

Article

# Na<sub>2</sub>S-Mediated One-Pot Selective Deoxygenation of $\alpha$ -Hydroxyl Carbonyl Compounds including Natural Products

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**Abstract:** A practical method for the deoxygenation of  $\alpha$ -hydroxyl carbonyl compounds under mild reaction conditions is reported here. The use of cheap and easy-to-handle Na<sub>2</sub>S·9H<sub>2</sub>O as the reductant in the presence of PPh<sub>3</sub> and *N*-chlorosuccinimide (NCS) enables the selective dehydroxylation of  $\alpha$ -hydroxyl carbonyl compounds, including ketones, esters, amides, imides and nitrile groups. The synthetic utility is demonstrated by the late-stage deoxygenation of bioactive molecule and complex natural products.

**Keywords:** deoxygenation; chlorination; dechlorination; one-pot



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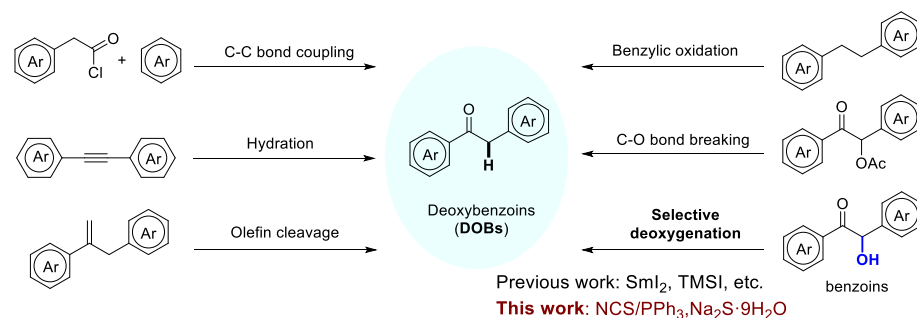
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## 1. Introduction

Deoxybenzoin (DOB) motifs are commonly found in many natural products, pharmaceutically-active molecules and fire-resistant polymers [1–4]. In addition, some DOB derivatives have been sporadically reported to possess activities such as  $\beta$  estrogenic agonist, antiallergic, anti-inflammatory and antimicrobial activities [5–7]. DOBs are industrially prepared from arylacetic acid and arenes by AlCl<sub>3</sub>-catalyzed C–C bond coupling. The process requires the functionalization of phenylacetic acid to phenylacetyl chloride by stoichiometric PCl<sub>3</sub> or SOCl<sub>2</sub> prior to the C–C bond coupling [8–12]. Other elegant strategies, including hydration [13], olefin cleavage [14], benzylic oxidation [15] and C–O bond breaking protocols [16–18], have also been developed to access DOBs in recent years (Scheme 1). However, these methods generally required the prefunctionalization of starting molecules or, alternatively, the use of expensive substrates [13–16]. Thus, it is highly desirable to develop practical processes for DOB production using cheap and easy-to-handle feedstocks.



**Scheme 1.** Reported methods for the synthesis of DOBs.

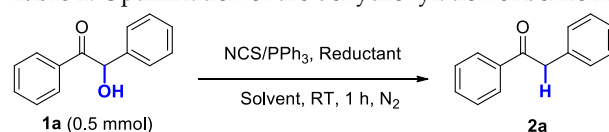
On the other hand, benzoin is classically prepared by the cyanide-mediated benzoin condensation of aromatic aldehydes, and, more generally, acyloins have long been

efficiently synthesized from esters by the acyloin condensation by using dissolving metals [19–21]. Most notably, a wide range of benzoin is commercially available and inexpensive. Therefore, the selective dehydroxylation of benzoin is undoubtedly one of the most powerful and attractive methodologies to access these valuable DOBs products. However, there are currently few methods for directly transforming acyloins to ketones via a dehydroxylation strategy. Moreover, each of the reported methods has limitations, such as the need for metal catalysis, moisture-sensitive reagents, high temperatures, bases, additives or expensive reactants, along with low chemoselectivity or unsatisfactory yields [22–30]. In fact, the selective dehydroxylation of such  $\alpha$ -hydroxyl carbonyl compounds is nontrivial, as the hydroxyl group is a poor leaving group and the adjacent carbonyl moiety is also susceptible to these reduction conditions. In this context, it is of high interest for developing efficient, mild and economical methodologies for this useful transformation. In view of this, we wish to report a practical and selective one-pot method for the dehydroxylation of benzoin to corresponding DOBs in excellent yields through the in situ chlorination of alcohols and reductive dechlorination using cheap and easy-to-handle  $\text{PPh}_3/\text{NCS}$  and  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  as a chlorinated reagent and reductant, respectively.

