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A novel transition metal-free conjugate reduction of α,β-unsaturated ketones with tosylhydrazine as a hydrogen source

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ABSTRACT

A novel and efficient method has been developed for the chemoselective conjugate reduction of α,β-unsaturated ketones with tosylhydrazine as a hydrogen source to the corresponding saturated ketones in moderate to good yields. The present protocol does not require the use of transition metal, and is efficient being applicable to a wide range of substrates (25 examples).

The conjugate reduction of α,β-unsaturated ketones is an important functional group transformation for the synthesis of natural products, pharmaceuticals, and functional materials.[1–4] A great amount of progress has been made in this area, the most promising method for performing this transformation is transition-metal catalyzed transfer hydrogenations using molecular hydrogen,[5] silicon hydride,[6] or formate[7] as a hydrogen source. However, due to their expensive nature, inadequate accessibility, and toxicity of these often used metals, there is an urgent need to develop less expensive and easily available catalyst systems for sustainable hydrogenation protocols. Recent methods based on organo-catalyzed transfer hydrogenations can overcome these limitations. In particular, readily available Hantzsch esters are competent hydrogen sources for iminium ion-, Brønsted acid- and hydrogen bonding-catalyzed reactions.[8] These methodologies give often unsurpassed degrees of stereocontrol in the reduction of α,β-unsaturated ketones, cyclic/acyclic imines and activated olefins.[9] Subsequently, several other hydrogen transfer reagents containing amino functional groups also have been fully investigated such as imidazoline,[10] thiazoline,[11] lithium amide,[12] and tertiary amines.[13] Recently, use of alcohol as a hydrogen source has been widely studied,[14] especially, the reduction of the ketones to alcohols has been achieved with relative ease.[15] Notably, the conjugate reduction of α,β-unsaturated ketones using alcohol as a hydrogen source, has also been investigated. For example, Zhang and co-workers developed an elegant method for conjugate reduction of α,β-unsaturated ketones using ^{n}BuOH as a hydrogen source and solvent, good to excellent yields were obtained for various substrates even with reducible groups.[16] On the other hand, hydrous hydrazine is considered as a promising candidate for a hydrogen source since it is much easier in handling, safer, and more stable than hydrogen. Subsequently, various methods for the catalytic hydrogenation of unsaturated hydrocarbons with hydrous hydrazine have been sought both in industrial and academic laboratories.[17] However, a transition metal was needed in these reactions, because hydrous hydrazine as a hydrogen source firstly was decomposed to hydride intermediates that are common to those of the hydrogenation of unsaturated bonds with hydrogen. Furthermore, the scope of substrates is still limited, using hydrous hydrazine for C=C double bonds is not compatible with the presence of carbonyl groups, such as chalcone, which was reduced to 1,3-diphenylpropanone with only 30% chemoselectivity along with the formation of pyrazoles as by-products.[17c] Therefore, developing a process for transition metal-free and highly chemoselective conjugate reduction of α,β-unsaturated ketones, is still challenging but greatly should be omitted highly desirable.

In recent years, tosylhydrazone has attracted extensive attention because of their various transformations of carbonyl compounds. For example, elegant methods have recently been explored furnishing synthetically useful C–C[18], C–O[19], C–N[20] and C–S[21] bonds via reductive coupling of tosylhydrazone under metal-catalyzed and metal-free conditions. Therefore, we assumed

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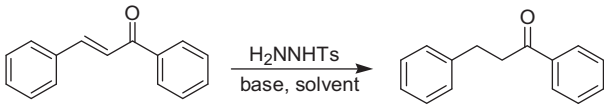
that the hydroxy group of the resulting intermediate *o*-hydroxychalcone tosylhydrazone **2a** as a nucleophile could intramolecularly attack the diazo intermediate to afford correspondingly 2*H*-chromene **3a** (Scheme 1). In an initial demonstration of this hypothesis, we chose to evaluate substrate **1a** for the preparation of 2-phenyl 2*H*-chromenes **3a** according to the conditions described by Valdes[18] (K_2CO_3/dioxane, 110 °C for 24 h). However, the corresponding ring closure product 2*H*-chromene **3a** was not detected. Unexpectedly, the conjugate reduction product *o*-hydroxyl dihydrochalcone **4a** was obtained in 78% yield. With the encouraging initial result, herein, we will describe a novel approach for transition metal-free conjugate reduction of α,β-unsaturated ketones with tosylhydrazine as a hydrogen source.

