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PAPER

An excellent dual recycling strategy for the hypervalent iodine/nitroxyl radical mediated selective oxidation of alcohols to aldehydes and ketones†

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Using a recyclable hypervalent iodine reagent **1**, the authors have constructed versatile and green methods for the hypervalent iodine and nitroxyl radical-mediated selective oxidation of alcohols to aldehydes and ketones. The recyclable reagent **1** having a unique tetraphenyladamantane structure exhibited almost the same reactivity as the ordinary reagent, phenyliodine diacetate (PIDA), in the hypervalent iodine(III)/2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO)-mediated oxidation. For recycling, the reagent **1** could be nearly quantitatively recovered as the reduced tetraiodide **2** by filtration after reaction completion, utilizing the insolubility of the formed **2** in a polar solvent, specifically, methanol. Based on the confirmed reactivity and excellent recycling operation of the reagent **1**, the methodology has been further extended to a greener dual recycling strategy. By combining the recyclable iodine reagent **1** and silica-supported TEPMO catalyst, a variety of alcohols were effectively oxidized to the desired aldehydes, and the two types of used reagent and catalyst, the iodine **1** and immobilized TEMPO **5**, could be separately recovered by an easy workup, and both repeatedly used without any loss of their original activities for at least four cycles.

Introduction

The hypervalent iodine reagent is now widely used as a safe and user-friendly tool in synthetic chemistry for performing environmentally benign oxidations which meet the standards of green chemistry. The inherent low toxicity and ready availability of the hypervalent iodine reagent, combined with its attractive reactivity—similar to those of toxic heavy metal-based oxidants, such as lead, mercury, and thallium elements—have gained it considerable interest among modern synthetic chemists. The initial role of the hypervalent iodine reagent in 20th century organic synthesis seemed to be a safer replacement of the toxic heavy metal oxidants, but this situation rapidly changed with the recent outstanding advances of hypervalent iodine chemistry in developing metal catalyst-free reactions. Consequently, a variety of useful transformations utilizing the mild and selective oxidizing properties of hypervalent iodine reagents have been frequently reported for constructing complex organic molecules, which can now partially replace classical methods that require highly toxic heavy metals as well as other metal catalysts.[1]

The hypervalent iodine atoms can oxidize substrates, with the accompanying formation of more stable monovalent iodine compounds as the driving force. Despite the environmentally benign characteristics of the hypervalent iodine reagent as a green oxidant, a general problem in its use in chemical reactions occurs from the co-production of stoichiometric amounts of iodoarenes. Therefore, several types of recyclable alternatives to hypervalent iodine reagents have already appeared to facilitate the separation of the iodine co-product from the reaction mixture as well as the reuse of the reagents (Fig. 1).[2] Attaching the reagent to an insoluble polymer support, such as polystyrene, is a promising strategy for its recycling, and accordingly, the polymer-supported hypervalent iodine reagents of type **I**, poly(diacetoxyiodo)styrene (PDAIS) and poly[bis(trifluoroacetoxyiodo)]styrene (PBTIS), incorporating phenyliodine diacetate (PIDA) and phenyliodine bis(trifluoroacetate) (PIFA) in their polymer backbones were first independently introduced by Togo *et al.*[3] and Ley *et al.*[4] for synthesis. With recent progress in

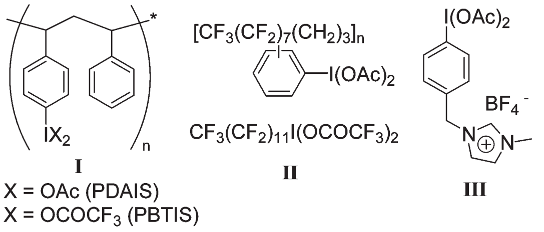

Fig. 1 Representative types of recyclable iodine(III) reagents.

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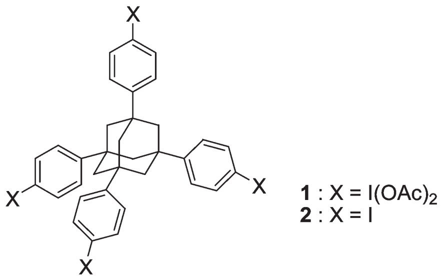
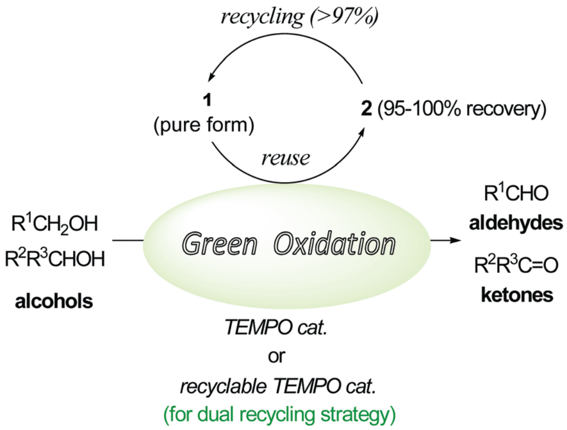


Fig. 2 Adamantane-based recyclable hypervalent iodine reagent.



Scheme 1 Hypervalent iodine/TEMPO mediated greener oxidation of alcohols to aldehydes and ketones.

fluorous chemistry and use of ionic liquid mediums, Gladysz, Qian, and Handy reported the preparation and use of hypervalent iodine compounds bearing type **II** fluorous tags and ionic supports, such as type **III** imidazolium salt, as recyclable.[5,6] Other various useful recyclable reagents have also been systematically reported by Zhdankin and other research groups.[7,8]

Usually, these recyclable hypervalent iodine reagents were solely employed during the reactions, and the combined use with other types of recyclable reagents was rarely considered. This is mainly due to the reasons based on the following two issues:[9] (1) the significant change in reactivity, and (2) difficult separation from each other in the multiple recycling systems. When combining one reagent with another recyclable component, the reactivity change was sometimes too critical to smoothly reproduce the reactions of conventional hypervalent iodine reagents. Furthermore, contamination of the two used reagents frequently occurred during their recovery. As a result, either the hypervalent iodine reagent or the other recyclable component cannot be effectively reused. A recyclable hypervalent iodine reagent satisfying the reactivity requirements and recovery has never been suggested for use in a combined reagent system.

