



Cite this: *Green Chem.*, 2019, **21**, 5896

Received 26th July 2019,
Accepted 25th September 2019

DOI: 10.1039/c9gc02605c

rs.c.li/greenchem

Oxidation of secondary alcohols using solid-supported hypervalent iodine catalysts†

Frederic Ballaschk and Stefan F. Kirsch *

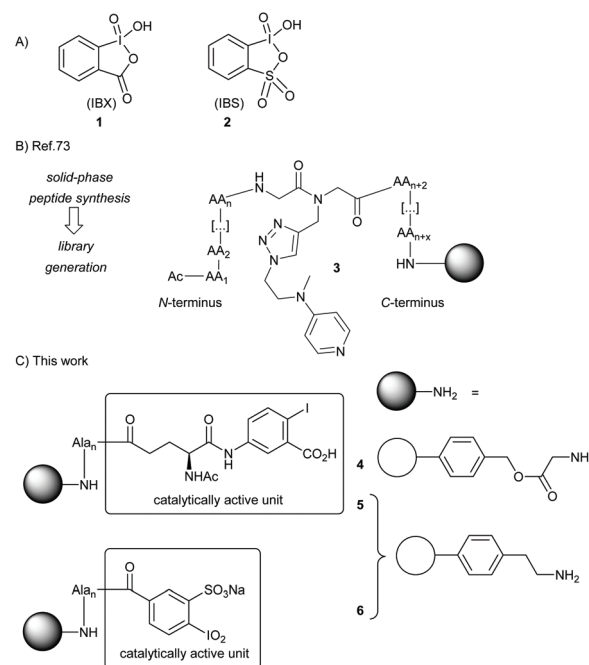
It is shown how secondary alcohols are oxidized to provide the corresponding ketones by use of Oxone® and solid-supported hypervalent iodine catalysts. Under experimentally simple conditions with acetonitrile at elevated temperatures, excellent conversions were achieved with low catalyst loadings (0.2–5 mol%) when employing the conjugates **5** and **6** derived from IBX and IBS. The catalysts are broadly applicable to a range of alcohol substrates. Of primary importance with respect to sustainability issues, the metal-free catalysts are easily removed from the reaction mixture through filtration, and they can be re-used in oxidation processes for multiple times, without loss of catalytic activity.

Introduction

The formation of carbonyls through alcohol oxidation is one of the most fundamental reactions in contemporary chemistry. A great plethora of methods already exist to fulfill this task, and hypervalent iodine reagents belong to the most applied oxidation agents.^{1–5} For example, the Dess–Martin periodiane (DMP) became the standard textbook reagent for all kinds of alcohol oxidation, after its invention in 1983.⁶ Its parent compound, 2-iodoxybenzoic acid (IBX, **1**),^{7–9} is even older and was reported first in 1893 by Hartmann and Meyer (Scheme 1).¹⁰ Since then, IBX was mainly forgotten over more than half a century before it experienced a renaissance with the breakthrough reports by Frigerio and Santagostino in 1994: IBX was shown to be a moisture-stable and easy-to-handle reagent for the mild oxidation of alcohols in DMSO at room temperature.^{11,12} The IBX oxidation of alcohols then emerged as a standard transformation in organic synthesis with numerous applications in complex molecule synthesis.¹³ Nowadays IBX is considered one of the most versatile oxidizing agents, with an extraordinary array of reactivities beyond alcohol oxidation, including phenol oxidation,^{14–17} functional group transfer onto activated methylene compounds,^{18–22} and dehydrogenations.^{23,24}

Despite the many advantages IBX offers, several issues are unattractive to practitioners: (i) similar to many other beloved oxidation agents, stoichiometric amounts of the hypervalent iodine compound are required for alcohol oxidation. This is particularly problematic since IBX is reported to be shock- and

heat-sensitive,^{25,26} at least under certain conditions, thus weakening its routine for large-scale applications. (ii) The regeneration of the IBX species from the 2-iodosobenzoic acid (IBA) formed during the oxidative process is typically avoided, resulting in significant amounts of “organic waste”.²⁷ (iii) DMSO is the preferred solvent for all variants of IBX oxidations,^{28,29} requiring sophisticated work-up protocols to remove the remainder of the hypervalent iodine reagent, for



Scheme 1 A) Structures of IBX and IBS. (B) DMAP-peptide conjugates through Fmoc-SPPS on Boc-Gly Merrifield resin. (C) Solid-supported oxidation catalysts derived from IBX and IBS.

Organic Chemistry, Bergische Universität Wuppertal, Gaußstr. 20, 42119 Wuppertal, Germany. E-mail: sfkirsch@uni-wuppertal.de

†Electronic supplementary information (ESI) available: Experimental procedures, analytical data and copies of ¹H, ¹³C NMR-spectra. See DOI: 10.1039/c9gc02605c



example by addition of chlorinated solvents. It is therefore reasonable to summarize that IBX and its derivatives are not the ideal reagents with respect to the principles of Green Chemistry^{30,31} since they are mostly used as stoichiometric and non-recyclable reagents.

