, entries 8-11). The reaction was most efficient when it was conducted at 130 °C, and lower temperatures resulted in lower yields (Table 1, entry 12). By decreasing the amount of $EtOCS_2K$ (1.5 equiv), the yield was reduced to 90%, respectively (Table 1, entry 13). (See SI for more details)

Table 1. Optimization of reaction conditions[a,b]

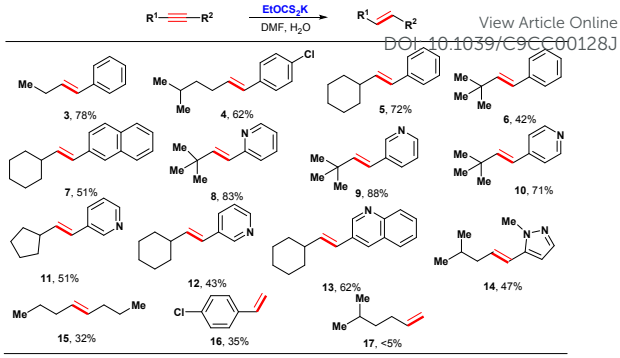


Entry	"Sulphur" source	Solvent	Yield[b] (%)
1	-	DMF	n.r.
2	Thiourea	DMF	trace
3	Thioacetamide	DMF	16
4	Dimethylammonium dimethyldithiocarbamate	DMF	7
5	Sodium dimethyldithiocarbamate	DMF	32
6	$EtOCS_2K$	DMF	98
7	Potassium isopropyl xanthate	DMF	95
8	$EtOCS_2K$	DMSO	92
9	$EtOCS_2K$	DMAc	90
10	$EtOCS_2K$	xylene	n.r.
11	$EtOCS_2K$	H_2O	< 5
12[c]	$EtOCS_2K$	DMF	31
13[d]	$EtOCS_2K$	DMF	90

[a] Reaction conditions: alkyne **1** (1.0 mmol), "sulphur" source (2.0 mmol) and H_2O (2 mmol) in solvent (2.0 mL) at 130 °C for 12 h; [b] Isolated Yield; [c] Reaction was carried out at 120 °C; [d] 1.5 equiv $EtOCS_2K$ was used.

With the optimized reaction conditions in hand, we turned our attention to the semi-hydrogenation reaction by varying alkyne components (Scheme 2). Various substituted alkyl alkynes were found to be compatible under the optimized conditions. First, aryl alkyl alkynes underwent efficient semi-hydrogenation to afford the corresponding (*E*)-alkenes **3–7** in moderate to good yields. The reactions of pyridyl-substituted alkyl alkynes also proceeded smoothly, furnishing the E-alkenes **8–12** in moderate yields. The semi-hydrogenation was also applicable to quinolyl alkynes, as exemplified by the synthesis of (*E*)-3-(2-cyclohexylvinyl)quinoline **13** in 62% yield. Heterocyclic substituted internal alkynes, such as pyrazole, can complete the reaction to obtain the desired product in acceptable yields. The terminal alkyne *p*-chlorophenylacetylene also successfully completed the reaction, indicating that the semi-hydrogenation reaction is characterized by good functional group tolerance. Unfortunately, the reaction of terminal alkyl alkynes, such as 5-methylhex-1-yne, produced a mixture of products.

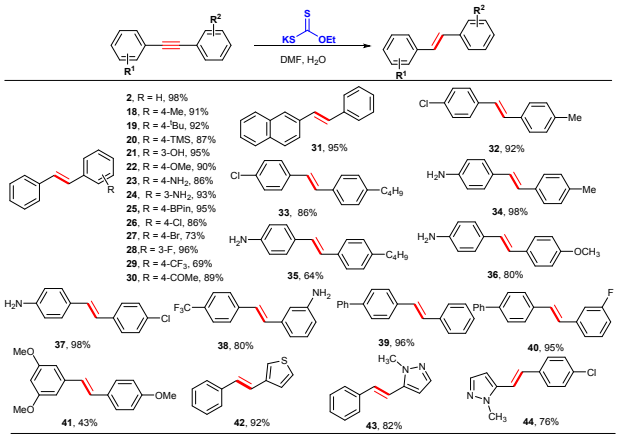
Scheme 2. $EtOCS_2K$-promoted semi-hydrogenation of alkyl alkyne[a]



[a] Standard conditions: alkyne (1.0 mmol), $EtOCS_2K$ (2.0 mmol), H_2O (2.0 mmol), DMF (2.0 mL), 150 °C, 24 h. [b] Isolated yields.