## 2. Results

Our investigation began with the evaluation of reaction parameters using benzoin (**1a**) as the model substrate (Table 1). Given the cheap and easy-to-handle nature of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ , it was chosen as the reductant for our model reaction. After systematically screening the reaction parameters, we found that **1a** could be quantitatively converted to ketone **2a** in the presence of  $\text{NCS}/\text{PPh}_3$  at room temperature in one hour when  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  and DMF were used as the reductant and solvent, respectively (Entry 2). No other side products were formed under the optimized conditions. Three points should be highlighted. (1) The screening of solvents showed that the use of *N,N*-dimethylformamide (DMF) is superior, as no improvement of yield was observed when the solvent was switched from DMF to  $\text{CH}_2\text{Cl}_2$ , toluene, THF or  $\text{CH}_3\text{CN}$  (Table 1, Entries 1–5). This might be because of the better solubility of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  in DMF than in other solvents. (2) When other sulfur-containing reducing agents, such as  $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ ,  $\text{K}_2\text{S}$ ,  $\text{NaSH}$ ,  $\text{NaSH}\cdot \text{H}_2\text{O}$  or  $\text{S}_8$ , were employed, the desired product **2a** was isolated in relatively lower yields (Entries 6–10). (3) To eliminate the influence of the alkalinity of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  on dehalogenation [30], both organic and inorganic bases, including imidazole, pyridine and  $\text{NaOH}$ , were all investigated, and they all give rise to chloride intermediate instead of DOB **2a** (Entries 11–13).

**Table 1.** Optimization of the dehydroxylation of benzoin (**1a**)<sup>(a)</sup>.



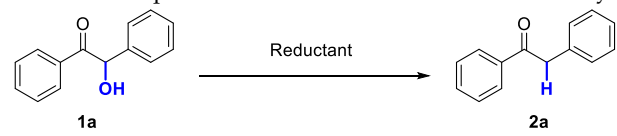
Entry	Reductant	Solvent	Yield [%] <sup>(b)</sup>
1	$\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$	$\text{CH}_2\text{Cl}_2$	32
2	$\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$	DMF	93
3	$\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$	toluene	64
4	$\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$	THF	72
5	$\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$	$\text{CH}_3\text{CN}$	80
6	$\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$	DMF	78
7	$\text{K}_2\text{S}$	DMF	45
8	$\text{NaSH}$	DMF	28
9	$\text{NaSH}\cdot \text{H}_2\text{O}$	DMF	88
10	$\text{S}_8$	DMF	trace
11 <sup>(c)</sup>	Imidazole	DMF	-
12 <sup>(c)</sup>	Pyridine	DMF	-
13 <sup>(c)</sup>	$\text{NaOH}$	DMF	-

<sup>(a)</sup> Reaction conditions: 0.5 mmol of benzoin (**1a**), 0.5 mmol of *N*-chlorosuccinimide (NCS), 0.5 mmol of triphenylphosphine ( $\text{PPh}_3$ ), 0.5 mmol of reductant and 2 mL of mentioned solvents at room temperature for one hour.

<sup>(b)</sup> Isolated yields. <sup>(c)</sup> Only chlorinated intermediate was determined by GC–MS.

The preliminary results show that the  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  as reductant is a good supplement to many of the conventional reductants, such as Zn [22], Sn [23], P [24],  $\text{P}(\text{OEt})_3$  [25] and TMSI [26], for the dehydroxylation of benzoin (Table 2) in terms of the economy and safety of the reagent, as well as the gentleness and efficiency of the reaction.

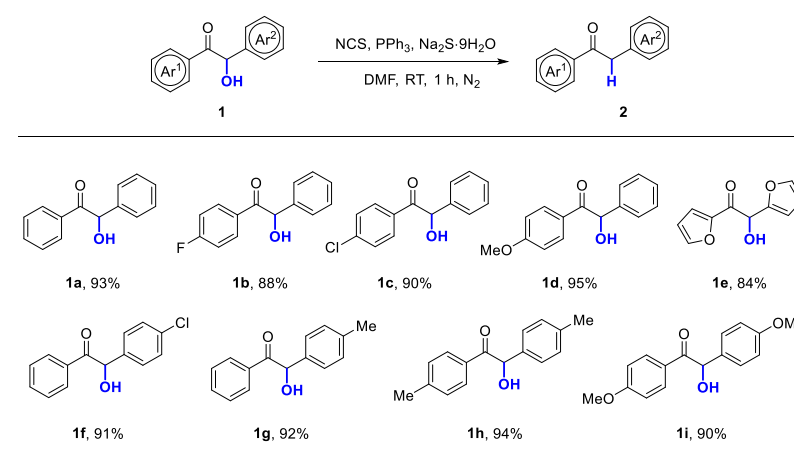
**Table 2.** Comparison of different reductants for the dehydroxylation of benzoin.