Several strategies were developed to tackle those issues. For example, modified IBX reagents^{32–37} for the use in common solvents other than DMSO and safer formulations^{38,39} of IBX with reduced explosive properties were described. Experimental procedures that aimed at the effective recovery of the reduced form of the hypervalent iodine compounds using biphasic protocols or fluororous techniques led to further improvements.^{40–44} Polymer-supported IBX reagents were also reported, with the goal to ease work-up protocols and to improve recyclability,⁴⁵ including polymer-supported variants of IBX,^{46–50} IBX-amides,^{51–56} IBX-esters,⁵⁷ and 2-iodylphenol ethers.⁵⁸ In addition, the oxidation with catalytic amounts of IBX^{59–61} and particularly 2-iodoxybenzenesulfonic acid (IBS, 2)^{62–65} was shown to be highly efficient.⁶⁶ Those catalytic methods typically rely on Oxone® as the stoichiometrically used co-oxidant,^{67–74} a reagent that is considered environmentally safe, non-toxic and non-explosive.⁷⁵ To facilitate the recovery of the hypervalent iodine organocatalyst, fluororous IBX was recently introduced.⁷⁶ However, the catalytic use of hypervalent iodine oxidants bound to a polymer support was not reported, until now. This is despite the fact that there would be obvious advantages: the iodine-based catalysts are an environmentally sustainable alternative to transition metals, relatively inexpensive and easily recoverable.⁷⁷

In this paper, we present two new solid-supported hypervalent iodine reagents for the oxidation of secondary alcohols, derived from readily available starting materials: one is based on IBX, and the other is an IBS derivative. In the presence of Oxone®, the two reagents are shown to be highly effective catalysts when using a water–acetonitrile solvent mixture, with catalyst loadings as low as 1 mol%. We also demonstrate that the two metal-free organocatalysts are easily reusable, and work-up protocols consist of simple filtrations. Therefore, our hypervalent iodine compounds may become attractive ‘green catalysts’ in the ever-evolving fields of alcohol oxidations and other challenging oxidative processes.^{30,31,78–81}

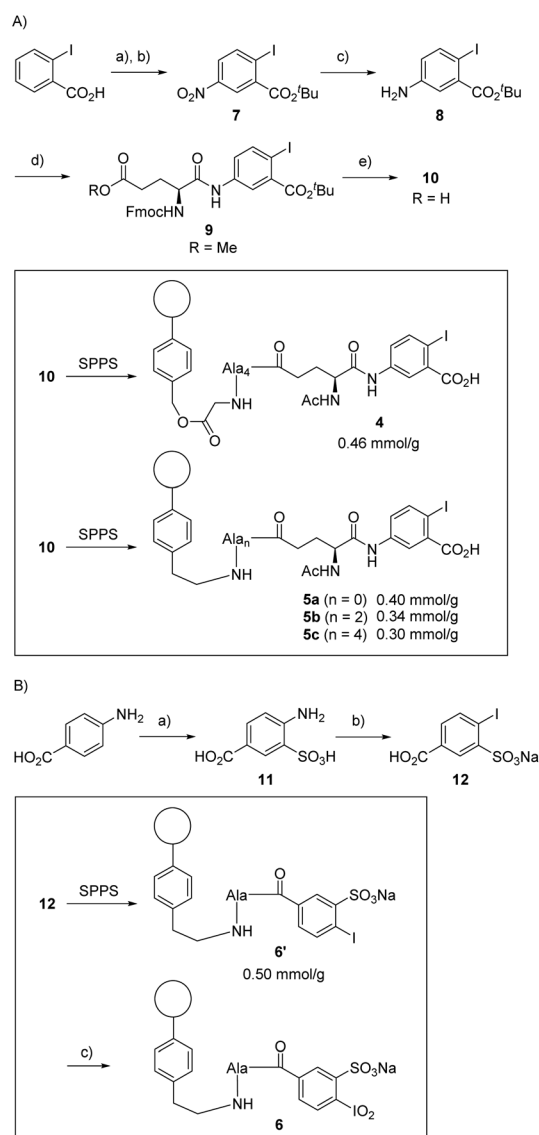
Results and discussion

We recently presented the use of solid-supported DMAP–peptide conjugates **3** for the highly regioselective acylation of polyhydroxylated small molecules (Scheme 1).^{82,83} We now expanded this concept to connect hypervalent iodine precursor units with peptide-modified resins. Our initial plan was to study conjugates **4** consisting of the glycine-modified Merrifield resin and a (poly)alanine linker, the N-terminus of which was connected to the iodine-containing catalyst. For reasons detailed below, we also generated the conjugates **5** and **6** where the (poly)alanine linker was attached to an aminoethyl polystyrene resin. While **5** is based on the same

IBX-derived catalytically active unit used for **4**, the solid-supported catalyst **6** was designed as a variant of IBS.

