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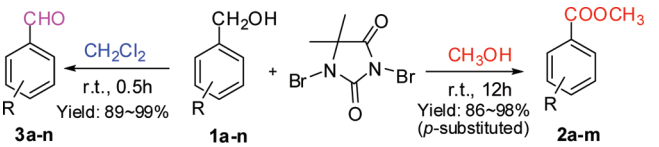
SELECTIVE AND EFFICIENT OXIDATION OF BENZYLIC ALCOHOLS TO BENZALDEHYDES AND METHYL BENZOATES BY DIBROMO-5,5-DIMETHYLHYDANTOIN

Zhongzhou Li, Wei Zhu, Jinlong Bao, and Xinzhuo Zou
Department of Chemistry, East China Normal University, Shanghai, China

GRAPHICAL ABSTRACT



Abstract *A selective and efficient method of oxidizing benzyl alcohols to benzaldehydes and methyl benzoates by using 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) as oxidant is developed. One-step conversion of benzyl alcohols to methyl benzoates in methanol at room temperature for 12 hours is achieved without any catalysts. Moreover, para-substituted benzyl alcohols are obtained in 86–98% yield. When dichloromethane is used as solvent, further oxidation of benzaldehydes to esters is well controlled, selectively affording benzaldehydes in 89–99% yield within 30 minutes.*

[Supplementary materials are available for this article. Go to the publisher's online edition of Synthetic Communications® *for the following free supplemental resource(s): Full experimental and spectral details.]*

Keywords Benzaldehyde; chemoselective; dibromo-5,5-dimethylhydantoin; methyl benzoate; oxidation

INTRODUCTION

The oxidation of alcohols is a fundamental procedure in synthetic organic chemistry.[1] The products such as benzaldehydes, benzoic acids, or benzoates are valuable in the fine chemical, pharmaceutical, and agrochemical industries. Thus, chemists are focused on developing an efficient route to synthesize these compounds,[2] and many related studies have been recently conducted. Approximately 500 works have been reported on the oxidation of alcohols from 2008 to 2012 based on the query results of SciFinder using the search words "oxidation of alcohols." Studies on the oxidation of alcohols mainly focus on oxidation control

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and oxidant use. The oxidation of alcohols usually suffers from overoxidation.[3] Accordingly, highly selective oxidation of alcohols under mild conditions is attractive and challenging for organic synthesis and green chemistry. Some excellent methods have been developed to address this challenge.[4] However, research on selectively synthesizing aldehydes and directly producing esters from alcohols with the same reagents as those used for solvato-control methods is limited. Such compounds are also traditionally synthesized by oxidizing their alcohol analogs with large amounts of noxious or hazardous oxidants based on transition metals (such as chromate[5] and permanganate[6]) as well as with organic nitrogen-containing and organometallic compounds as catalysts.[7] However, these oxidations cannot often be used in large-scale manufacturing because of inherent safety concerns and wastege of by-products.[8] The best oxidants are molecular oxygen[9] and hydrogen peroxide.[10] Although the use of molecular oxygen or air as oxidant is attractive, numerous challenges in terms of activating the O=O bond at a low temperature (typically < 160 °C) are encountered.[11] As one of the cleanest terminal oxidants with only water as the by-product, hydrogen peroxide is attracting increased attention in modern organic synthesis.[10(a),12] However, the use of oxygen or hydrogen peroxide as oxidant usually requires expensive active metal catalysts such as gold,[13] palladium,[14] and ruthenium.[15] Recently, the use of halogenating agents as oxidants, including *N*-bromosuccinimide (NBS), *N*-iodosuccinimide, 1,3-dibromo-5,5-dimethylhydantoin (DBDMH), and trichloroisocyanuric acid, has been reported.[16]

Given the low cost of DBDMH, it is widely used as a sanitizer for swimming pools, a brominating reagent for ethylene propylene diene monomer rubber, an additive in plastics to promote photodegradation, and a fungicide.[16(a),17] Our group has studied some aspects of the use of 1,3-dichloro-5,5-dimethylhydantoin (DCDMH) and DBDMH as halogenated reagents and described methods involving DCDMH or DBDMH.[18] Moreover, our group has applied DBDMH in the synthesis of hydroxyotobain derivatives. One-pot synthesis of 6-bromo piperonyl aldehyde (**3n**) was achieved with piperonyl alcohol (**1n**) as starting material, indicating that DBDMH can serve as an oxidant and a bromination reagent in the reaction (Scheme 1).