We have previously developed a structurally new recyclable hypervalent iodine reagent **1**, namely, 1,3,5,7-tetrakis[4-(diacetoxyiodo)phenyl]adamantane (Fig. 2), which has a very similar reactivity to that of the conventional PIDA and an easily accomplishable recovery by precipitation, utilizing the insolubility of the tetraiodide **2**, stoichiometrically produced from **1** after the reactions, in common polar solvents.[10–12] The adamantane reagent **1** has high thermal stability (mp (decomp.) 195–196 °C) like PIDA, and is not sensitive to air and moisture. As a continuation of our research studies, a dual recycling strategy which enables effective recovery and reuse of the two types of the reagent and catalyst is now reported based on the advantageous use of the adamantane reagent **1**, for performing the hypervalent iodine and nitroxy radical-mediated green and selective oxidation of alcohols to aldehydes and ketones in high yields (Scheme 1).

Results and discussion

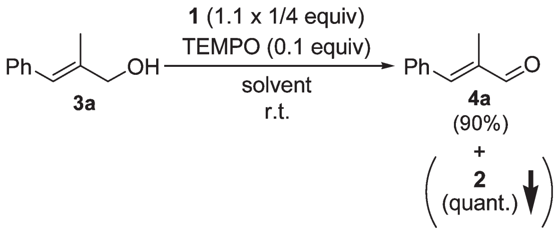
Selective conversions of alcohols to the corresponding partially-oxidized aldehydes and ketones are important and fundamental chemical processes in accordance with the broad utilization of carbonyl compounds in organic synthesis. The recent direction toward environmentally friendly chemical processes has strongly motivated chemists to develop milder, safer, and cleaner synthetic methods using less-toxic oxidants. A survey of the metal-free conditions for the selective oxidation of alcohols has been significantly studied in recent decades, as it appears to surely reduce the undesirable environmental and economical impact caused by the use of a metal oxidant and catalyst.[13] One of the attractive routes to the metal-free selective oxidation of alcohols to aldehydes and ketones includes a method utilizing stable nitroxyl radicals, *e.g.*, 2,2,6,6-tetramethyl-piperidine 1-oxyl (TEMPO), as a mediator.[14a] In the presence of a stoichiometric oxidant, the strategy requires only catalytic amounts (typically, <10 mol%) of TEMPO as an organocatalyst.[14]

For the transformation of natural products and other complex molecules, the combination of hypervalent iodine(III) reagents, that is, PIDA, and TEMPO[15a] (or its derivatives)[15b,c] is specifically known to promote the efficient and chemoselective oxidation of alcohols for access to highly functionalized carbonyl compounds. The oxidative process is mild enough to even be compatible with easily racemized compounds and substrates having many oxidation-sensitive functional groups, such as ethers, sulfides, selenides, allyl, furyl, epoxides, and alkenes, which makes it the promising choice among the other known methods. In addition, this protocol shows a perfect selectivity for the oxidation of primary alcohols to aldehydes, without any over-oxidation to carboxylic acids, in preference to primary alcohols over secondary ones. Upon reaction completion, the only quantitative waste was iodobenzene, a PIDA-derived co-product. To facilitate isolation of the carbonyl product as well as removal and recovery of the stoichiometric organoiodide, several kinds of recyclable hypervalent iodine reagents have already been envisioned for use.[16] The polymer-supported iodine reagent was first selected as the recyclable alternative to PIDA in the TEMPO-mediated oxidation of alcohols.[16a] However, as claimed by Zhdankin *et al.*[7a] and other groups,[5,6] including our own,[10] the polymer reagents are usually much less reactive than PIDA due to steric hindrance of the iodine(III) sites in the polymer structures and the low solubility in various solvents. Moreover, degradation of the resin frequently occurred when it was repeatedly used, which made the maintenance of the original reactivity of the polymer reagents difficult, thus resulting in the limited availability for their recycling and the somewhat unsatisfactory overall recycling yield. Hence, the efforts to develop more suitable types of recyclable hypervalent iodine reagents have recently appeared.[16b,c]

Based on these criteria, we also aimed to further establish a greener hypervalent iodine and TEMPO-mediated alcohol oxidation strategy with an improved overall recycle yield based on the sustainable use of our recyclable hypervalent iodine reagent **1**.

Selective oxidation of alcohols to aldehydes and ketones using the recyclable adamantane reagent 1

