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An efficient method for selective oxidation of 1,2-diols in water catalyzed by Me_2SnCl_2†

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Dimethyltin(IV)dichloride-catalyzed selective oxidation of 1,2-diols in water was achieved using dibromoisocyanuric acid (DBI) or Br_2 as oxidants. The catalyst activates the 1,2-diol moiety through the formation of stannylene acetal in addition to enhancing selectivity. Various cyclic and acyclic 1,2-diol substrates have been selectively oxidized affording α-hydroxyketones in good to excellent yields. This method is safe and simple in operation.

Introduction

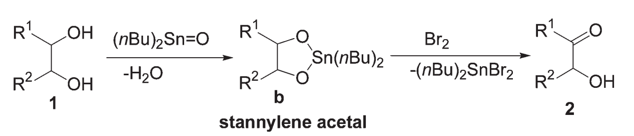
Organic reactions in water as a solvent or co-solvent have attracted a lot of attention recently. This is because of the unique properties of water and its key role as a solvent for green chemistry.[1] With increasing regulatory pressure targeting organic solvents, the development of nonhazardous alternatives is of great importance.[2] Selective oxidation of 1,2-diols to their corresponding α-hydroxyketones is a basic and an important organic reaction.[3] This is because α-hydroxyketone units are found in some antitumor antibiotics and important natural products like olivomycin A,[4] kurasoin A and B.[5] However, the few methods available for selective oxidation of 1,2-diols to α-hydroxyketones,[6–11] suffer from drawbacks such as relatively low yields and side reactions accompanying C–C bond cleavage.[10] Use of Bu_2SnO,[12] has been recognized as a highly selective method. It proceeds in two stages: formation of stannylene acetal **b** by azeotropic condensation of 1,2-diol **1** with Bu_2SnO followed by the oxidation of **b** by Br_2 (Scheme 1).

This method has been applied to the synthesis of (+)-spectinomycin[13] and to the oxidation of sugars into oxo-sugars.[14] Unfortunately, it is unfavourable from an environmental viewpoint and also requires more than 1 equimolar amount of Bu_2SnO. So far, a handful of methods on selective oxidation of 1,2-diols in organic solvents have been presented using organotin catalysts,[15] chiral copper compounds,[16] and electrochemical methods.[15,17] But to the best of our knowledge no report on selective oxidation in water has been presented. Our most recent report on selective monobenzoylation of 1,2-diols in water,[18] and other reports on selective monobenzoylation in organic solvents,[19] greatly motivated this investigation. In these reports, Me_2SnCl_2 catalyst activates the 1,2-diol moiety through the formation of stannylene acetal and also facilitate selectivity. We envisioned that if we introduce a suitable oxidizing agent to a stannylene acetal in water, then selective oxidation may be achieved.

Results and discussion

We began our investigation on catalytic selective oxidation of 1,2-diols in water using *cis*-cyclooctane-1,2-diol **1a** as a model substrate and halogen cation "source" oxidants. After a series of optimization studies, we found that monoselective oxidation of **1a** proceeded efficiently in the presence of 10 mol% of Me_2SnCl_2, 1.2 equiv. potassium carbonate, and 1.5 equiv. Br_2 in water at low temperature (0 °C) under shielding the light for 1 h to afford **2a** in (85%) yield (entry 1, Table 1).

Temperature optimization experiments revealed that −5 °C was the optimum temperature for oxidation of **1a** using Br_2, affording (91%) yield (entry 1–3). Reducing the amount of Br_2 to 1.0 equiv. led to a drop in yield (78%) (entry 4). Commonly known mild oxidizing agents, *N*-bromosuccinimide (NBS) and *N*-iodosuccinimide (NIS) afforded lower yields at 0 °C (entries 5 and 6), while *N*-chlorosuccinimide (NCS) only afforded a trace amount of the desired product (entry 7). Dibromoisocyanuric acid



Scheme 1 Oxidation of 1,2-diols *via* stannylene acetal.