Next, various diarylacetylenes were successfully semi-hydrogenated under standard conditions, demonstrating the generality of the approach and providing exceptional trans-stereoselectivity. Both electron-donating and -withdrawing substituents on the aromatic rings were compatible under the standard conditions. Electron-donating groups, such as -Me, -^{t}Bu, -TMS, -OH, -OMe, and -NH_2, were also successfully hydrogenated (Scheme 3, **18–25**, 86%–98% yield). In particular, the alkaline-sensitive TMS group was easily hydrolysed and yielded (*E*)-trimethyl(4-styrylphenyl)silane **20** in 87% yield. The borate group remained intact and is very useful in transition-metal-catalysed Suzuki coupling reactions (Scheme 3, **25**). An important feature of this reaction is the tolerance for halides, including F, Cl, Br, and CF_3, with no dehalogenated material observed. Interestingly, no reduction of the keto group occurred during the hydrogenation of 1-(4-(phenylethynyl)phenyl)ethan-1-one, and the keto group remained intact (Scheme 3, **30**). It is important to note that the carbonyl group was easily reduced to alcohol in the presence of Pd/C-H_2 or $NaBH_4$. Moreover, the semi-hydrogenation of 1,3-dimethoxy-5-((4-methoxyphenyl)ethynyl)benzene resulted in the formation of the precursor of *trans*-resveratrol **41** that was isolated in 43% yield. The synthesis of *trans*-resveratrol analogues is important in modern organic chemistry because of their wide range of biological activities and pharmaceutical applications.[23] Substrates bearing heterocycles, such as 5-pyrazolyl or 3-thienyl groups, also produced the corresponding semi-hydrogenation products **42–44** in good yields.

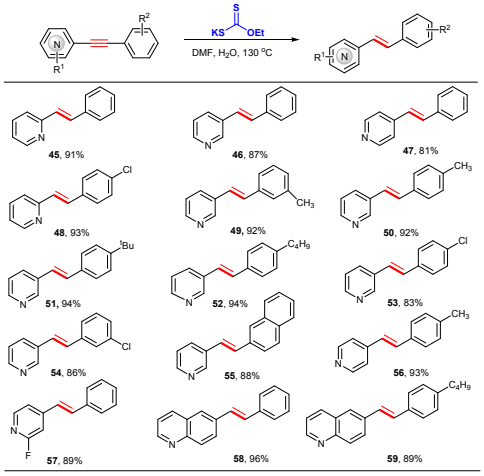
Scheme 3. $EtOCS_2K$ promoted semi-hydrogenation of diaryl alkynes[a]



[a] Standard conditions: alkyne (1.0 mmol), $EtOCS_2K$ (2.0 mmol), H_2O (2.0 mmol), DMF (2.0 mL), 130 °C, 12 h. [b] Isolated yields.

To continue our investigation of the reaction scope, we explored various pyridine-based substrates for this process under the optimized reaction conditions (Scheme 4). Overall, it was found that most of the substrates could be converted to the corresponding (*E*)-alkenes in good to excellent yields. Furthermore, when the pyridine ring was substituted at the ortho-, meta-, and para-positions, the yields were not affected (Scheme 4, **45**–**47**). These results show the semi-hydrogenation is not affected by electron-withdrawing or -donating substituents on the benzene ring or the pyridine ring, and the desired product can be successfully obtained. Next, when 3-(naphthalen-2-ylethynyl)pyridine was employed as the substrate, the expected semi-hydrogenation product **55** was obtained in 88% yield. Finally, 6-(phenylethynyl)quinoline showed excellent selectivity towards the corresponding (*E*)-alkenes in our semi-hydrogenation protocol.