Synthesis of the solid-supported precatalysts **4**, **5** and **6**

We started the synthesis of the precatalyst **4** as summarized in Scheme 2A, using 2-iodobenzoic acid as the commercially available and cheap starting material. Nitration of the aromatic core gave the 5-nitro analogue in 65% yield, as pure substance after simple recrystallization. Subsequent conversion into the



Scheme 2 A) Synthesis of solid-supported precatalysts **4** and **5**: (a) i) 0 °C, 15 min, (ii) rt, 30 min, (iii) 130 °C, 90 min, (H₂SO₄/HNO₃), 65%; (b) Boc₂O (2.5 eq.), DMAP (0.3 eq.), 70 °C, 4 h, (t-BuOH), >99%; (c) H₂ (8 bar), Pd/C (10 mol%), rt, 18 h, (EtOAc), 82%; (d) Fmoc-Glu(OMe)-OH (1.35 eq.), HATU (1.5 eq.), DIPEA (2 eq.), rt, 18 h, (DMF), 90%; (e) LiOH·H₂O (1 eq.), 0 °C to rt, 18 h, (THF/H₂O), 73%. (B) Synthesis of solid supported precatalyst **6**: (a) H₂SO₄/SO₃ (25%), (H₂SO₄), 69%; (b) i) NaOH (1.0 eq.), 0 °C, (ii) H₂SO₄ (20 eq.), 0 °C, (iii) NaNO₂ (1.1 eq.), –2 °C, 60 min, (iv) urea (2.0 eq.), –2 °C, 60 min, (v) NaI (1.5 eq.), 0 °C to rt, 18 h, (water), 47%; (c) TBA-Oxone® (5 eq.), MeSO₃H (5 eq.), rt, 5 h, (CH₂Cl₂).



tert-butyl ester furnished **7** in excellent yields. Reduction of the nitro group with palladium on charcoal and H₂ pressure (8 bar) led to the desired aniline derivative **8** in 82% yield. The iodobenzoic acid variant was coupled to a protected glutamic acid with classical conditions providing the unnatural amino acid **9** in 90% yield. The methyl ester was then saponified while the *tert*-butyl ester remained untouched: this step was achieved with lithium hydroxide in aqueous THF in 73% yield.

With the Fmoc-protected amino acid **10** in hand, the immobilization on glycin-modified Merrifield resin was accomplished using standard solid-phase peptide synthesis (see ESI† for details). Of note, alanine was chosen as the linker amino acid because of the ease of its introduction with SPPS techniques, its lack of functional groups, and its stability toward oxidative conditions (particularly in comparison to glycine). We decided to start with the conjugate **4** having four alanines as linker unit since, at the outset of our studies, we expected that the use of an elongated and flexible linker that provides a spatial separation of the catalytically active part from the polymer body will be advantageous.⁵¹ The loading of the resin was determined to be around 0.46 mmol g⁻¹ *via* UV-VIS measurements (see ESI†). The amino acid **10** was also linked to the aminoethyl polystyrene resin giving conjugates **5**. We constructed those conjugates with several linker lengths for further tests, with **5a** having no alanine unit (*n* = 0), **5b** having two alanines (*n* = 2) and **5c** having four alanines (*n* = 4). In all cases, a loading between 0.3 and 0.4 mmol g⁻¹ was achieved.

We next focused on the synthesis of the solid-supported precatalyst **6** (Scheme 2B), relying on our previous synthetic approach to the oxidant IBX-SO₃K.^{37,84,85} We began with 4-aminobenzoic acid, which was selectively sulfonylated with fuming sulfuric acid to give the acid **11**. Sandmeyer-type conditions furnished iodide **12**. All the steps of this sequence are high-yielding without the need for a chromatographic purification, and multiple runs were successfully and reproducibly carried out in multigram scale. The carboxylic acid **12** was then coupled to the polymer resin bearing a single alanine linker to give the conjugate **6'** with a loading of 0.50 mmol g⁻¹. We note that the direct coupling of **12** to the resin was slow and low-yielding when no alanine was involved. The polymer-supported iodoxy reagent **6** was easily obtained upon oxidation of **6'** with the Oxone® tetrabutylammonium salt (TBA-Oxone®).

Oxidations with the solid-supported precatalysts **4**, **5** and **6**

We then started to test the potential of our new catalytic system **4**, choosing the oxidation of borneol **13a** as a suitable benchmark reaction. Following previous reports on the catalysed oxidation with IBX and IBS with stoichiometric amounts of Oxone®, the oxidation was initially attempted with 1.6 equivalents of Oxone® at 70 °C in aqueous acetonitrile (70%), in the presence of 4 mol% of polymer bound IBX precatalyst **4**. As shown in Table 1 (entry 2), borneol was completely converted into the corresponding ketone **14a** under the conditions after 18 h; isolated yields of **14a** were high. In a similar way, a range of secondary alcohols including 4-nonanol, menthol, 1,3-diphenylpropan-2-ol and 2,2-dimethyl-1-phenylpropan-1-ol

Table 1 Recycling tests with precatalyst **4**, **5**, **6**

Entry	Catalyst (mol%)	Cycle no. ^a	13a/14a ^b
1	—	—	92/8
2	4 (4)	1 (initial)	0/100
3	4 (4)	2 (1 st reuse)	18/82
4	4 (4)	3 (2 nd reuse)	64/36
5	4 (4)	4 (3 rd reuse)	82/18
6	4 (4)	5 (4 th reuse)	85/15
7	5c (5)	1 (initial)	0/100
8	5c (5)	2 (1 st reuse)	0/100
9	5c (5)	3 (2 nd reuse)	0/100
10	5c (5)	4 (3 rd reuse)	0/100
11	5c (5)	5 (4 th reuse)	19/81
12 ^c	6 (1)	1 (initial)	21/79
13 ^c	6 (1)	2 (1 st reuse)	14/86
14 ^c	6 (1)	3 (2 nd reuse)	12/88
15 ^c	6 (1)	4 (3 rd reuse)	14/86
16 ^c	6 (1)	5 (4 th reuse)	19/81
17 ^c	6 (1)	6 (5 th reuse)	22/78