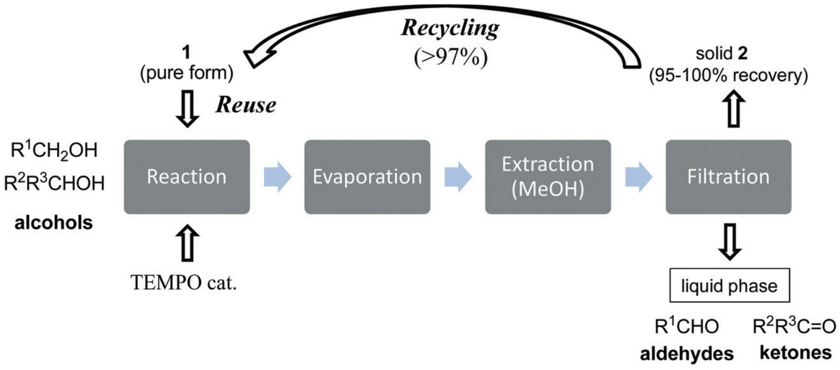
We first confirmed the reactivity with regard to the recyclable hypervalent iodine reagent **1** for the selective oxidation of primary alcohol **3a** to the corresponding aldehyde **4a** under the regulatory conditions using the TEMPO catalyst (Scheme 2). The test reaction was carried out in dichloromethane since the chlorinated solvent is most popularly employed for the PIDA/TEMPO-mediated oxidation of alcohols in previous studies that excludes the solubility problem of some substrates, otherwise polar solvents, such as acetonitrile, are potentially applicable (see the results in ESI†).[14,15] Thus, after dissolving the adamantane reagent **1** (1.1 × 1/4 equiv. relative to the alcohol **3a**, which corresponds to 110 mol% I(III)) in dichloromethane,[17] the oxidation of **3a** was demonstrated in the presence of the TEMPO catalyst (10 mol%) at room temperature in an open flask without any particular precautions and optimization, producing the desired partially-oxidized aldehyde **4a** in 90% yield. No over-oxidized carboxylic acid was detected during the reaction. At the same concentration of the substrate **3a** (0.2 M), the PIDA/TEMPO combination[14a] produced **4a** in a similar yield (92%) for the same reaction time (3 h). Similar to other investigations, our consensus of the high reactivity of **1** as the recyclable equivalent of PIDA was supported even for this type of alcohol oxidation by this reactivity check and comparison of the reagents. Nonetheless, the reaction hardly occurred in the absence of the TEMPO catalyst for both the adamantane reagent **1** and PIDA.[18]



Scheme 2 TEMPO-mediated selective oxidation of primary alcohol **3a** to aldehyde **4a** with the adamantane reagent **1**.

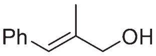
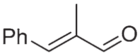
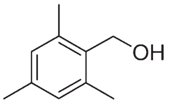
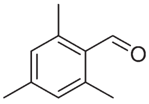
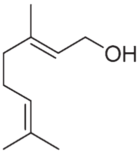
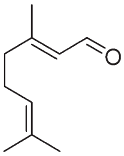
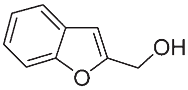
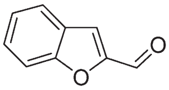
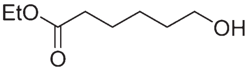
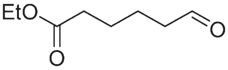
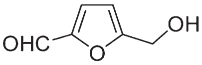
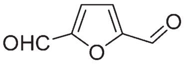
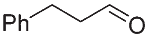
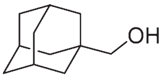
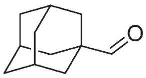
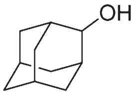
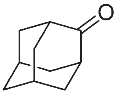
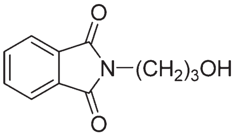
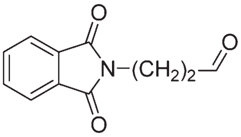
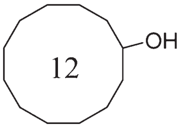
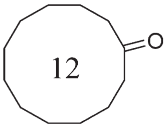
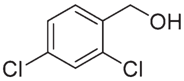
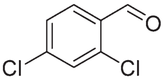
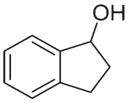
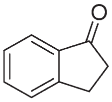
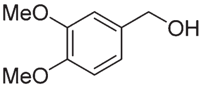
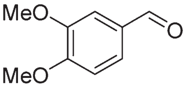
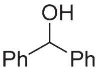
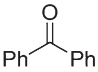
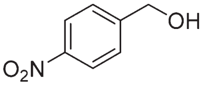
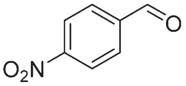
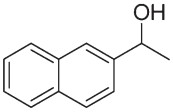
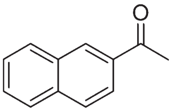
On the other hand, the recovery of **1** could be conducted by utilizing the insolubility of the co-produced tetraiodide **2** in a polar solvent, specifically, methanol (see Scheme 3).[19] The operation usually started with the removal of the used solvent. Thus, the flask containing the homogeneous reaction mixture was attached to a rotary evaporator, and the solvent was removed. To the resulting oily mixture, methanol was added to extract the aldehyde **4a**, while the highly symmetrical and hardly soluble tetraiodide **2** simultaneously precipitated as a powder. The heterogeneous solution was then filtered, and the solid on the filter was washed several times with small amounts of methanol to nearly quantitatively recover **2**. From the filtrate, a crude **4a** with small amount of impurities and TEMPO was obtained, which was further purified by short column chromatography on silica gel. The pure **4a** was thus obtained, and the co-produced **2** could be easily recovered from the reaction mixture by a simple solid/liquid separation technique (*i.e.*, filtration). The latter was then recycled for a second run as the initial adamantane reagent **1** after the treatment of the recovered **2** with *m*-chloroperbenzoic acid in acetic acid (see Experimental section).[10] Consequently, the present method should be a facile, simple, clean, and convenient method for the recycling of the hypervalent iodine reagent **1** as well as for the isolation of the aldehyde **4a**.

With this generalized procedure, a number of alcohols including the representative substrates reported in the conventional PIDA/TEMPO-mediated oxidation[14,15] were evaluated using the present recycle method with **1**. The same experimental procedure for all the substrates in Table 1 led to the successful production of the expected partially oxidized aldehydes **4a–m** from the corresponding primary alcohols **3a–m** or the ketones **4n–r** from the secondary alcohols **3n–r** at room temperature. Less than trace amounts of carboxylic acids were produced in all cases. The substrate versatility and availability of the functional groups were not dramatically changed to those of the ordinary method using the PIDA/TEMPO combination.[14,15a] Thus, the adamantane reagent **1** could promote the formation of the target aldehydes **4b** and **4c** from geraniol **3b**[15a] and an aliphatic alcohol **3c**[14] in comparable efficiencies to that of PIDA (entries 2 and 3). Several other aliphatic and benzylic alcohols having electron-



Scheme 3 Recycling procedure for the adamantane reagent **1**.