Reductant	Equivalent	Temperature	Time [Hour]	Yield [%]
$\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$	1.0	RT	1	93
Zn	1.0	120 °C	8	82
Sn	1.8	100 °C	24	88
P	0.4	80 °C	1	80
$\text{P}(\text{OEt})_3$	1.2	180 °C	10	42
TMSI	3.0	RT	4	55

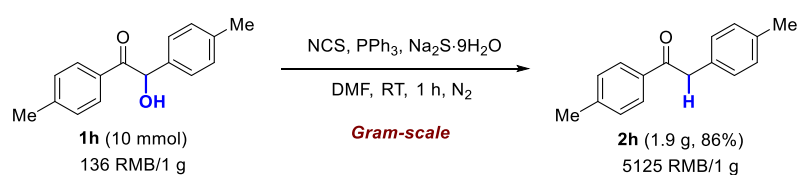
### 3. Discussion

With an optimized set of reaction conditions established, the scope of dehydroxylation was investigated (Scheme 2). The substituents of fluoro, chloro and methoxy at the para position of the benzoyl ring could be well tolerated and they reacted smoothly under the standard conditions, providing the corresponding DOB products with 88–95% yields (1b–1d). Similarly, the introduction of either electron-withdrawing or electron-donating substituents on the phenyl ring did not alter the reaction efficiency as demonstrated by the chloro and methyl substituents (1f–1g). To our delight, one representative heteroaromatic furan-derived 1e was well tolerated enough to afford the corresponding product 2e a 84% yield. Moreover, the dehydroxylation of 1h and 1i bearing two substituents on the benzoyl and phenyl rings also worked efficiently.



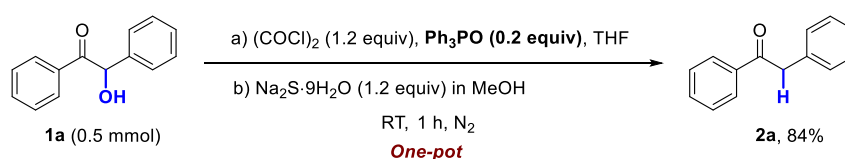
**Scheme 2.** Substrate scope of benzoin. Reaction conditions: 0.5 mmol of 1, 0.5 mmol of NCS, 0.5 mmol of triphenylphosphine ( $\text{PPh}_3$ ), 0.5 mmol of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ , and 2 mL of DMF at room temperature for one hour. The yield refers to isolated yields.

Moreover, our dehydroxylation strategy could be scaled up the Gram-scale smoothly, providing a new and practical way for the synthesis of high value-added ketone 2h from the cheap substrate 1h at a 86% yield under mild conditions (Scheme 3). The price of ketone 2h is 38 times higher than that of the start material [31].



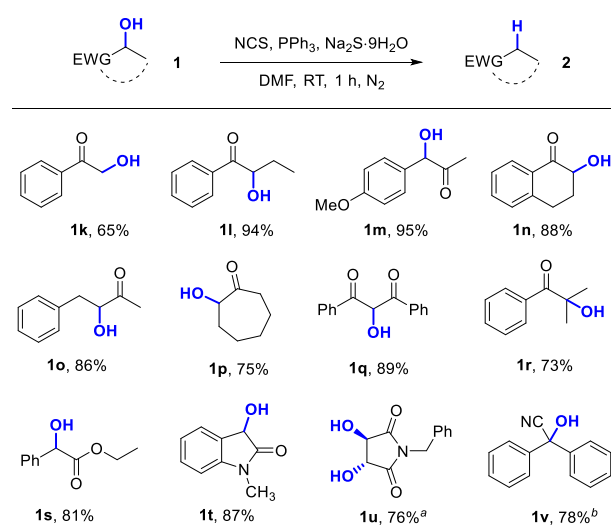
**Scheme 3.** Gram-scale reaction.

To avoid the problem of the use of stoichiometric Ph<sub>3</sub>P possibly causing the tedious separation of the phosphine-derived byproduct from the desired products, a modified one-pot procedure which includes the triphenylphosphine oxide-catalyzed chlorination reaction of the alcohol **1a** to afford chloride [32] and then dechlorination using Na<sub>2</sub>S·9H<sub>2</sub>O as reductant in MeOH has been established. As shown in Scheme 4, this modified and atom-efficient procedure provides a convenient purification, delivering the product at a good yield.