Accordingly, the present investigation was aimed to study the oxidizing function of DBDMH further. A convenient method of selectively oxidizing benzyl alcohols to corresponding benzaldehydes and methyl benzoates by using DBDMH as oxidant and by selecting the appropriate solvent is proposed.

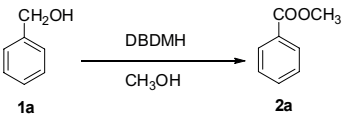
Scheme 1. One-pot synthesis of 6-bromo piperonyl aldehyde by using DBDMH.

RESULTS AND DISCUSSION

The possibility of the one-step oxidation of benzyl alcohols to methyl benzoates was initially screened by reacting benzyl alcohol with DBDMH at a ratio of 1:2 in methanol at room temperature. The result showed that 50% benzaldehyde and 50% methyl benzoate were obtained (Table 1, entry 1). Then, the effect of the molar ratio of benzyl alcohol to DBDMH on oxidation to methyl benzoate was investigated (Table 1). When 3 equivalents of DBDMH was used, the methyl benzoate was obtained in 90% yield (Table 1, entry 2). With increased DBDMH amounts (1:4 molar ratio), the yield of benzoate further increased to 98% (Table 1, entry 3). Subsequently, the effect of reaction time on the oxidation was investigated. The result showed that only 88% methyl benzoate was obtained within 10 h of reaction time (Table 1, entry 4). However, no further improvement in the yield was achieved with prolonged reaction time to 30 h (Table 1, entry 5). No yield improvement was observed with increased temperature by refluxing (Table 1, entry 6). The results show that room temperature was the best for this oxidation.

Under the aforementioned optimized conditions, substrate generality was examined, and the results are presented in Table 2. The *para*-substituted benzyl alcohols (**1b–1g**) were transformed to corresponding methyl benzoates in similar yields (86–94%; Table 2, entries 2–7). The substrates with a strongly electron-donating group (**1e** and **1m**) underwent methyl esterification and even concomitant ring bromination to afford methyl 3-bromo-4-methoxybenzoate **2e** and methyl 5-bromo-2-methoxybenzoate **2m** in 93% and 73% yields, respectively (Table 2, entries 5 and 13). The substrates with a strongly electron-withdrawing group in the *para*-position (**1f** and **1g**) had slightly decreased yields (Table 2, entries 6 and 7). The oxidation of the heterocyclic benzyl alcohol compound **1h** afforded **2h** in 75% yield (Table 2, entry 8). The substrate with a strongly electron-withdrawing group and steric hindrance in the *meta*-position on its benzene ring (**2i**) was obtained in 64% yield (Table 2, entry 9). The *ortho*-substituted benzyl alcohols were oxidized to methyl benzoates in relatively

Table 1. Optimization of conditions for oxidation of benzyl alcohol to methyl benzoate with DBDMH[a]

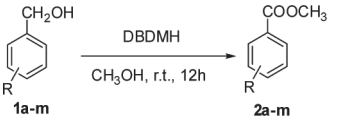


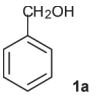
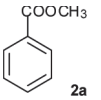
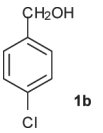
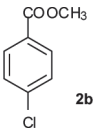
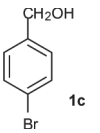
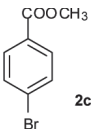
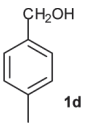
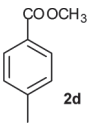
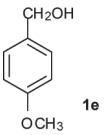
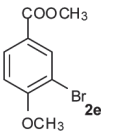
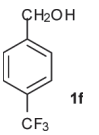
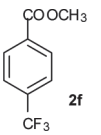
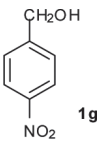
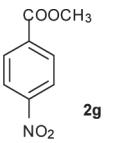
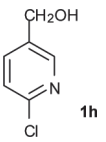
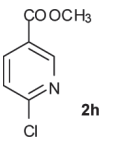
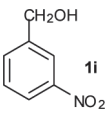
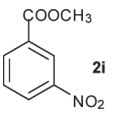
1a 2a