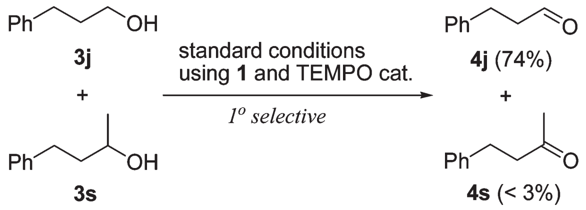
Table 1 Green and selective oxidation of alcohols **3** using a recyclable hypervalent iodine reagent **1** and TEMPO catalyst[a]

Entry	Alcohols (**3**)	Carbonyl compound (**4**), yield	Entry	Alcohols (**3**)	Carbonyl compound (**4**), yield
1	 **3a**	 **4a**, 90%	10	 **3j**	 **4j**, 81%
2	 **3b**	 **4b**, 93%	11	 **3k**	 **4k**, 83%
3	 **3c**	 **4c**, 92%	12	 **3l**	 **4l**, 60%
4	 **3d**	 **4d**, 73%	13	 **3m**	 **4m**, 83%
5	 **3e**	 **4e**, 90 %	14	 **3n**	 **4n**, 72%
6	 **3f**	 **4f**, 71%	15	 **3o**	 **4o**, 91%
7	 **3g**	 **4g**, 80%	16	 **3p**	 **4p**, 89%
8	 **3h**	 **4h**, quant.	17	 **3q**	 **4q**, 85%
9	 **3i**	 **4i**, 83%	18	 **3r**	 **4r**, quant.

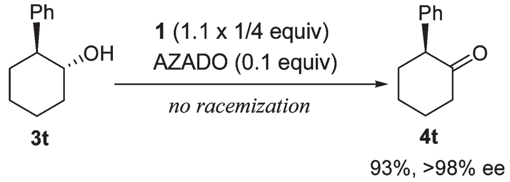
[a] The reactions were performed overnight using the adamantane **1** (1.1 × 1/4 equiv. relative to alcohol **3**) in dichloromethane at room temperature in the presence of TEMPO catalyst (10 mol%). See the general procedure in Experimental section. The provided yields are determined based on the alcohols **3** used.

rich and deficient aromatic moieties were converted to the corresponding aldehydes **4c–j** in satisfactory yields (entries 3–10). As the functional groups, several oxidation-sensitive alkenes (entries 1 and 2), electron-rich aromatic and heteroaromatic rings (entries 8, 11, and 12), and alkyne (entry 13) were well tolerated. Both the aliphatic and aromatic secondary alcohols **3n–r** could be smoothly oxidized (entries 14–18). In comparison to PIDA, no significant decrease in the reaction rate and product yield were observed in each substrate case when using **1**, except for entry 12 (for PIDA, 72% of the product **4l** was obtained). In addition, 95–100% of the reagent was constantly recovered as the tetraiodide **2** from the reaction mixtures. The reactions were performed overnight to completely decompose **1** to **2**, although most of the starting alcohols **3** disappeared within a few hours in each case.

The conventional hypervalent iodine/nitroxyl radical-mediated oxidation protocol is known to be mild enough to provide pronounced chemoselectivities of the functional groups under the standard reaction conditions.[14,15] The almost perfect preference of primary alcohols in the competitive oxidation, even in the presence of structurally close secondary alcohols, is quite noteworthy.[15a] It became clear that a similar chemoselective nature was now maintained under the conditions with our recyclable iodine reagent **1** (Scheme 4). In fact, a cross-over experiment for a 1 : 1 mixture of 3-phenylpropanol **3j** and 4-phenyl-2-butanol



Scheme 4 Cross-over experiment: selectivity between primary and secondary alcohols.



Scheme 5 Oxidation of optically active alcohol **3t** to an enolizable ketone **4t**; AZADO = 2-azaadamantane-*N*-oxyl.

3s using **1** in the presence of 10 mol% TEMPO resulted in the exclusive consumption of the primary alcohol **3j** leading to the corresponding aldehyde **4j**, whereas the ketone **4s** from the secondary alcohol **3s** was produced in less than a measurable amount (it was also judged by confirming a 97–98% recovery of the secondary alcohol **3s**). The conventional PIDA could also exclusively deliver a 79% yield of the aldehyde **4j**.

Another important benefit of the present methodology is exemplified by the non-racemic oxidation of an optically active alcohol **3t** to the enolizable ketone **4t** (Scheme 5). With the adamantane reagent **1**, oxidation of **3t** could proceed in good yield without any decrease in the enantiomeric excess values of the product. Due to the low reactivity of TEMPO toward **3t**, the less hindered class of nitroxyl radicals, 2-azaadamantane-*N*-oxyl (AZADO),[15b,c] was used at this point as a specific catalyst for **3t**. Under such conditions, no evidence of racemization was found during the course of the reaction.[20]

As stated above, the adamantane reagent **1** is a promising recyclable alternative to PIDA that can provide valuable advantages over the conventional hypervalent iodine/nitroxyl radical mediated oxidation of alcohols. We suppose that the remarkably high reactivity of **1** among the recyclable reagents should be responsible for the well-defined tetrahedral structure at which the introduction sites of the four iodine(III) functions are fully controlled. Based on an X-ray crystallographic analysis,[21] the interatomic distance between the iodine(III) atoms of **1** is about 13 Å, and thus, these iodine sites are sufficiently separated from each other and do not interfere during the reactions. Based on this molecular design and its high solubility toward organic solvents, **1** showed an excellent ability that is compatible with PIDA in the reactions. Furthermore, no degradation of the molecules of **1** and **2** was observed in the overall single recycling (recovery, reactivation, and reuse) in Scheme 3, because the reagent **1** and tetraiodide **2** are very stable under oxidative conditions.[22]

Nevertheless, recovery of the nitrosyl radical, *i.e.*, TEMPO, still remained untackled at this point, which is the next challenge to be addressed in our methodology.