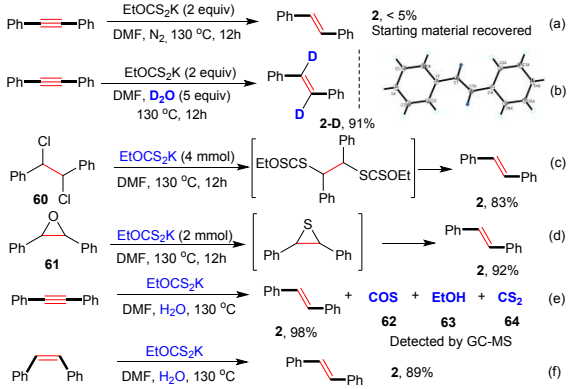
Scheme 4. $EtOCS_2K$-promoted semi-hydrogenation of alkynylpyridine[a]



[a] Standard conditions: alkyne (1.0 mmol), $EtOCS_2K$ (2.0 mmol), H_2O (2.0 mmol), DMF (2.0 mL), 130 °C, 12 h. [b] Isolated yields.

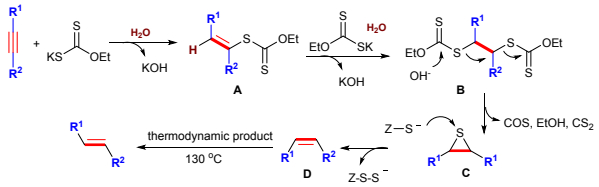
To gain mechanistic insights, deuteration experiments were conducted to verify the hydrogen donors to the alkene. When anhydrous DMF was used as the solvent under N_2, the reaction did not proceed (Scheme **5a**). However, when DMF and D_2O were used, the deuterium product **2-D** was obtained in 91% yield (Scheme **5b**). These results indicate that water acts as a proton donor in this transformation. When 1,2-dichloro-1,2-diphenylethane **60** used as the substrate reacted with $EtOCS_2K$ under the standard semi-hydrogenation reaction conditions, the reaction may be a nucleophilic substitution reaction that obtains biscarbonodithioate intermediate[24], after which the 1,2-diphenylethenes are obtained (Scheme **5c**). Unfortunately, we were unable to isolate the biscarbonodithioate intermediate. When we use 2,3-diphenyloxirane **61** and $EtOCS_2K$ under the standard semi-hydrogenation reaction conditions, the reaction may pass through 2,3-diphenylthiirane intermediate[25], and finally, desulphurization yields the 1,2-diphenylethenes (Scheme **5d**).[26] In this semi-hydrogenation reaction, we found that 1,2-diphenylethyne and potassium ethyl xanthate gave (*E*)-1,2-diphenylethene in good yield under the standard conditions. Importantly, we also detected the COS **62**, EtOH **63** and CS_2 **64** by GC-MS (Scheme **5e**). In the standard condition, the cis-stilbenes isomerised into *trans*-stilbenes in good yield (Scheme **5f**). This discovery may help us understand the reaction mechanism.

Scheme 5. Control experiments.



The postulated reaction mechanism based on the literature and our experimental results is depicted in Scheme 6. In this reaction, the semi-hydrogenation reaction is initiated by the double nucleophilic addition of $EtOCS_2K$ to alkynes, yielding 1,2-diphenylethane-1,2-diyl) O,O'-diethyl bis(carbonodithioate) **B**, and is followed by the formation of episulphide **C** with the aid of OH^-.[27] In this process, the ZS^- represents any sulphur anion in the medium (xanthate and sulphide, etc.). Then, episulphide **C** under a desulphurization reaction generates *cis*-alkenes **D** [26] and the *cis*-alkenes isomerised into *trans*-stilbenes under thermodynamic conditions (Scheme **5f**).

Scheme 6. Proposed reaction mechanism.



In summary, we established a novel and practical method for highly selective semi-hydrogenation of alkynes to the corresponding (*E*)-alkenes using $EtOCS_2K$ as the accelerant and H_2O as the hydrogen donor in a transition-metal-free system. Mechanism verification revealed that H_2O acts as the hydrogen donor, and the reduction process is facilitated by intermediate vinyl xanthates. This method is safe, simple, and chemoselective. In view of the method's generality and excellent functional group compatibility, this semi-hydrogenation transformation will find more applications in organic synthesis.

Conflicts of interest

There are no conflicts to declare.

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An environmentally sustainable alternative for the chemoselective reduction of the Csp-Csp triple bond through double hydrosulfuration and desulphurization procedure by Xanthate was reported. This old reagent xanthate, first isolated in 1822, promoted the trans-selective semihydrogenation of the alkynes using H_2O as the hydrogen donors under transition-metal-free condition.