To explore the general reactivity of conjugate reduction of α,β-unsaturated ketones with tosylhydrazine as a hydrogen source, we selected chalcone **1b** as the model substrate and the results are listed in Table 1. As shown, initial studies were carried out in the above reaction condition (K_2CO_3/Dioxane, 110 °C for 24 h), gratifyingly, the model substrate **1b** was reduced via 1,4-reduction pathway and afforded the 1,4-adduct **4b** in 73% yield without the formation of pyrazoles (Table 1, entry 1).[22] To get optimum reaction conditions, firstly, a variety of bases were examined, we found that strong bases such as NaOH and ^{t}BuOK were inefficient and afforded the desired product in poor yields (Table 1, entries 2 and 3). However, other bases such as K_3PO_4, AcONa, and Et_3N can only afford moderate yields (Table 1, entries 4–6). Next, under the same condition (Table 1, entry 1), we screened various solvents (Table 1, entries 7–10), all the reactions proceeded smoothly to afford the desired product, however, only moderate yields were obtained. Finally, the amounts of base were screened, interestingly, we found that increasing the amounts of base to 2.0 equiv is insignificant to activity and a similar yield was obtained (Table 1, entry 11 vs 1), while the yield of dihydrochalcone was decreased to 66% when the amounts of base were reduced to 1.0 equiv (Table 1, entry 12). The influence of the reaction temperature and time were also investigated and it was confirmed that reactions run at 110 °C gave the best results. Based on the result of the above systematically screening experiments, the optimized conditions for the conjugate reduction of α,β-unsaturated ketones with tosylhydrazine were obtained as follows: 1.1 equiv of tosylhydrazine and 1.5 equiv of K_2CO_3 in dioxane at 110 °C for 24 h under N_2.

Under the above optimum reaction conditions, the substrate scope and limitation of the conjugate reduction were then explored. As summarized in Table 2, a variety of chalcones with diverse substitution patterns of electron donating groups in both the rings smoothly underwent the transformation and gave their corresponding products ranging from 48% to 81% (Table 2, **1b**–**u**). For instance, chalcones with various groups in both the rings such as methyl and methoxyl were successfully reduced to their corresponding products in good yields (Table 2, **1b**–**h**). It was interesting that the chlorine on the aromatic rings was tolerated under this

Table 1
Optimization of conjugate reduction of chalcone **1b** with tosylhydrazine[a]



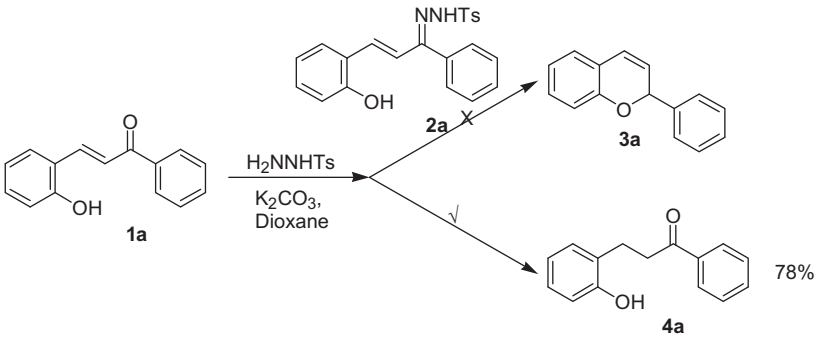
1b **4b**

Entry	Solvent (equiv)	Base	Yield[b] (%)
1	K_2CO_3 (1.5)	Dioxane	73
2	NaOH (1.5)	Dioxane	41
3	^{t}BuOK (1.5)	Dioxane	46
4	K_3PO_4 (1.5)	Dioxane	56
5	AcONa (1.5)	Dioxane	58
6	Et_3N (1.5)	Dioxane	52
7	K_2CO_3 (1.5)	Pyridine	50
8	K_2CO_3 (1.5)	Toluene	48
9	K_2CO_3 (1.5)	DMSO	54
10	K_2CO_3 (1.5)	Acetonitrile	49
11	K_2CO_3 (2.0)	Dioxane	72
12	K_2CO_3 (1.0)	Dioxane	66

[a] Reaction conditions: chalcone **1b** (1.0 mmol), tosylhydrazine (1.1 mmol), K_2CO_3 (1.5 mmol) , dioxane (2 mL), 110 °C, 24 h, under N_2.
[b] Isolated yield based on **1b**.

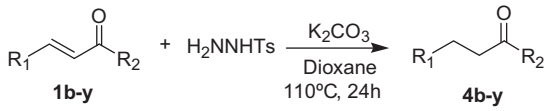
present protocol and gave the corresponding conjugate reduction products up to 81% yields which can undergo additional transformations by metal-catalyzed cross-couplings (Table 2, **1i**–**l**). Moreover, substrates with the dimethylamino group proceeded smoothly to afford the conjugate reduction products in moderate yields (Table 2, **1m**–**o**). The steric effect on the reactivity was not significant by the *ortho*-substituents on the aromatic ring, when we introduced a substituent on the *ortho* position of the aromatic ring, the yields of products are slightly lower than those which possess a *para* substituent group such as methyloxyl or bromo (Table 2, **1p**–**t**). The reaction of substrate **1u**, bearing a furyl ring proceeded smoothly to afford the desired product **4u** in 55% yield (Table 2, **1u**). Furthermore, we found substrates with nitro group which are sensitive to ordinary hydrogenation conditions, remained intact in this process and afforded the conjugate reduction product in 58% yield (Table 2, **1v**). Notably, the diketene substrate **1w** was a suitable substrate under the modified conditions, giving the double conjugate reduction product **4w** in 46% yield (Table 2, **1w**). As for substrates, bearing ketones derived from aliphatic aldehydes such as **1x** and **1y**, only moderate yields were obtained along with the minor formation of pyrazole as by-products (Table 2, **1x** and **1y**). Unexpectedly, substrates derived from aliphatic ketones were unsuitable in the present protocol, giving the corresponding pyrazoles.[22]