Regarding recycling of nitroxyl radical

To facilitate the removal and reuse of the nitroxyl radicals, continuous efforts have been made to provide a recyclable alternative to TEMPO and its derivatives.[23] These approaches for the oxidation of alcohols using a hypervalent iodine reagent as a stoichiometric oxidant include the nitroxyl radicals attached to the soluble or insoluble polymers,[9,24a,b] the fluorous tags,[24c,d] and the ionic supports.[24e,f] The many successes of the construction of practical and ecological reaction systems with these recyclable nitroxyl radicals have recently received considerable attention. Such examples might be a good counterpart for PIDA, but these were hardly employed for the recyclable hypervalent iodine reagent. In a combination of the polymer-supported iodine reagent, PDAIS,[9] the immobilized TEMPO catalyst exhibited a significant decrease in reactivity, and an excess amount (∼2 equiv.) of PDAIS was needed to complete oxidation. Moreover, the separation of the employed polymer-supported iodine reagent and nitroxyl radical was quite difficult once mixed. Hence, the release of the stoichiometric amounts of iodobenzene as waste or the poorer recovery of the reagent and catalyst are serious drawbacks when using the recyclable nitroxyl radicals as catalysts in this methodology.[25]

These facts certainly inspired us to consider the opportunity to use the adamantane reagent **1** as a specific counterpart of the recyclable TEMPO catalyst for realizing a more efficient and greener strategy based on the dual recycling of the hypervalent iodine reagent as well as the nitroxyl radical in the selective oxidation of alcohols **3** to aldehydes **4**.

Combination of the recyclable hypervalent iodine reagent 1 and silica-supported TEMPO catalyst 5: a dual recycling strategy for greener oxidation

The adamantane reagent **1** and its recoverable form, the tetraiodide **2**, are both soluble during the reactions, and thus the removal and recovery of the catalyst nitroxyl radical based on the solid/liquid phase separation from the reaction mixture was anticipated. The catalyst separation can be easily accomplished by simple filtration by utilizing the insoluble nitroxyl radical, while the recovery of **1** from the filtrate is followed by the described workups in Scheme 3. For this purpose, we have been particularly interested in the use of the silica-supported TEMPO **5**[26,27] as a suitable heterogeneous counterpart of the soluble reagent **1** (Fig. 3). The immobilized silica reagents having nitroxyl radical sites on the silica surface areas were originally introduced as more reactive and stable alternatives to the corresponding polystyrene analogues of TEMPO. These types of insoluble nitroxyl radicals, to our knowledge, were first introduced by Tsubokawa *et al.*[27a] during the stage of alcohol oxidation, and those with commercial applications, having a relatively high degree of loading (>0.7 mmol g^{-1}), are now readily available.

As we supposed, the replacement of regular TEMPO with the insoluble silica-supported TEMPO was successful. The yield of the products was maintained—in most cases under the same reaction conditions—since the reactivity of **1** is similar to that of the conventionally used PIDA. Nonetheless, the reaction usually took a longer time than the soluble TEMPO due to the heterogeneous nature of **5** when the same molar amount of the catalyst was used. The reaction rates for **1** and PIDA when using the immobilized **5** were nearly identical. Thus, we decided to use 20 mol% of the catalyst **5** which would not negatively affect the net reaction outcomes for the dual use of the recycling of **1** and **5**.[28] Considering the excellent reusability of the immobilized TEMPO **5** (see below) (recyclability, selectivity, *etc.*) and efficiencies of the alcohol oxidation, rather the reactions under such conditions including the high quantity of the catalyst sometimes faced the obvious enhancement of the product yields. The reactions of the alcohols **3** in Table 1 proceeded smoothly without problems, and Table 2 represents the results of the examined oxidations to the aldehydes. No tedious pre-treatment of the silica TEMPO **5** in the solvent for swelling was required. The reactions could thus be initiated by just adding **5** to the homogeneous mixture of **1** and **3** or adding the readily soluble **1** to the heterogeneous solution of **5** and **3**.

We could readily develop a facile operation procedure based on the solid/liquid separation strategy for isolation of **1** and insoluble **5** from the reaction mixtures. Scheme 6 schematically illustrates the experimental procedure. First, the used insoluble **5** could be absolutely removed from the heterogeneous reaction mixtures by filtration, and directly reused for the next run after rinsing. From the homogeneous liquid phase, the used **1** could be recovered as the tetraiodide **2** according to the already mentioned general procedure in Scheme 3 involving the second solid/liquid separation. Indeed, the use of the silica-supported TEMPO catalyst and the adamantane reagent satisfactorily met the purpose of the dual recycling of the hypervalent iodine reagent and catalyst nitroxyl radical with a high degree of recyclability (95–100% recovery of **1** and quantitative recovery of **5**). Also, it should be noted that we can save the effort of isolation of the aldehyde **3** in the dual recycling system compared to the method of using the soluble TEMPO. In addition, the procedure can be carried out without the difficulty of removing the TEMPO.

To our delight, the reuse of both the adamantane reagent **1** and immobilized TEMPO **5** was successful using the efficient