Entry	Alcohol: DBDMH (mol ratio)	Time (h)	Temp. (°C)	Yield (%)[b]
1	1:2	12	25	50
2	1:3	12	25	90
3	1:4	12	25	98
4	1:4	10	25	88
5	1:4	30	25	95
6	1:4	12	Reflux	92

[a]All reactions were run with benzyl alcohol using DBDMH in methanol.
[b]GC yield.

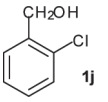
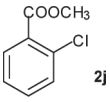
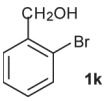
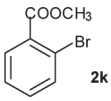
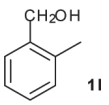
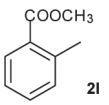
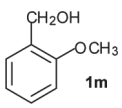
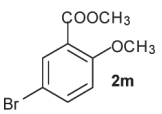
Table 2. Substrate scope for the oxidation of benzyl alcohols to methyl benzoates with DBDMH in methanol[a]



Entry	Substrate	Product	Yield (%)[b]
1	 1a	 2a	98
2	 1b	 2b	95
3	 1c	 2c	94
4	 1d	 2d	93
5	 1e	 2e	93
6	 1f	 2f	89
7	 1g	 2g	86
8	 1h	 2h	75
9	 1i	 2i	64

(*Continued*)

Table 2. Continued

Entry	Substrate	Product	Yield (%)[b]
10	 **1j**	 **2j**	30 (18)[c]
11	 **1k**	 **2k**	24 (25)[c]
12	 **1l**	 **2l**	12
13	 **1m**	 **2m**	73

[a]Substrate (5 mmol), methanol (30 ml), and DBDMH (20 mmol) were stirred at room temperature for 12 h.

[b]GC yield.

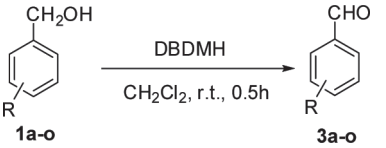
[c]Reflux.

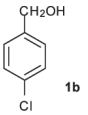
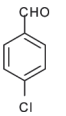
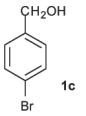
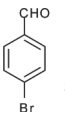
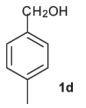
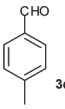
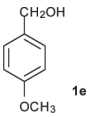
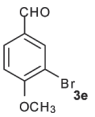
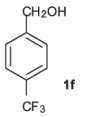
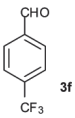
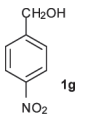
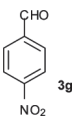
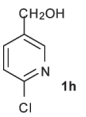
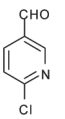
poor yields (Table 2, entries 10–12). As shown in Table 2, **1j** transformed to **2j** in 30% yield (Table 2, entry 10). The yield of the methyl esterification of **1k** (with a large atomic radius) substituted in the *ortho*-position decreased to 24% (Table 2, entry 11). The yield of the ortho-methyl-substituted **1l** decreased to 12% (Table 3, entry 12). The result showed that steric hindrance affected the efficiency of oxidation to methyl benzoates. However, increased temperature to reflux did not markedly improve the yields of **2j** and **2k** from of **1j** and **1k** (Table 2, entries 10 and 11).