**Scheme 4.** Catalytic triphenylphosphine oxide (Ph<sub>3</sub>PO) mediated reaction.

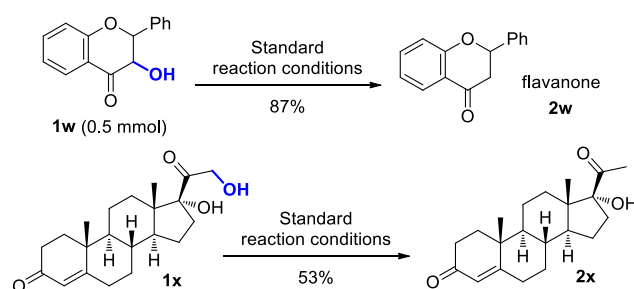
To further explore the scope of our system, other types of  $\alpha$ -hydroxyl carbonyl compounds have also been evaluated (Scheme 5). Firstly, the primary alcohol (**1k**) in positions  $\alpha$  of a ketone group under our conditions reacted well, yielding the corresponding acetophenone **2k** in a moderate yield. Unexpectedly, the secondary alcohols (**1l** and **1m**) also facilitated this transformation, more efficiently than that of primary alcohol (**1k**) under same conditions. In addition, the tertiary alcohol (**1r**) could also be converted to the corresponding dehydroxylation product at a 73% yield, which indicates that the steric effect of substituents in the  $\alpha$ -positions of a ketone group had a marginal influence on the yield. Aside from simple phenylacetyl group (**1l**), a broad range of  $\alpha$ -hydroxyl carbonyl compounds bearing the aliphatic (**1o**), cyclic (**1p**) and dicarbonyl groups (**1q**) also reacted smoothly.



**Scheme 5.** Substrate scope of versatile  $\alpha$ -hydroxy carbonyl compounds. Reaction conditions: 0.5 mmol of  $\alpha$ -hydroxy carbonyl compounds (**1**), 0.5 mmol of *N*-chlorosuccinimide (NCS), 0.5 mmol of triphenylphosphine (PPh<sub>3</sub>), 0.5 mmol of Na<sub>2</sub>S·9H<sub>2</sub>O and 2 mL of DMF at room temperature in one hour. Isolated yields. <sup>(a)</sup> 1.0 mmol of NCS, 1.0 mmol of PPh<sub>3</sub>, and 1.0 mmol of Na<sub>2</sub>S·9H<sub>2</sub>O. <sup>(b)</sup> Reaction time: 2 h.

Pleasingly, the desired dehydroxylation strategy could be extended to other carbonyl-based electron-withdrawing groups, including the ester (**1s**), amide (**1t**) and imide groups (**1u**), as shown by the conversion of these commercially available start materials to give the desired products in good yields (73–87%). In the case of substrate bearing a nitrile group (**1v**) [33,34], the reaction system afforded the dehydroxylation product efficiently, albeit with the requirement of a relatively longer reaction time. Interestingly, as shown in the conversion of a *trans*-3,4-dihydropyrrolidine-2,5-dione derivative **1u** into the corresponding **2u**, double dehydroxylation was possible by using the 2.0 equiv. of NCS/PPh<sub>3</sub> and Na<sub>2</sub>S·9H<sub>2</sub>O.

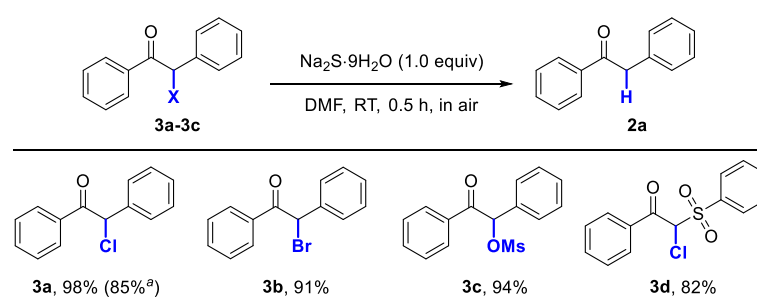
To further demonstrate the synthetic value of our methodology, the dehydroxylation protocol has been applied for the synthesis of bioactive molecules and the late-stage modification of natural products (Scheme 6). For example, flavanone is a natural plant flavonoid found to inhibit tumor cells *in vitro* [35,36]. The 3-hydroxyflavanone **1w** could be easily transformed into flavanone under our standard reaction conditions. Additionally, cortexolone **1x** could be deoxygenated in a selective manner without affecting the tertiary hydroxyl group. The latter case represents an advantage over the competing SmI<sub>2</sub>-mediated dehydroxylation reaction [28], as the enone moiety is compatible in our case. These examples further demonstrated that our strategy represents an efficient and versatile method for the dehydroxylation of  $\alpha$ -hydroxyl carbonyl compounds under mild conditions.