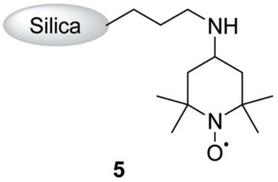


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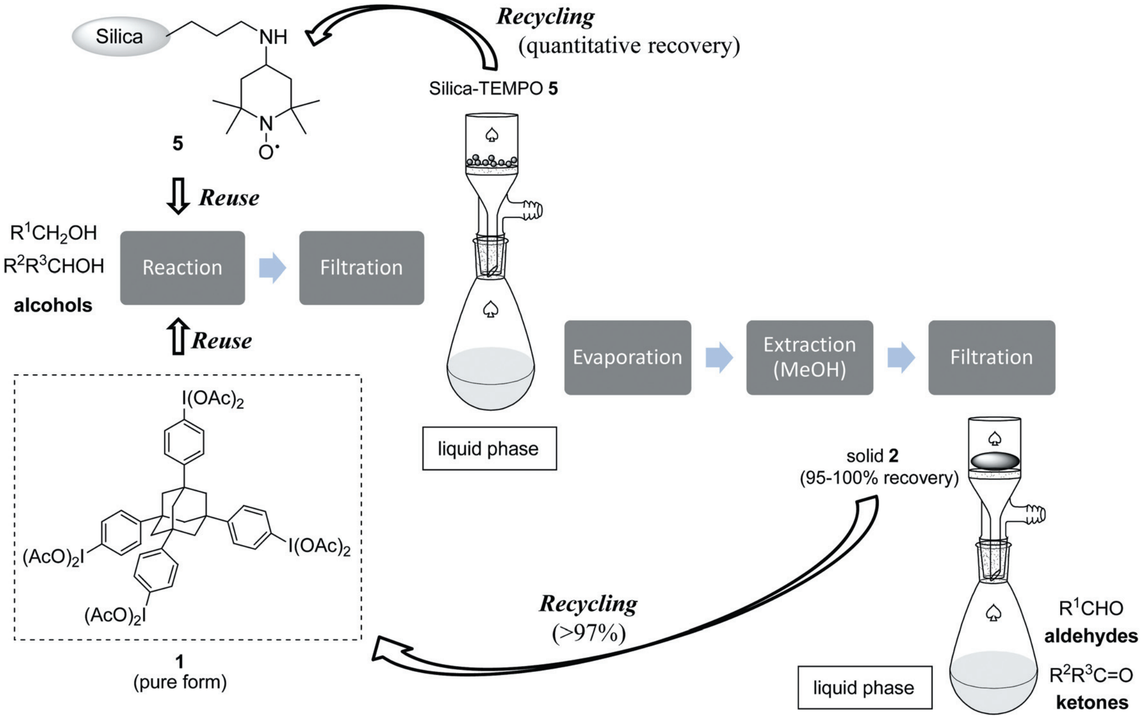
Fig. 3 Silica-supported recyclable TEMPO catalyst **5**.

Table 2 A combined use of two recyclable reagents, **1** and silica-supported TEMPO **5**: selected examples of greener aldehyde synthesis[a]

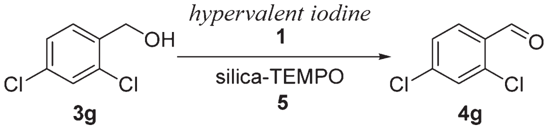
Entry	Alcohol (**3**)	Aldehyde (**4**)	Yield (%)
1	**3a**	**4a**	88
2	**3b**	**4b**	83
3	**3c**	**4c**	76
4	**3f**	**4f**	78
5	**3g**	**4g**	85
6	**3h**	**4h**	96
7	**3i**	**4i**	75
8	**3j**	**4j**	72
9	**3k**	**4k**	93

[a] The results were obtained from the reaction using the adamantane **1** (1.1 × 1/4 equiv.) and calcd 20 mol% of the silica-supported TEMPO catalyst **5** in dichloromethane overnight at room temperature.



Scheme 6 Schematic drawing of dual recycling strategy of hypervalent iodine reagent **1** and silica-supported TEMPO **5**.

Table 3 Repeated uses of the two recyclable reagents[a]



(1)

Entry	Reuse	Yield (%)
1	—	85
2	1	93
3	2	90
4	3	88
5	4	86

[a] The reactions were repeated using the (reused) adamantane **1** (1.1 × 1/4 equiv. relative to the primary alcohol **3g**) and (reused) silica-supported TEMPO catalyst **5** (calcd 20 mol%) at room temperature for 12 hours. Isolated yield of the aldehyde **4g** is indicated for each run.

dual recycling strategy. Reuse of the recovered **1** and **5** was evaluated for at least four cycles using the alcohol **3g** as a model substrate (eqn (1), Table 3), which suggests no remarkable loss in the activity of the reagent and catalyst during alcohol oxidation and their recycling. The yields and reaction rates after the subsequent recyclings were almost constant for both the reagent and catalyst, proving the structure of the adamantane reagent **1** and the amine linkage of the immobilized TEMPO catalyst **5** are sufficiently stable to withstand repeated uses. The reused reagent and catalyst did not add any harmful impurities to the reaction. The aldehyde **4g** was thus selectively produced by the reused materials, and over-oxidation of the product **4g** was neglectable even after the prolonged stirring of the reaction mixtures for 24 h.

At this stage, the aim to realize a dual recycling strategy for the selective oxidation of alcohols to aldehydes and ketones that can separately recover the hypervalent iodine reagent and nitroxyl radical has been accomplished along with high levels of recycling efficiency.

Conclusions

In this paper, we have clarified the excellent ability of the adamantane reagent **1**[10] as a recyclable hypervalent iodine reagent in the universally used nitroxyl radical-catalyzed oxidation of alcohols. The series of versatile and green oxidation systems using **1**, that consist of combination of (1) TEMPO catalyst, and (2) insoluble silica-supported TEMPO **5**, have been developed for the selective oxidation of alcohols **3** to aldehydes or ketones **4**, in which the recyclable reagent **1** having the well-defined tetrahedral structure showed a promising reactivity similar to the classically used phenyliodine diacetate, PIDA. In the latter combined case, notably, both **1** and **5** could be recovered and isolated on the basis of practical operation techniques, *i.e.*, successive solid/liquid separations, and the only waste material released into the environment from the reactions was then the nontoxic acetic acid.

Upon recycling, **1** can be typically recovered in 95–100% quantities as a fine solid *via* filtration by utilizing the insolubility of the co-produced tetraiodide **2** that was formed from **1** after the reactions in the polar solvent, methanol. The tetraiodide **2** was then recycled for a second run as the initial adamantane form **1** after the treatment with *m*-chloroperbenzoic acid in acetic acid (see Experimental section). No degradation of the molecule was detected for the reagent **1** during the reactions and the regeneration step. Thus, the repeated use of **1** as well as **5** was possible for at least four cycles since the recovered materials maintained high reactivity.

