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Short Communication

Efficient and eco-compatible transition metal-free Oppenauer-type oxidation of alcohols

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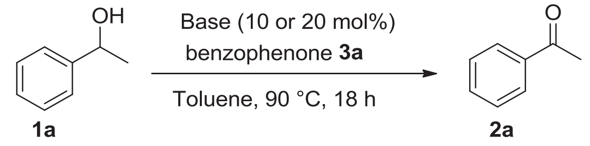
ABSTRACT

Catalytic amounts of cheap, non-toxic, easy-to-handle and non-sensitive sodium tert-butoxide are able to promote the dehydrogenative oxidation of a wide array of secondary alcohols using inexpensive benzophenone as the H-acceptor. The corresponding ketones, highly important intermediates and targets throughout life and material sciences, are very selectively obtained under mild conditions.

1. Introduction

The oxidation of alcohols to their corresponding carbonyl compounds constitutes a very important reaction in organic synthesis [1]. Classical methods involve stoichiometric amounts of chromium [2] or manganese oxides [3], and activated DMSO [4] or hypervalent iodine derivatives [5]. Most of these oxidants are difficult-to-handle, hazardous and the high amounts of wastes produced are of environmental concern [2–5]. The search for catalytic, cheap and eco-compatible methods is thus crucial for laboratory- and large-scale processes. Along these lines, transition metal-based systems are able to catalytically promote oxidations of alcohols in the presence of oxygen or peroxides [6–9]. However, these catalysts are generally sophisticated and often expensive. Additionally, oxidations consisting in the hydrogen transfer (H-transfer) from the alcohol to an H-acceptor (e.g. ketone) also constitute attractive methodologies [10–12]. Discovered by Oppenauer in the 1930s, such oxidations initially involved stoichiometric amounts of aluminum or alkali alkoxides [10–14]. Afterwards, lanthanides [11] and transition metals (ruthenium [15–17], iridium [18–20], iron [21–24]) were found to achieve Oppenauer-type oxidations catalytically. Besides, we and others recently reported that catalytic amounts of alkali hydroxides and alkoxides were able



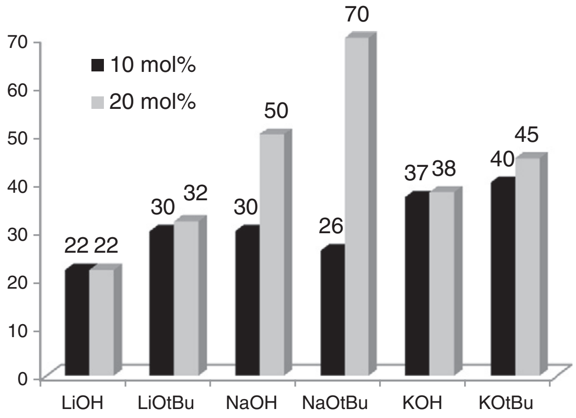


Fig. 1. Oxidation of **1a** into **2a** catalyzed by various alkali bases: yields of **2a** (%)[a,b] ([a]base (0.1 or 0.2 mmol), **1** (1 mmol), **3a** (2 mmol), toluene (2 mL); [b]conversions of **1a** determined by ^1H NMR with 1,3-dimethoxybenzene as standard (selectivities >98%)).

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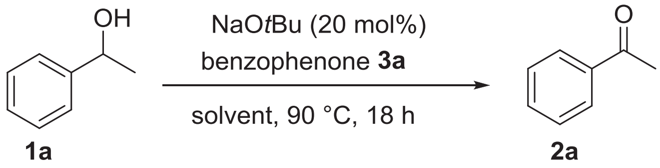
Table 1
Oxidation of **1a** into **2a** via H-transfer in the presence of NaO*t*Bu in various solvents.[a,b]



	Solvent	Conversions of **1a** (%)[b]
1	DMSO[c]	37
2	Acetonitrile[c]	40
3	Dioxane	43
4	Dichloromethane	47
5	THF	50
6	Toluene	70

[a] **1a** (1 mmol), NaO*t*Bu (0.2 mmol), **3a** (2 mmol), solvent (2 mL).
[b] Determined by ^{1}H NMR with 1,3-dimethoxybenzene as standard (selectivities >99%).
[c] Side aldol condensation and crotonization. Selectivities: in DMSO: 50%; and in acetonitrile: 70%.

to promote the reverse Meerwein–Ponndorf–Verley reduction of ketones using alcohols as H-donors [25–29]. Hence this paper reports the route to cheap and non-toxic alkali-based catalytic systems for the complementary Oppenauer-type oxidation of alcohols [10–12,30,31]. These results have been patented [26].

2. Experimental

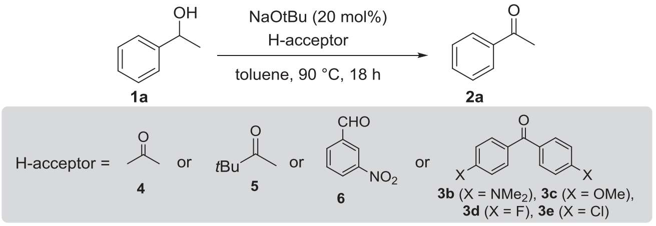
2.1. Materials and instruments

Reactants were purchased from commercial sources and used without purification. NaO*t*Bu (99.9%, Aldrich and 97%, Alfa Aesar), KO*t*Bu (99.99%, Aldrich), LiO*t*Bu (99.9%, Alfa Aesar), NaOH (99.99%, Aldrich), KOH (99.99%, Aldrich), and LiOH (99.9%, Alfa Aesar), were carefully ground to a fine powder before use. Column chromatography was performed with SDS 60 Å C.C. silica gel and thin layer chromatography using Merck silica gel 60 F_{254} plates. NMR spectra were recorded on a Bruker 400 spectrometer and GC/MS on an Agilent 6890N instrument.

2.2. General procedures for the oxidation of alcohols with NaOtBu

A Radley tube (Carousel RR98030) with a magnetic stirring bar was charged with NaO*t*Bu (Aldrich (99.9%) and Alfa Aesar (97%), 0.2 mmol), benzophenone (2 mmol), alcohol (1 mmol) and toluene (2 mL). The tube was closed, stirred and heated. After cooling, dichloromethane

Table 2
Oxidation of **1a** into **2a** via H-transfer in the presence of different H-acceptors.[a]



	H-acceptor	Conversions of **1a** (%)[b]
1	**4**	2
2	**4**[c]	10
3	**5**	35
4	**6**	20[d]
5	**3b**	26
6	**3c**	55
7	**3d**	70
8	**3e**	85

[a] **1a** (1 mmol), NaO*t*Bu (0.2 mmol), H-acceptor (2 mmol), toluene (2 mL).
[b] Determined by ^{1}H NMR with 1,3-dimethoxybenzene as standard (selectivities >99%).
[c] **4** used as the solvent.
[d] Aldol condensation between **2a** and **6** (selectivity: 60%).