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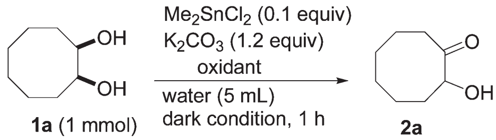
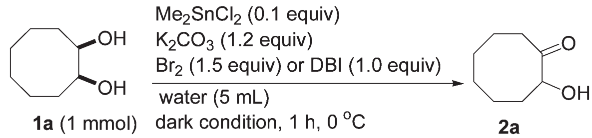
Table 1 Selective oxidation of 1,2-diol **1a** in water using various oxidants



Entry	Oxidant (equiv.)	Temp. (°C)	Yield (%)[a]
1	Br_2 (1.5)	0	85
2	Br_2 (1.5)	−5	91
3	Br_2 (1.5)	−10	89
4	Br_2 (1.0)	−5	78
5	NBS (2.0)	0	40
6	NIS (2.0)	0	29
7	NCS (2.0)	0	trace
8	DBI[b] (1.0)	0	90
9	DBI[b](1.5)	0	83
10	DBDMH[c] (1.5)	0	86
11	DIDMH[d] (1.5)	0	45
12	H_2O_2 (2.0)	0	0

[a] Isolated yield. [b] Dibromoisocyanuric acid. [c] 1,3-Dibromo-5,5-dimethylhydantoin. [d] 1,3-Diiodo-5,5-dimethylhyndantoin.

Table 2 Selective oxidation study by varying various parameters



Entry	Variation from the "standard" conditions	Yield (%)[a]
1[b]	Under O_2	90
2[b]	Under Ar	73
3[b]	0.05 equiv. Me_2SnCl_2	78
4[b]	0.01 equiv. Me_2SnCl_2	63
5[b]	Absence of Me_2SnCl_2 for 1 h	54
6[b]	Absence of Me_2SnCl_2 for 5 h	40
7[b]	Absence of K_2CO_3	43
8[b]	Without shielding the light	65
9[c]	Absence of Me_2SnCl_2	<1
10[c]	0.05 equiv. Me_2SnCl_2	76
11[c]	Absence of K_2CO_3	60

[a] Isolated yield. [b] 1.5 equiv. Br_2 was used. [c] 1.0 equiv. DBI was used.

(DBI), first reported by Gottardi[20] as a mild but more effective brominating agent than NBS,[21] afforded the desired product in an excellent yield of 90% with 1 equiv. (entry 8). Increasing the amount of DBI to 1.5 equiv. led to the formation of some diketone product, resulting in a drop in yield of the desired product (entry 9). 1.5 equiv. 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) gave comparable results. However, a closely related 1,3-diiodo-5,5-dimethylhydantoin (DIDMH) was not efficient in effecting this oxidation (entries 10 and 11). Efforts to use H_2O_2 as oxidant failed as it did not oxidize our reaction.

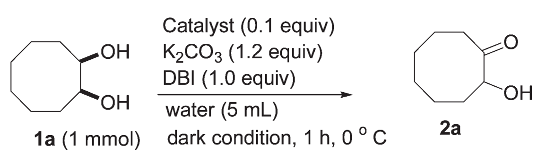
We next investigated the effect of a number of different reaction parameters on the efficiency of selective oxidation of 1,2-diol **1a** in water with Br_2 or DBI. The results are summarized in Table 2.

With bromine as the oxidant, the 90% yield was maintained under oxygen atmosphere, while in argon there was a drop to 73% (entries 1 and 2). Reducing the catalyst loading to 0.05 equiv. and 0.01 equiv. led to a drop in yields (entries 3 and 4). As expected, poor yield was obtained in the absence of the catalyst (entry 5). Extending the reaction time to 5 h in the absence of Me_2SnCl_2, resulted in the formation of the diketone and associated drop in the yield of the monoketone (entry 6). Similarly, absence of the base (potassium carbonate) or performing the reaction in presence of light led to drop in yields (entries 7 and 8). In the reaction with DBI as the oxidant but without the catalyst, essentially no reaction was observed (entry 9). As with bromine as the oxidant, reducing the catalyst loading to 0.05 equiv., also led to a drop in yield (76%) (entry 10). Similarly, the yield dropped in the absence of the base (entry 11).