^a Recycling and reuse of catalyst by filtration. ^b Ratio **13a/14a** was determined *via* GC-FID (calibrated with stock solutions of **13a** and **14a**) after 18 h. ^c With 40 mol% of ⁿBu₄NHSO₄, 2 h, MeCN.

were easily oxidized by use of catalyst **4**. The formation of by-products was not detected *via* ¹H NMR or GC-FID analysis of the crude reaction mixture. Hence, the performance of the oxidation reactions was easily screened by determining the ratio of starting substrate **13** and oxidation product **14** with GC-FID in a standardized way. In the absence of precatalyst **4**, 8% conversion of the starting substrate were observed after 18 h, thus indicating a minor background reaction with no synthetic use (entry 1). However, it was truly disappointing that the polymeric system **4** lacked a main asset: it was not reusable. A loss of activity was already found in the second cycle when reusing **4** after simple filtration for the borneol oxidation (entry 3). A markedly lowered conversion of 82% was observed after 18 h, under otherwise identical conditions. This trend continued, and the fifth reaction with the same batch of catalyst gave only 15% conversion, demonstrating that resin-supported catalyst **4** had no recyclability of value.

The failure of **4** was attributed to the weakness of the ester bond between the Merrifield resin and the glycine linker toward hydrolysis under the reaction conditions. Indeed, control experiments showed that esters were partly hydrolysed in aqueous acetonitrile at 70 °C in the presence of Oxone® while amide bonds remained fully stable. As a result, column chromatography was required to obtain analytically pure oxidation products when employing precatalyst **4**. Simple filtration, on the other hand, gave the ketones with traces of impurities that were not unequivocally identified, but may certainly stem from the partial hydrolysis of **4**. The design error of **4** then led us to carefully study the systems **5** and **6** where the hypervalent iodine precursor units were connected to the aminoethyl polystyrene resin *via* more stable amide bonds.



Gratifyingly, it was easily possible to reuse the catalysts **5** and **6** for multiple times, after recycling of the resins through simple filtration. As shown in Table 1 (entries 7–11), the IBX-derived system **5c** kept its activity over five cycles, and complete oxidation of borneol was achieved using 5 mol% of the catalyst with 1.6 equivalents of Oxone® at 70 °C in aqueous acetonitrile. Lower catalyst loadings (<2.5 mol%) were shown to provide incomplete conversions, even after elongated reaction times. The IBS variant **6** was effectively reused for five times (Table 1, entries 12–17), accomplishing a constant conversion between 78% and 88%, albeit with lowered catalyst loading (1 mol%) and reduced reaction times (2 h). As a result of the recycling tests, we decided that both systems **5** and **6** based on the aminoethyl polystyrene resin qualify well for catalyzing the oxidation of secondary hydroxy groups under the premise that they deliver easy work-up and multiple reuses.

Our optimization attempts with catalyst **5c** then showed that a broad range of reaction conditions is feasible, and the oxidation proceeds equally well in water-free MeNO₂, aqueous MeNO₂ (30% water) and aqueous MeCN (5–30% water). However, the use of dry acetonitrile as solvent led to signifi-

cantly diminished yields. Best conversions were achieved between 70 °C and 90 °C, while temperatures below 60 °C did not provide the product of oxidation. To our surprise, the linker length had almost no influence on the catalyst efficiency. As summarized in Table 2, similar conversions were achieved when using 2.5 mol% of the polymers **5a**, **5b** for the oxidation of nonanol **13b**.

The IBS-derived catalyst system **6** turned out to be markedly more active, compared to **5**: Table 3 demonstrates that 3 mol% of **6** or of its unoxidized precursor **6'** are sufficient to achieve an excellent conversion at 70 °C in aqueous acetonitrile. The required reaction times were notably shorter than with IBX derivative **5**. Under non-aqueous conditions in acetonitrile or nitromethane, the oxidation proceeded slowly, and the weak conversions were attributed to the low solubility of Oxone® (entries 3 and 4). The addition of substoichiometric amounts of *n*Bu₄NHSO₄ as phase transfer catalyst resulted in a tremendous rate enhancement.⁶² In the presence of 0.4 equivalents of *n*Bu₄NHSO₄, it was easily possible to use **6** with extremely low catalysts loadings of 1 mol% and 0.2 mol% to accomplish useful conversions (entries 8 and 9). Under the conditions, a TON up to 455 was reached with regard to each catalytic center (with a TOF of around $5.3 \times 10^{-3} \text{ s}^{-1}$).