As highlighted in the dual recycling strategy, the utility of **1** for the hypervalent iodine/nitroxyl radical-mediated selective oxidation of alcohols to aldehydes and ketones has been first demonstrated in this study. It is beneficial to use **1** in hypervalent iodine-mediated oxidation in terms of reactivity, solubility, removal, recovery, and recycling, for extending the methodology to dual recycling. Considering the versatility and salient features of **1**,[10,11] the dual recycling strategy is not only a reliable choice for alcohol oxidation, but also a model case for the construction of other potential multi-component recyclable reagent systems in further extended research studies. Hence, we believe that this demonstration provides a useful concept and general guideline of green chemistry for oxidation using recyclable hypervalent iodine reagents.[29]

Experimental

Preparation of the recyclable hypervalent iodine reagent 1: the regeneration step from the recovered tetraiodide 2

To a stirred solution of the (recovered) tetraiodide **2**[30] (1.42 g, 1.5 mmol) in dichloromethane (150 mL) and acetic acid (150 mL) was added *m*-chloroperbenzoic acid (*m*CPBA) (*ca.* 69% purity, 3.12 g, 18 mmol) at room temperature. The mixture was stirred for 12 h under the same reaction conditions until the cloudy solution became clear. The resultant mixture was filtered, and dichloromethane was removed from the filtrate using a rotary evaporator. Hexanes were added to the residue to precipitate 1,3,5,7-tetrakis[4-(diacetoxyiodo)phenyl]adamantane **1**. After filtration, the crude **1** was washed several times with the hexanes, and then dried *in vacuo* to give **1** (2.09 g, 97%) as a white solid.

1,3,5,7-Tetrakis[4-(diacetoxyiodo)phenyl]adamantane (1).[10a] Colorless crystal; mp (decomp.) 195–196 °C (from AcOH–dichloromethane-hexanes by vapor diffusion method); ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.01 (s, 24H), 2.20 (s, 12H), 7.56 (d, J = 8.7 Hz, 8H), 8.09 (d, J = 8.7 Hz, 8H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ = 20.4, 39.6, 46.4, 119.5, 127.7, 135.2, 151.9, 176.5 ppm; elemental analysis: calcd for $C_{50}H_{52}I_4O_{16}\cdot 2H_2O$: C 41.34, H 3.89, I 34.95; found: C 41.30, H 3.70, I 35.03.

Typical procedure for TEMPO catalyzed oxidation of alcohols 3 to aldehydes 4 using the recyclable hypervalent iodine reagent 1 (Table 1)

The reagent **1** (77.9 mg, 0.22 × 1/4 mmol) was added to a dichloromethane solution (1 mL) including the alcohol **3**

(0.20 mmol) and catalytic amount of TEMPO (3.1 mg, 0.02 mmol). The reaction mixture was stirred until the alcohol **3** was no longer detectable by TLC. After removal of the solvent using a rotary evaporator, methanol (5 mL) was added to the residue to precipitate the tetraiodide **2**. After filtration, the crude **2** on the filter was washed several times with small amounts of methanol, and the residue was nearly quantitatively recovered as the pure tetraiodide **2**. From the filtrate, the crude product **4** was obtained after evaporation, which was purified by short column chromatography on silica gel to give the pure aldehyde or ketone.

Cross-over experiment: selective synthesis of aldehyde 4j from primary alcohol 3j in the presence of a secondary alcohol 3s (Scheme 4)

The reagent **1** (88.5 mg, 0.25 × 1/4 mmol) was added to a dichloromethane solution (1.2 mL) containing the alcohol **3j** (34.0 mg, 0.25 mmol), 4-phenyl-2-butanol **3s** (37.5 mg, 0.25 mmol), and a catalytic amount of TEMPO (3.9 mg, 0.025 mmol) at 0 °C. The reaction mixture was stirred until the alcohol **3j** was no longer detectable by TLC. Workup of the reaction mixture and recovery of the tetraiodide **2** were conducted according to the typical procedure already described. From the filtrate, the crude product **4j** and remaining 4-phenyl-2-butanol **3s** were obtained as a mixture after evaporation, which was separated by short column chromatography on silica gel to give the pure aldehyde **4j** in 73% yield with a 97% recovery of the 4-phenyl-2-butanol **3s**.

Non-racemic synthesis of enolizable ketone 4t (Scheme 5)

The enolizable ketone **4t** was obtained in the optically pure form from the corresponding alcohol **3t** by a procedure similar to that described for the alcohols in Table 1 using AZADO instead of TEMPO. The optical purity of the obtained ketone **4t** was measured by HPLC (Daicel OD column, hexane–*i*-PrOH = 95 : 5, flow rate 0.8 mL min^{-1}, t_R = 10.0 min. [(*S*)-(–)-enantiomer].[20]

General experimental procedure for green oxidation of alcohols using a combination of the recyclable hypervalent iodine reagent 1 and supported TEMPO catalyst: a dual recycling strategy (Tables 2 and 3)

The reagent **1** (77.9 mg, 0.22 × 1/4 mmol) was added to a stirred solution of the alcohol **3** (0.20 mmol) and catalytic amount of silica-supported TEMPO **5**[26] (65.6 mg, 0.04 mmol) in dichloromethane (1 mL) at room temperature. After consumption of the alcohol **3**, the insoluble TEMPO **5** was recovered in a quantitative amount by filtration after washing several times with dichloromethane. After removal of the solvent from the filtrate, methanol (5 mL) was added to the residue to precipitate the tetraiodide **2**. After filtration, the crude **2** was washed several times with small amounts of methanol, and the residue on the filter was nearly quantitatively collected as the pure **2**. From the filtrate, the crude product **4** was obtained after evaporation, which was purified by short column chromatography on silica gel to give the pure aldehyde or ketone if required.