The effect of DBDMH amount on the selective oxidation of benzyl alcohols to benzaldehydes was then examined. To oxidize benzyl alcohol to methyl benzoate, 1 mol of DBDMH was reacted with 1 mol of benzyl alcohol in methanol at room temperature. The reaction was monitored by thin-layer chromatography (TLC). After 1 h, 75% benzaldehyde was obtained (Table 4, entry 2). The yield of benzaldehyde remained at approximately 50–74% regardless of decreased DBDMH amount and reaction time. Esters and other complex compounds were also obtained (Table 4, entries 2–4). On one hand, the further oxidation of aldehyde to ester with methanol as solvent was inevitable. On the other hand, dichloromethane was used as postprocessing extractant in this work. Then dichloromethane was used as reaction solvent instead of methanol. Interestingly, a satisfactory yield of benzaldehyde was obtained at room temperature within 0.5 h with dichloromethane as solvent (Table 4, entry 5). However, reducing the amount of DBDMH to 0.75 equiv. resulted in a lower yield of benzaldehyde (Table 4, entry 6). Therefore, the final optimum conditions were 1:1 DBDMH-to-substrate ratio in dichloromethane at room temperature for 0.5 h.

The scope of the proposed method was demonstrated with various benzyl alcohols (Table 3). Benzyl alcohols with halogen groups can be oxidized to afford

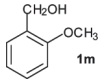
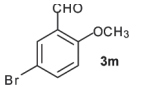
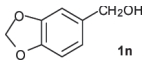
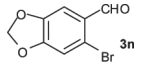
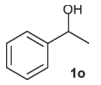
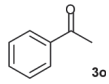
Table 3. Substrate scope for the selectivity oxidation of benzyl alcohols to benzaldehyde with DBDMH in dichloromethane[a]



Entry	Substrate	Product	Yield (%)[b]
1			93
2			97
3			92
4			92
5			55
6			89
7			99
8			89
9			92
10			93

(*Continued*)

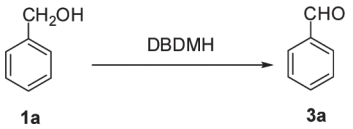
Table 3. Continued

Entry	Substrate	Product	Yield (%)[b]
11			94
12			98
13			66
14			78
15			98

[a]Substrate (1 mmol), dichloromethane (20 ml), and DBDMH (1 mmol) were stirred at room temperature for 0.5 h.
[b]GC yield.

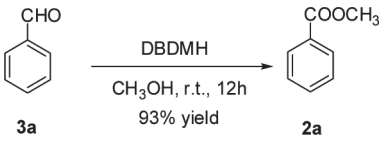
benzaldehydes in satisfactory yields (>90%; Table 3, entries 2, 3, 10, and 11). The substrates with a strongly electron-withdrawing group, namely, **1f**, **1g**, and **1i**, afforded products **3f**, **3g**, and **3i** in 89%, 99%, and 92% yields, respectively (Table 3, entries 6, 7, and 9). The substrates with an electron-donating group in their benzene ring (**1d** and **1l**) were also oxidized to afford **3d** and **3l** in good yields (>90%; Table 3, entries 4 and 12). The oxidation of the heterocyclic benzyl alcohol compound **1h** afforded **3h** in 89% yield (Table 3, entry 8). The result showed that electronic structures did

Table 4. Optimization of conditions for oxidation of benzyl alcohol to benzaldehydes with DBDMH[a]



Entry	Alcohol: DBDMH (mol. ratio)	Solvent	Time (h)	Temp. (°C)	Yield (%)[b] 3a	2a
1	1:4	CH_3OH	12	25	n.d.[c]	98
2	1:1	CH_3OH	1	25	75	10
3	1:0.75	CH_3OH	1	25	74	13
4	1:0.5	CH_3OH	12	25	50	28
5	1:1	CH_2Cl_2	0.5	25	93	n.d.[c]
6	1:0.75	CH_2Cl_2	0.5	25	79	n.d.[c]

[a]All reactions were run with benzyl alcohol using DBDMH.
[b]GC yield.
[c]Not detected by GC.