The scope of the catalyzed oxidation of secondary alcohols with Oxone® was then explored, using the solid-supported compounds **5c** and **6** under standardized conditions. As summarized in Table 4, various structurally diverse secondary alcohols **13** were examined as substrates using method A [**5c** (5 mol%), Oxone® (1.6 equiv.), 18 h, 70 °C, MeCN–H₂O (7 : 3)] and method B [**6** (5 mol%), Oxone® (1.6 equiv.), *n*Bu₄NHSO₄ (0.4 equiv.), 18 h, 70 °C, MeCN]. We point out that the addition of the phase transfer agent was only required when using non-aqueous conditions (method B); aqueous solvent mixtures (method A) do not require the additive since Oxone® is easily dissolved under the conditions. A general trend was that the performance of the IBS-derived catalyst **6** was superior. In par-

Table 2 Effect of the linker length of precatalysts **5a**, **5b**, **5c**

Entry	Catalyst	13b / 14b ^a
1	5a	1/99
2	5b	3/97
3	5c	3/97

^a Ratio **13b**/**14b** was determined *via* GC-FID (calibrated with stock solutions of **13b** and **14b**) after 18 h.

Table 3 Optimization of the oxidations with IBS-derived catalysts **6** and **6'**

Entry	Catalyst (mol%)	Additive	Solvent	13b / 14b ^a
1 ^b	6' (3)	—	MeCN–H ₂ O (7 : 3)	5/95
2 ^b	6 (3)	—	MeCN–H ₂ O (7 : 3)	3/97
3 ^c	6 (2.5)	—	MeCN	94/6
4 ^c	6 (2.5)	—	MeNO ₂	91/9
5 ^c	6 (2.5)	<i>n</i> Bu ₄ NHSO ₄ (10 mol%)	MeCN	43/57
6 ^c	6 (2.5)	<i>n</i> Bu ₄ NHSO ₄ (10 mol%)	MeNO ₂	63/37
7 ^c	6 (2.5)	<i>n</i> Bu ₄ NHSO ₄ (20 mol%)	MeCN	3/97
8 ^d	6 (1)	<i>n</i> Bu ₄ NHSO ₄ (40 mol%)	MeCN	2/98
9 ^e	6 (0.2)	<i>n</i> Bu ₄ NHSO ₄ (40 mol%)	MeCN	9/91
10 ^d	—	<i>n</i> Bu ₄ NHSO ₄ (40 mol%)	MeCN	94/6

^a Ratio **13b**/**14b** was determined *via* GC-FID (calibrated with stock solutions of **13b** and **14b**). ^b 6 h. ^c 2 h. ^d 4 h. ^e 24 h.



Table 4 Scope of the oxidations with catalysts **6** and **5c**

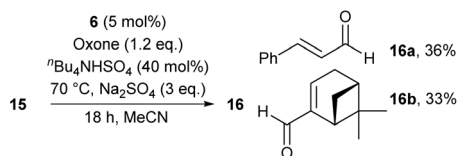
<div>method A or method B</div> <div><div><div><div>R^1</div><div>R^2</div><div>OH</div></div><div>13</div></div><div><div>R^1</div><div>R^2</div><div>O</div></div><div>14</div></div> <div>method A: 5c (5 mol%), Oxone® (1.6 equiv.), 18 h, 70 °C, MeCN-H₂O (7:3) method B: 6 (5 mol%), Oxone® (1.6 equiv.), <i>n</i>Bu₄NHSO₄ (0.4 equiv.), 18 h, 70 °C, MeCN</div>											
Entry	Alcohol 13	#	Ketone 14	Yield [%] ^{a,b}		Entry	Alcohol 13	#	Ketone 14	Yield [%] ^{a,b}	
				A	B					A	B
1		a		79	91 ^c	11		k		76	98
2		b		70	79 ^c	12		l		82	84
3		c		80	85 ^c	13		m		71	97 ^f
4		d		32	65 ^d	14		n		n.r.	89
5		e		71	83	15		o		0	66 ^c
6		f		0	32 ^e	16		p		0	66 ^c
7		g		82	85	17		q		95	96
8		h		84	84	18		r		0	61
9		i		n.r.	98 ^c	19		s		0	78 ^g
10		j		75/58/69/ 82/63	86/79/85/ 86/82	20		t		n.r.	75 ^h

^a Isolated yield. ^b n.r. = experiment was not run. ^c 3 h. ^d 24 h. ^e 72 h in acetone. ^f 90% from benzoin. ^g 18 h in toluene. ^h Determined *via* GC-FID (calibrated with stock solutions of **13t/14t**).

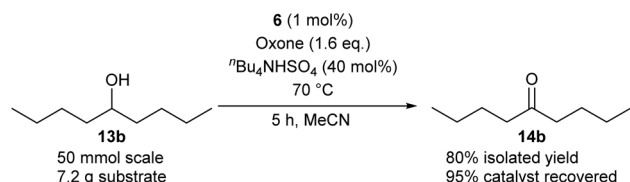
ticular, sterically demanding secondary alcohols (e.g., **13a**, **13d**, **13f** and **13k**) were easier oxidized to the corresponding ketones using method B. The reaction times until full conversion of the starting substrate were also markedly shorter with

6, compared to **5c** (method A). Another advantage of catalyst **6** was that it was employed in a combination with *n*Bu₄NHSO₄ under non-aqueous conditions, allowing to use other solvents than acetonitrile if required due to solubility issues of the sub-





Scheme 3 Oxidation of primary allylic alcohols **15** by use of **6**.