Lack of reaction with DBI in the absence of Me_2SnCl_2 prompted us to study the effects of other organotin compounds as potential catalysts in reactions involving different 1,2-diols with 1.0 equiv. of this oxidant. The results are summarized in Table 3. Me_2SnBr_2 was found to be effective as a catalyst in place of Me_2SnCl_2, although at the expense of slight erosion in selectivity (entry 1). Dialkyltin dichloride catalysts gave moderate yields of mono-oxidation products (entries 2–4), while dialkyltin oxide and Cu salts did not show impressive activities (entries 5–7 and 8–9).

We next explored the substrate applicability to the oxidation system involving Me_2SnCl_2 as the catalyst and Br_2 or DBI as the oxidants. Generally, selective oxidation using 1.5 equiv. Br_2 and 1.0 equiv. DBI gave comparable yields for all substrates screened (Table 4). All *meso*- and *trans*-cyclic-1,2-diols, underwent selective oxidation affording mono-oxidized products in moderate to excellent yields (entries 1–6). A number of acyclic-1,2-diols were selectively oxidized at elevated temperature of 50 °C,[22] affording corresponding α-hydroxy-ketones in excellent to moderate yields (entries 7–9). Next, we carried out selective oxidation of 1,2-diols having both primary and secondary alcohols. When 1,2-diols **1k**, **1l**, **1m**, **1n**, and **1o** were treated under these catalytic conditions,

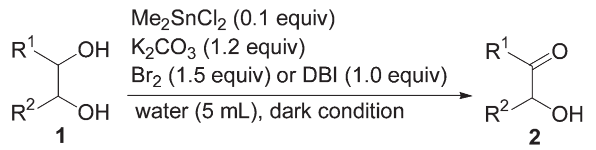
Table 3 Screening of catalyst with DBI as oxidant



Entry	Catalyst	Yield (%)[a]
1	Me_2SnBr_2	87
2	n-Oct_2SnCl_2	61
3	n-Bu_2SnCl_2	68
4	Ph_2SnCl_2	57
5	n-Bu_2SnO	23
6	Ph_2SnO	58
7	Me_2SnO	30
8	$CuCl_2$	15
9	$Cu(OTf)_2$	10

[a] Isolated yield.

Table 4 Scope of substrates with Br_2 or DBI as oxidants

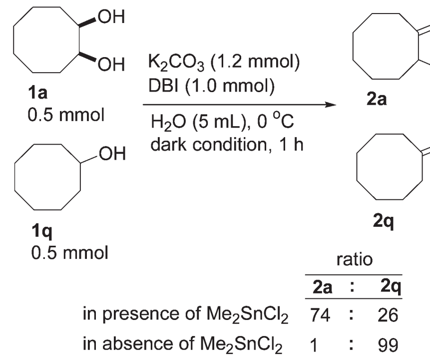


Entry	1,2-diol	Temp (Time)	Product	Yield (%)[a] Br$_2$	DBI
1	1b-d	0 °C (1 h)	2b-d; **b**: n = 3	93	91
2		0 °C (2 h)	**c**: n = 2	72	69
3		0 °C (3 h)	**d**: n = 1	55	57
4	1e-g	−5 °C (0.5 h)	2a,c,d; **a,e**: n = 4	81	85
5		0 °C (2 h)	**c,f**: n = 2	73	71
6		0 °C (3 h)	**d,g**: n = 1	57	57
7	1h	50 °C (1 h)	2h	92	91
8	1i	50 °C (1 h)	**2h**	89	88
9	1j	50 °C (1 h)	2j	56	59
10	1k	0 °C (2 h)	2k	82	87
11	1l	rt (2 h)	2l	86	82
12	1m	rt (3 h)	2m	34	37
13	1n	0 °C (1 h)	2n	69	67
14	1o	0 °C (1 h)	2o	85	80
15	1p	0 °C (2 h)	2p	60	56