In summary, we have developed a novel approach for the transition metal-free conjugate reduction of α,β-unsaturated ketones to the corresponding saturated ketones with tosylhydrazine as a hydrogen source under mild condition. The method is versatile



Scheme 1. Conjugate reduction reaction of chalcone **1a** using tosylhydrazine as a hydrogen source.

Table 2
Conjugate reduction of α,β-unsaturated ketones with tosylhydrazine[a]



Substrate	R_1	R_2	Product	Yield[b] (%)	Substrate	R_1	R_2	Product	Yield[b] (%)
1b	ph	ph	**4b**	77	**1n**	4-Me_2N-C_6H_4	4-Me-C_6H_4	**4n**	60
1c	ph	4-Me-C_6H_4	**4c**	72	**1o**	4-Me_2N-C_6H_4	4-MeO-C_6H_4	**4o**	63
1d	ph	4-MeO-C_6H_4	**4d**	73	**1p**	2-MeO-C_6H_4	ph	**4p**	59
1e	4-Me-C_6H_4	ph	**4e**	67	**1q**	2-MeO-C_6H_4	4-Me-C_6H_4	**4q**	60
1f	4-Me-C_6H_4	4-Me-C_6H_4	**4f**	71	**1r**	2-MeO-C_6H_4	3-MeO-C_6H_4	**4r**	61
1g	4-Me-C_6H_4	4-MeO-C_6H_4	**4g**	73	**1s**	2-Br-C_6H_4	ph	**4s**	66
1h	4-MeO-C_6H_4	ph	**4h**	65	**1t**	2-Br-C_6H_4	4-MeO-C_6H_4	**4t**	48
1i	4-Cl-C_6H_4	ph	**4i**	66	**1u**	2-Furyl	4-MeO-C_6H_4	**4u**	55
1j	4-Cl-C_6H_4	4-Me-C_6H_4	**4j**	81	**1v**	4-NO_2-C_6H_4	ph	**4v**	58
1k	4-Cl-C_6H_4	4-MeO-C_6H_4	**4k**	70	**1w**	ph	CH=CH-C_6H_5	**4w**	46[c]
1l	4-Cl-C_6H_4	3-MeO-C_6H_4	**4l**	61	**1x**	$C_6H_5CH_2$	ph	**4x**	51
1m	4-Me_2N-C_6H_4	ph	**4m**	58	**1y**	Et	ph	**4y**	36

[a] Reaction conditions: α,β-unsaturated ketones (1.0 mmol), tosylhydrazine (1.1 mmol), K_2CO_3 (1.5 mmol) , dioxane (2 mL), 110 °C, 24 h, under N_2.
[b] Isolated yield based on **1**.
[c] Diketene (1.0 mmol), tosylhydrazine (2.2 mmol), K_2CO_3 (3.0 mmol).

for various α,β-unsaturated ketones and affords the corresponding saturated ketones in moderate to good yields. This method is cheap, easy-to-handle, and a convenient alternative to traditional catalytic hydrogenation. Further investigations to the reaction mechanism and utilization of this reduction system in organic synthesis are currently in progress.

Experimental section

General methods

All reactions were carried out under nitrogen. Chemicals were purchased from Aldrich, Acros, or Alfa Aesar, and, unless otherwise noted, were used without further purification. Flash chromatography was performed on silica gel (silica gel, 200–300 mesh). ^1H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz and Bruker 100 MHz spectrometers with $CDCl_3$ as the solvent.

Typical experimental procedure

A flask equipped with a magnetic stirring bar was charged with α,β-unsaturated ketone **1** (1.0 mmol), tosylhydrazine (1.1 mmol), K_2CO_3 (1.5 mmol), and dioxane (2 ml). The reaction mixture was stirred under a nitrogen atmosphere at 110 °C for 24 h. The reaction mixture was cooled to room temperature; the reaction mixture was extracted with diethyl ether (5 × 3 ml). The combined extracts were washed with brine and dried over $MgSO_4$, and the crude product was adsorbed onto silica gel and purified by column chromatography (silica gel, petroleum ether/ethyl acetate 20:1) giving the pure saturated carbonyl compounds **4**.

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Supplementary data

Supplementary data (Detailed experimental procedures, characterization data, and copies of ^1H and ^{13}C NMR spectra for all of the products **2a**–**y**.) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.07.063.

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