Scheme 4 Oxidation of **13b** on a 50 mmol-scale by use of **6**.

strate. For example, 5 α -cholestan-3 β -ol **13s** was successfully oxidized with Oxone® and **6** in toluene under otherwise identical conditions (entry 19). The main advantage of method A (with **5c**) was the simple work-up protocol consisting only of filtration to remove **5c** and subsequent extraction of the aqueous layer. If the starting material was completely converted, further purification by column chromatography was typically not necessary. In the case of method B (with **6**), an additional filtration over silica for the removal of the tetrabutylammonium salts was required to obtain analytically pure compounds; the phase transfer agent was not recovered.

We point out that primary alcohols also provide oxidation products under the conditions of method B. However, aldehydes were produced in markedly reduced yields and mixed with various products of over-oxidation, thus limiting the use of the catalytic system tremendously. In the case of primary allylic alcohols **15**, it was possible to isolate the corresponding aldehydes in pure form and moderate yields, as outlined for **16a** and **16b** in Scheme 3. Two other limitations of our catalyst system for the oxidation of secondary alcohols were identified in the course of our studies: (1) phenols are not stable under the conditions,^{14,15} and (2) amines are not tolerated due to various competing condensation and oxidation reactions that were not further analyzed.

Method B using IBS-derived polymer **6** is also easily applicable to larger scales, as demonstrated in Scheme 4 for the conversion of secondary alcohol **13b** into ketone **14b**: 50 mmol of **13b** led to the isolation of the desired ketone with 80% yield after 5 h, using only 1 mol% of catalyst **6**. Of note, 95% of the supported catalyst were recovered for re-uses.

Conclusions

We have presented two new catalytic systems **5c** (based on IBX) and **6** (based on IBS) that are outstanding tools for the oxidation of secondary alcohols with Oxone® under ketone formation. The catalysts, derived from hypervalent iodine

reagents linked to a polymer support, are highly active, and a broad scope is demonstrated for both catalysts. However, the catalytic oxidation with **6** proceeded more rapidly and cleanly. After completion of the reaction, the catalysts were recovered through simple filtration, and it was possible to reuse them for multiple times, thus rendering them highly attractive for the objectives of Green Chemistry: recoverable and prepared from readily available starting materials consisting of abundant chemical elements.

Our future studies will make use of the catalyst systems for chemoselective oxidations, by varying the linker units. We will also show in due course how the immobilized catalysts are of use in flow chemical oxidation processes.

Conflicts of interest

There are no conflicts to declare.

Notes and references

- 1 A. Yoshimura and V. V. Zhdankin, *Chem. Rev.*, 2016, **116**, 3328–3435.
- 2 V. V. Zhdankin, *ARKIVOC*, 2009, 1–62.
- 3 V. V. Zhdankin, *J. Org. Chem.*, 2011, **76**, 1185–1197.
- 4 A. Varvoglis, *Tetrahedron*, 1997, **53**, 1179–1255.
- 5 M. Uyanik and K. Ishihara, *Chem. Commun.*, 2009, 2086–2099.
- 6 D. B. Dess and J. C. Martin, *J. Org. Chem.*, 1983, **48**, 4155–4156.
- 7 A. Duschek and S. F. Kirsch, *Angew. Chem., Int. Ed.*, 2011, **50**, 1524–1552.
- 8 T. Wirth, *Angew. Chem., Int. Ed.*, 2001, **40**, 2812–2814.
- 9 V. Satam, A. Harad, R. Rajule and H. Pati, *Tetrahedron*, 2010, **66**, 7659–7706.
- 10 C. Hartmann and V. Meyer, *Ber. Dtsch. Chem. Ges.*, 1893, **26**, 1727–1732.
- 11 M. Frigerio and M. Santagostino, *Tetrahedron Lett.*, 1994, **35**, 8019–8022.
- 12 M. Frigerio, M. Santagostino, S. Sputore and G. Palmisano, *J. Org. Chem.*, 1995, **60**, 7272–7276.
- 13 J. L. F. Silva and B. Olofsson, *Nat. Prod. Rep.*, 2011, **28**, 1722–1754.
- 14 L. Pouységu, D. Deffieux and S. Quideau, *Tetrahedron*, 2010, **66**, 2235–2261.
- 15 S. Quideau, L. Pouységu and D. Deffieux, *Synlett*, 2008, 467–495.
- 16 D. Magdziak, A. A. Rodriguez, R. W. Van De Water and T. R. R. Pettus, *Org. Lett.*, 2002, **4**, 285–288.
- 17 S. Quideau, L. Pouységu, A. Ozanne and J. Gagnepain, *Molecules*, 2005, **10**, 201–216.
- 18 S. F. Kirsch, *J. Org. Chem.*, 2005, **70**, 10210–10212.
- 19 A. Duschek and S. F. Kirsch, *Chem. – Eur. J.*, 2009, **15**, 10713–10717.