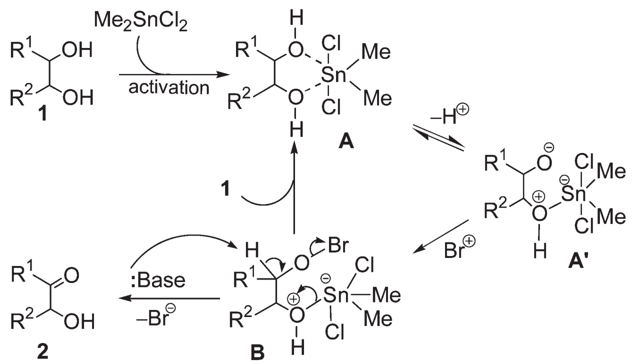
[a] Isolated yield.

the secondary alcohols were selectively oxidized preferentially affording products **2k**, **2l**, **2m**, **2n**, and **2o** respectively in moderate to excellent yields (entries 10–14). Additionally, 1,2,6-hexanetriol **1p** underwent selective oxidation at the secondary hydroxyl group of the 1,2-diol moiety affording **2p** in good yield (entry 15).

Competitive reaction between 1,2-diol **1a** and mono-ol **1q** was next tried (Scheme 2). In the presence of Me_2SnCl_2, **1a** and **1q** were oxidized to **2a** and **2q** in the ratio of 74 : 26 respectively. On the other hand, in the absence of Me_2SnCl_2, **2q** was predominantly obtained. These results clearly demonstrate the role of Me_2SnCl_2 in the activation of the hydroxyl groups of 1,2-diols and the versatility of the DBI as a promising oxidant for mono-ols in water.



Scheme 2 Competition reaction between *cis*-1,2-cyclooctanediol and cyclooctanol.



Scheme 3 Proposed reaction pathway for selective oxidation using Me_2SnCl_2 as a catalyst with Br_2 or DBI as the oxidant.

Finally a proposed reaction pathway for selective oxidation of 1,2-diols **1** is shown in Scheme 3. Chelate complex **A**[23] formed from the interaction of **1** with Me_2SnCl_2 or related complex **A′** (activated intermediates), could be oxidized by (Br^+) generated from the oxidant in water leading to **2**.

Conclusions

A catalytic process for selective oxidation of 1,2-diols in water under mild conditions has been achieved. This method not only provides a new approach to an environmentally benign process for selective oxidation 1,2-diols but also introduces an efficient oxidant (DBI) with superior results compared to NBS, which has commonly been used for selective oxidation in organic solvents. The method may also have potential in selective oxidation of specific hydroxyl groups in polyols. Selective oxidation using safer catalysts and enantioselective oxidation of 1,2-diols in water is currently ongoing in our lab.