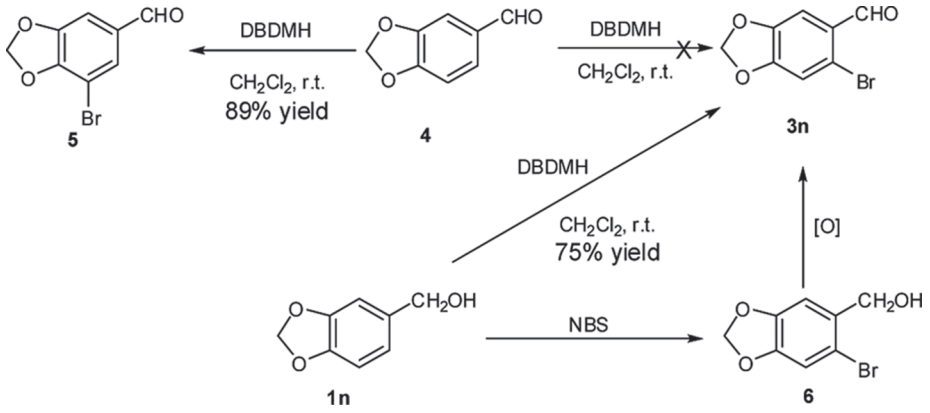
Scheme 2. Oxidation of benzaldehyde to methyl benzoate by using DBDMH.

not significantly affect the oxidation efficiency in terms of yield and chemoselectivity (Table 4, entries 2–5 and 8–9). However, the substrates with a strongly electron-donating group (**1e**, **1m**, and **1n**) underwent concomitant ring bromination to afford **3e**, **3m**, and **3n**, respectively, as well as a brominated product, in low yields (Table 4, entries 5, 13, and 14). Secondary alcohol **1o** was also oxidized to ketone **3o** in 98% yield (Table 3, entry 15).

Subsequently, the oxidation of benzaldehyde to methyl benzoate was investigated (Scheme 2). Methyl benzoate was obtained in 93% yield.

Moreover, the proposed method was used to synthesize **3n**, which was one of the intermediates in the synthesis of hydroxyotobain derivatives (Scheme 3). Generally, **3n** is prepared from **1n** in two steps.[19] In the current work, an attempt was made to synthesize **3n** by brominating compound **4** with DBDMH in dichloromethane. However, compound **5** was obtained as the major product. Interestingly, when the proposed method was used, **3n** was selectively obtained in one step with **1n** as starting material.

In summary, a mild and efficient method of chemoselectively converting benzyl alcohols to benzaldehyde and methyl benzoate using DBDMH was developed. Further oxidation of benzaldehyde to methyl benzoate was well controlled by changing the solvent from methanol to dichloromethane. Moreover, the reaction was metal-free and acid–base-free, and can thus be a valuable alternative to existing approaches for use at laboratory and industrial scales.



Scheme 3. Possible synthetic routes for 6-bromo piperonyl aldehyde.

EXPERIMENTAL SECTION

Representative Procedure for the Oxidation of Benzyl Alcohols to Methyl Enzoates (2b)[19] with DBDMH

DBDMH (20 mmol) was added in portions to a mixture of **1b** (5 mmol) and methanol (30 ml). The reaction was kept at room temperature. After the mixture was stirred for 12 h, the methanol was vacuum evaporated. The residue was dissolved by methyl-tert-butyl ether (MTBE) (30 ml) and washed with water (3×30 ml). The organic extracts were dried by anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel–petroleum ether/ethyl acetate, 30:1) to afford the product as light yellow solid (92% yield). Mp 42–44 °C (lit. 43°C). ^{1}H NMR (500 MHz, $CDCl_3$): δ°C 3.93 (s, 3H), 7.39 (d, 2H, J=8.0 Hz), 7.95 (d, 2H, J=8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ°C 52.2, 128.5, 128.6, 130.9, 139.3, 166.1.

Representative Procedure for the Oxidation of Benzyl Alcohols to Benzaldehyde (3b)[20] with DBDMH

DBDMH (1 mmol) was added to a mixture of **1b** (1 mmol) and dichloromethane (20 ml). The reaction was kept at room temperature. After the mixture was stirred for 0.5 h, it was washed with water (3×30 ml), dried with anhydrous $MgSO_4$, filtered, and vacuum evaporated. The residue was purified by column chromatography (silica gel–petroleum ether / ethyl acetate, 30:1) to afford the product as light yellow solid (93% yield). mp 47–48°C(lit. 48–50°C), ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22 (d, 2H, J=8.0 Hz), 7.92 (d, 2H, J=8.0 Hz), 9.97 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 129.4, 131.0, 134.9, 141.1, 190.7.

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