- 20 Y. Li, D. P. Hari, M. V. Vita and J. Waser, *Angew. Chem., Int. Ed.*, 2016, **55**, 4436–4454.
- 21 B. Crone and S. F. Kirsch, *Chem. Commun.*, 2006, 764–766.
- 22 T. Harschneck, S. Hummel, S. F. Kirsch and P. Klahn, *Chem. – Eur. J.*, 2012, **18**, 1187–1193.
- 23 K. C. Nicolaou, Y. L. Zhong and P. S. Baran, *J. Am. Chem. Soc.*, 2000, **122**, 7596–7597.
- 24 K. C. Nicolaou, T. Montagnon and P. S. Baran, *Angew. Chem., Int. Ed.*, 2002, **41**, 993–996.
- 25 M. Frigerio, M. Santagostino and S. Sputore, *J. Org. Chem.*, 1999, **64**, 4537–4538.
- 26 J. B. Plumb and D. J. Harper, *Chem. Eng. News*, 1990, 3.
- 27 T. K. Achar, S. Maiti and P. Mal, *RSC Adv.*, 2014, **4**, 12834–12839.
- 28 Z. Liu, Z.-C. Chen and Q.-G. Zheng, *Org. Lett.*, 2003, **5**, 3321–3323.
- 29 J. D. More and N. S. Finney, *Org. Lett.*, 2002, **4**, 3001–3003.
- 30 C. Parmeggiani, C. Matassini and F. Cardona, *Green Chem.*, 2017, **19**, 2030–2050.
- 31 F. Cavani and J. Henrique Teles, *ChemSusChem*, 2009, **2**, 508–534.
- 32 A. P. Thottumkara and T. K. Vinod, *Tetrahedron Lett.*, 2002, **43**, 569–572.
- 33 R. D. Richardson, J. M. Zayed, S. Altermann, D. Smith and T. Wirth, *Angew. Chem., Int. Ed.*, 2007, **46**, 6529–6532.
- 34 L.-Q. Cui, Z.-L. Dong, K. Liu and C. Zhang, *Org. Lett.*, 2011, **13**, 6488–6491.
- 35 S. Seth, S. Jhulki and J. N. Moorthy, *Eur. J. Org. Chem.*, 2013, 2445–2452.
- 36 J. N. Moorthy, K. Senapati, K. N. Parida, S. Jhulki, K. Sooraj and N. N. Nair, *J. Org. Chem.*, 2011, **76**, 9593–9601.
- 37 A. Bredenkamp, F. Mohr and S. F. Kirsch, *Synthesis*, 2015, **47**, 1937–1943.
- 38 I. M. Kumanyaev, M. A. Lapitskaya, L. L. Vasiljeva and K. K. Pivnitsky, *Mendeleev Commun.*, 2012, **22**, 129–131.
- 39 A. Ozanne, L. Pouységu, D. Depernet, B. François and S. Quideau, *Org. Lett.*, 2003, **5**, 2903–2906.
- 40 V. Tesevic and J. A. Gladysz, *Green Chem.*, 2005, **7**, 833–836.
- 41 H. Tohma, A. Maruyama, A. Maeda, T. Maegawa, T. Dohi, M. Shiro, T. Morita and Y. Kita, *Angew. Chem., Int. Ed.*, 2004, **43**, 3595–3598.
- 42 A. Kirschning, M. S. Yusubov, R. Y. Yusubova, K.-W. Chi and J. Y. Park, *Beilstein J. Org. Chem.*, 2007, **3**, 19.
- 43 M. S. Yusubov, R. Y. Yusubova, T. V. Funk, K.-W. Chi, A. Kirschning and V. V. Zhdankin, *Synthesis*, 2010, 3681–3685.
- 44 A. Yoshimura, C. T. Banek, M. S. Yusubov, V. N. Nemykin and V. V. Zhdankin, *J. Org. Chem.*, 2011, **76**, 3812–3819.
- 45 C. A. McNamara, M. J. Dixon and M. Bradley, *Chem. Rev.*, 2002, **102**, 3275–3300.
- 46 M. Mülbaier and A. Giannis, *Angew. Chem., Int. Ed.*, 2001, **40**, 4393–4394.
- 47 N. N. Reed, M. Delgado, K. Hereford, B. Clapham and K. D. Janda, *Bioorg. Med. Chem. Lett.*, 2002, **12**, 2047–2049.
- 48 G. Sorg, A. Mengel, G. Jung and J. Rademann, *Angew. Chem., Int. Ed.*, 2001, **40**, 4395–4397.
- 49 G. Sorg, B. Thern, O. Mader, J. Rademann and G. Jung, *J. Pept. Sci.*, 2005, **11**, 142–152.
- 50 Z. Lei, C. Denecker, S. Jegasothy, D. C. Sherrington, N. K. H. Slater and A. J. Sutherland, *Tetrahedron Lett.*, 2003, **44**, 1635–1637.
- 51 W.-J. Chung, D.-K. Kim and Y.-S. Lee, *Synlett*, 2005, 2175–2178.
- 52 U. Ladziata, J. Willging and V. V. Zhdankin, *Org. Lett.*, 2006, **8**, 167–170.
- 53 H.-S. Jang, Y.-H. Kim, Y.-O. Kim, S.-M. Lee, J. W. Kim, W.-J. Chung and Y.-S. Lee, *J. Ind. Eng. Chem.*, 2014, **20**, 29–36.
- 54 B. M. Bizzarri, I. Abdalghani, L. Botta, A. R. Taddei, S. Nisi, M. Ferrante, M. Passacantando, M. Crucianelli and R. Saladino, *Nanomaterials*, 2018, **8**, 516.
- 55 W.-J. Chung, D.-K. Kim and Y.-S. Lee, *Tetrahedron Lett.*, 2003, **44**, 9251–9254.
- 56 D.-K. Kim, W.-J. Chung and Y.-S. Lee, *Synlett*, 2005, 279–282.
- 57 H.-S. Jang, W.-J. Chung and Y.-S. Lee, *Tetrahedron Lett.*, 2007, **48**, 3731–3734.
- 58 R. R. Karimov, Z.-G. M. Kazhkenov, M. J. Modjewski, E. M. Peterson and V. V. Zhdankin, *J. Org. Chem.*, 2007, **72**, 8149–8151.
- 59 P. C. B. Page, L. F. Appleby, B. R. Buckley, S. M. Allin and M. J. McKenzie, *Synlett*, 2007, 1565–1568.
- 60 R. D. Richardson and T. Wirth, *Angew. Chem., Int. Ed.*, 2006, **45**, 4402–4404.
- 61 F. V. Singh and T. Wirth, *Chem. – Asian J.*, 2014, **9**, 950–971.
- 62 M. Uyanik, M. Akakura and K. Ishihara, *J. Am. Chem. Soc.*, 2009, **131**, 251–262.
- 63 M. Uyanik, R. Fukatsu and K. Ishihara, *Org. Lett.*, 2009, **11**, 3470–3473.
- 64 M. Uyanik, T. Mutsuga and K. Ishihara, *Molecules*, 2012, **17**, 8604–8616.
- 65 L.-Q. Cui, K. Liu and C. Zhang, *Org. Biomol. Chem.*, 2011, **9**, 2258–2265.
- 66 T. Dohi and Y. Kita, *Chem. Commun.*, 2009, 2073–2085.
- 67 S. K. Alla, P. Sadhu and T. Punniyamurthy, *J. Org. Chem.*, 2014, **79**, 7502–7511.
- 68 R. Bikshapathi, P. S. Prathima and V. J. Rao, *New J. Chem.*, 2016, **40**, 10300–10304.
- 69 F. Drouet, G. Masson and J. Zhu, *Org. Lett.*, 2013, **15**, 2854–2857.
- 70 J. N. Moorthy and K. N. Parida, *J. Org. Chem.*, 2014, **79**, 11431–11439.
- 71 A. Schulze and A. Giannis, *Synthesis*, 2006, 257–260.
- 72 A. P. Thottumkara, M. S. Bowsher and T. K. Vinod, *Org. Lett.*, 2005, **7**, 2933–2936.
- 73 A. Yoshimura, K. R. Middleton, M. W. Luedtke, C. Zhu and V. V. Zhdankin, *J. Org. Chem.*, 2012, **77**, 11399–11404.
- 74 A. Yoshimura, K. R. Middleton, A. D. Todora, B. J. Kastern, S. R. Koski, A. V. Maskaeve and V. V. Zhdankin, *Org. Lett.*, 2013, **15**, 4010–4013.