Acknowledgements

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Notes and references

1 (*a*) P. A. Grieco, *Organic Synthesis in Water*, Blackie Academic & Professional, London, 1998; (*b*) C.-J. Li and T. H. Chan, *Organic Reactions in Aqueous Media*, John Wiley & Sons, New York, 1997.
2 (*a*) U. M. Lindstrom, *Chem. Rev.*, 2002, **102**, 2751; (*b*) D. Sinou, *Adv. Synth. Catal.*, 2002, **344**, 221; (*c*) U. M. Lindstrom and F. Andersson, *Angew. Chem., Int. Ed.*, 2006, **45**, 548; (*d*) M. C. Pirrung, *Chem.–Eur. J.*, 2006, **12**, 1312; (*e*) C.-J. Li and L. Chen, *Chem. Soc. Rev.*, 2006, **35**, 68–82.
3 Recent reviews: (*a*) R. Noyori, M. Aoki and K. Sato, *Chem. Commun.*, 2003, 1977; (*b*) R. Irie and T. Katsuki, *Chem. Rec.*, 2004, **4**, 96; (*c*) T. Mallat and A. Baiker, *Chem. Rev.*, 2004, **104**, 3037; (*d*) M. J. Schultz and M. S. Sigman, *Tetrahedron*, 2006, **62**, 8227.
4 R. Uchida, K. Shiomi, J. Inokoshi, R. Masuma, T. Kawakubo, H. Tanaka, Y. Iwai and S. Omura, *J. Antibiot.*, 1996, **49**, 932.
5 V. Kumar, W. A. Remers and W. T. Bradner, *J. Med. Chem.*, 1980, **23**, 376.
6 (*a*) L. D. Accolti, A. Detomaso, C. Fusco, A. Rosa and R. Curci, *J. Org. Chem.*, 1993, **58**, 3600; (*b*) W. Adam, C. R. Shaha-Mcller and C. G. Zhao, *J. Org. Chem.*, 1999, **64**, 7492; (*c*) B. Plietker, *Org. Lett.*, 2004, **6**, 289.
7 W. A. Cramp, F. J. Julietti, J. F. McGhie, B. L. Rao and W. A. Ross, *J. Chem. Soc.*, 1960, 4257.
8 M. Ftizon, M. Golfier and J. M. Louis, *J. Chem. Soc.*, 1969, 1102.
9 E. J. Corey and C. U. Kim, *Tetrahedron Lett.*, 1974, **15**, 287.
10 Y. Sakata and Y. Ishii, *J. Org. Chem.*, 1991, **56**, 6233.
11 (*a*) L. F. Walker, A. Bourghida, S. Connolly and M. Wills, *J. Chem. Soc., Perkin Trans. 1*, 2002, 965; (*b*) T. Yamato, T. Hironaka, T. Saisyo, T. Manabe and K. Okuyama, *J. Chem. Res.*, 2003, 63.
12 (*a*) S. David and A. Thieffry, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1568; (*b*) D. H. Crout and S. M. Morrey, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2435.
13 S. Hanessian and R. Roy, *J. Am. Chem. Soc.*, 1979, **101**, 5839.
14 Y. Tsuda, M. Hanajima, N. Matsuhira, Y. Okuno and K. Kanemitsu, *Chem. Pharm. Bull.*, 1989, **37**, 2344.
15 T. Maki, S. Iikawa, G. Mogami, H. Harasawa, Y. Matsumura and O. Onomura, *Chem.–Eur. J.*, 2009, **15**, 5364.
16 O. Onomura, H. Arimoto, Y. Matsumura and Y. Demizu, *Tetrahedron Lett.*, 2007, **48**, 8668.
17 T. Maki, K. Fukae, H. Harasawa, T. Ohishi, Y. Matsumura and O. Onomura, *Tetrahedron Lett.*, 1998, **39**, 651.
18 W. Muramatsu, J. M. William and O. Onomura, *J. Org. Chem.*, 2012, **77**, 754.
19 For the benzoylation of 1,2-diols catalyzed by organotin compounds, see: (*a*) F. Iwasaki, T. Maki, W. Nakashima, O. Onomura and Y. Matsumura, *Org. Lett.*, 1999, **1**, 969; (*b*) F. Iwasaki, T. Maki, W. Nakashima, O. Onomura and Y. Matsumura, *J. Org. Chem.*, 2000, **65**, 996; (*c*) Y. Demizu, Y. Kubo, H. Miyoshi, T. Maki, Y. Matsumura, N. Moriyama and O. Onomura, *Org. Lett.*, 2008, **10**, 5075.
20 W. Gottardi, *Monatsh. Chem.*, 1968, **99**, 815.
21 (*a*) W. D. Brown and A. H. Gouliaev, *Synthesis*, 2002, 83; (*b*) C. Virgil, in *Encyclopedia of reagents for organic synthesis*, ed, by L. A. Paquette, John Wiley&Sons, Chichester, 2001, pp. 1560–1561.
22 Performing the reaction at elevated temperatures improved the solubility of substrates which have poor solubility in water.
23 The change in oxidation potential in ref. 15 suggests the formation of a complex between the 1,2-diol and the Me_2SnCl_2.