**Scheme 6.** Synthetic applications.

In order to confirm the role of Na<sub>2</sub>S·9H<sub>2</sub>O, substituted acetophenones bearing various leaving groups at the  $\alpha$ -position have been evaluated. As shown in Scheme 7, benzoin derivatives bearing chloro (**3a**), bromo (**3b**) or methanesulfonate (**3c**) groups at the  $\alpha$ -position all reacted smoothly under the standard conditions, providing DOB **2a** at 91–98% yields. These results demonstrate that  $\alpha$ -chloro acetophenone might be the plausible intermediate. The use of air atmosphere or adding a radical scavenger, such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), to the reaction had almost no effect on the yield. Considering that the reaction could work smoothly in air or with TEMPO, it seems unlikely that the radical process might be involved in our transformation. Furthermore, when the load of Na<sub>2</sub>S·9H<sub>2</sub>O was decreased to 0.5 equiv., the reaction could also proceed smoothly to give **2a** at an 85% yield. As a comparison, the use of BnCl as the substrate only led to the isolation of BnSBn under our standard reaction conditions, indicating the essential role of the  $\alpha$ -carbonyl group for activating the substrate for the reaction. Apparently, further studies are necessary to shed light on the reaction mechanism.

Moreover, an  $\alpha$ -chloroacetophenone-bearing phenylsulfonyl (**3d**) group proved to be a competent substrate, affording the desired dechlorination product **2j** at an 82% yield under the standard reaction conditions. These results revealed that the leaving group at the  $\alpha$ -position of the carbonyl compounds was not limited to Cl, others such as Br- and OM-substituted analogues also worked well in our hand.



**Scheme 7.** Scope of leaving groups. Reaction conditions: 0.5 mmol of **3**, 0.5 mmol of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  and 2 mL of DMF at room temperature in 0.5 h. Isolated yields. <sup>(a)</sup> 0.25 mmol of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ .

#### 4. Materials and Methods

Unless otherwise noted, the reactions were carried out in oven-dried glassware or a sealed tube under ambient atmosphere. *N,N*-Dimethylformamide (DMF) was distilled from calcium hydride. Tetrahydrofuran (THF) was dried and distilled from sodium. Reactions were monitored by analytical thin-layer chromatography (TLC) on Merck silica gel 60 F<sub>254</sub> plates (0.25 mm), visualized by ultraviolet light (254 nm) or by staining with ceric ammonium molybdate. <sup>1</sup>H NMR spectra were obtained on a Bruker AVANCE 400 MHz spectrometer at ambient temperature. Data were reported as follows: chemical shift on the  $\delta$  scale using residual proton solvent as internal standard [ $\delta$  TMS: 0.00 ppm], multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets), integration and coupling constant (*J*) in hertz (Hz). <sup>13</sup>C NMR spectra were obtained with proton decoupling on a Bruker AVANCE (100 MHz) spectrometer and were reported in ppm with residual solvent for internal standard [ $\delta$  77.0 (CHCl<sub>3</sub>)].

#### 5. Conclusions

In summary, an efficient and mild method for the selective dehydroxylation of  $\alpha$ -hydroxyl carbonyl compounds was developed using a one-pot strategy, which includes the successive chlorination and reductive dechlorination with NCS/PPh<sub>3</sub> and  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ , respectively. The easy-to-handle protocol provides facile, rapid and chemoselective access to DOBs at room temperature without the need for hazardous reagents or expensive metals. The synthetic utility of the methodology has been demonstrated by the facile synthesis of the bioactive molecule, the late-stage dehydroxylation of the complex natural product and Gram-scale transformation into a high value-added chemical.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules27154675/s1>. References [15,18,37–49] are cited in the Supplementary Materials. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the products synthesized in this work are available online.

**Author Contributions:** B.L., Z.G. and M.C. participated in the synthesis, purification and characterization of the new compound. L.Y. and Z.-K.Z. participated in the interpretation of the spectroscopy of compounds and the review of the manuscript. X.X. and Z.-Y.C. participated in the interpretation of the results, writing, revision and correspondence with the journal of Molecules until the manuscript was accepted. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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