- 75 H. Hussain, I. R. Green and I. Ahmed, *Chem. Rev.*, 2013, **113**, 3329–3371.
- 76 T. Miura, K. Nakashima, N. Tada and A. Itoh, *Chem. Commun.*, 2011, **47**, 1875–1877.
- 77 M. S. Yusubov and V. V. Zhdankin, *Resour.-Effic. Technol.*, 2015, **1**, 49–67.
- 78 S. Hazra, M. Deb and A. J. Elias, *Green Chem.*, 2017, **19**, 5548–5552.
- 79 K.-J. Liu, S. Jiang, L.-H. Lu, L.-L. Tang, S.-S. Tang, H.-S. Tang, Z. Tang, W.-M. He and X. Xu, *Green Chem.*, 2018, **20**, 3038–3043.
- 80 S. Hazra, A. K. Kushawaha, D. Yadav, P. Dolui, M. Deb and A. J. Elias, *Green Chem.*, 2019, **21**, 1929–1934.
- 81 W. Schilling, D. Riemer, Y. Zhang, N. Hatami and S. Das, *ACS Catal.*, 2018, **8**, 5425–5430.
- 82 F. Huber and S. F. Kirsch, *Chem. – Eur. J.*, 2016, **22**, 5914–5918.
- 83 M. L. Tong, F. Huber, E. S. T. Kaptouom, T. Cellnik and S. F. Kirsch, *Chem. Commun.*, 2017, **53**, 3086–3089.
- 84 K. D. Umland, C. Mayer and S. F. Kirsch, *Synlett*, 2014, 813–816.
- 85 P. Klahn, H. Erhardt, A. Kotthaus and S. F. Kirsch, *Angew. Chem., Int. Ed.*, 2014, **53**, 7913–7917.