Reusability of the recovered adamantane reagent **1** and silica-supported TEMPO catalyst **5** for the alcohol oxidation was evaluated at least four times using the alcohol **3g** as a model substrate in the dual recycling strategy (see Table 3).

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17 The adamantane reagent **1** is readily soluble in chlorinated solvents (dichloromethane, chloroform, *etc.*) as well as many polar solvents (for examples, methanol, acetonitrile, and fluorinated alcohols). See our ref. 11.

18 We also evaluated the reactivity of a related reagent having the tetraphenylmethane core in ref. 10*b* for the oxidation of the alcohol **3a**. This adamantane analogue also worked well as an effective oxidant in terms of the yield of the product **4a** as well as the recovery, however, a high amount of solvent was needed to dissolve the alternative reagent and to make the homogeneous conditions. Thus, we specifically selected the adamantane reagent **1** in this study.

19 The measured solubilities of the tetraiodide **2**, a reduced form of the adamantane reagent **1**, in several (mixed) solvents at 25 °C are as follows: 0.04 mg mL^{-1} (methanol); 0.08 mg mL^{-1} (isopropanol); 0.26 mg mL^{-1} (acetonitrile); 5.3 mg mL^{-1} (ethyl acetate); 6.0 mg mL^{-1} (acetone); 0.06 mg mL^{-1} (methanol–ethyl acetate = 10:1); 0.08 mg mL^{-1} (methanol–ethyl acetate = 5:1); 0.42 mg mL^{-1} (methanol–ethyl acetate = 1:1).

20 We have confirmed the lack ofracemization of the product by comparing the obtained chiral **4t** to the authentic sample in ref. 11*g*.

21 CCDC 232058 contains crystallographic data of the adamantane reagent **1**.

22 The polymer-supported reagents of type **I** in Scheme 1 are not stable under various oxidative conditions. The degradation of the resin often occurred when they were repeatedly used, which caused a loss of activity and lower overall recycling efficiency. See ref. 7*a* and 10.

23 (*a*) S. Weik, G. Nicholson, G. Jung and J. Rademann, *Angew. Chem., Int. Ed.*, 2001, **40**, 1436.; For a review, see:R. A. Sheldon, I. W. C. S. Arends, G.-J. ten Brink and A. Dijksman, *Acc. Chem. Res.*, 2002, **35**, 774.

24 For the use of recyclable TEMPO catalysts in alcohol oxidation with PIDA, see ref. 9 and the following papers: (*a*) G. Pozzi, M. Cavazzini, S. Quici, M. Benaglia and G. Dell'Anna, *Org. Lett.*, 2004, **6**, 441; (*b*) M. A. Subhani, M. Beigi and P. Eilbracht, *Adv. Synth. Catal.*, 2008, **350**, 2903; (*c*) G. Pozzi, M. Cavazzini, O. Holczknecht, S. Quici and I. Shepperson, *Tetrahedron Lett.*, 2004, **45**, 4249; (*d*) O. Holczknecht, M. Cavazzini, S. Quici, I. Shepperson and G. Pozzi, *Adv. Synth. Catal.*, 2005, **347**, 677; (*e*) W. Qian, E. Jin, W. Bao and Y. Zhang, *Tetrahedron*, 2006, **62**, 556; (*f*) A. Fall, M. Sene, M. Gaye, G. Gomez and Y. Fall, *Tetrahedron Lett.*, 2010, **51**, 4501.

25 A combination of the ion-supported hypervalent iodine reagent and TEMPO catalyst was reported for the oxidation of the alcohols in ref. 24*e*. However, the perfect separation of the two ion-supported reagent and catalyst was difficult in principle as seen in ref. 9, and such a method typically caused partial contamination of the reagent and catalyst during their recovery. The recycling efficiency regarding the quantity of the recovered iodine reagent, a result of its repeated use, and isolation of the used TEMPO catalyst were not clearly determined. In addition, re-preparation of the ion-supported iodine reagent could proceed in only a 78% yield, which corresponds to a 22% loss of the reagent for the next overall recycling step.

26 Commercially available from Aldrich Co. Ltd (catalog No. 576344, 120–230 mesh, extent of labeling: 0.7 mmol g^{-1} loading).

27 (*a*) N. Tsubokawa, T. Kimoto and T. Endo, *J. Mol. Catal. A: Chem.*, 1995, **101**, 45; (*b*) A. Heeres, H. A. van Doren, K. F. Gotlieb and I. P. Bleeker, *Carbohydr. Res.*, 1997, **299**, 221; (*c*) C. Bolm and T. Fey, *Chem. Commun.*, 1999, 1795; (*d*) R. Ciriminna, M. Pagliaro, J. Blum and D. Avnir, *Chem. Commun.*, 2000, 1441; (*e*) D. Brunel, F. Fajula, J. B. Nagy, B. Deroide, M. J. Verhoef, L. Veum, J. A. Peters and H. van Bekkum, *Appl. Catal., A*, 2001, **213**, 73.

28 An alternative solution for improving the reaction rate is the use of the more reactive nitroxyl radical instead of the silica-supported TEMPO **5**. Other insoluble TEMPO catalysts onto silica, such as Silia*Cat*® TEMPO (M. Pagliaro, D. Avnir, J. Blum and G. Deganello, *U.S. Patent*, 6,797,773 B1, 2004; A. Michaud, G. Gingras, M. Morin, F. Beland, R. Ciriminna, D. Avnir and M. Pagliaro, *Org. Proc. Res. Dev.*, 2007, **11**, 766.), was applicable for the adamantane oxidant **1** to reduce the amount of the catalyst.

29 Recently, an elegant method for catalytic use of the hypervalent iodine reagent using a TEMPO-hybrid oxidant has been reported to produce carboxylic acids from primary alcohols. This method only produced carboxylic acids, rather than aldehydes. See: T. Yakura and A. Ozono, *Adv. Synth. Catal.*, 2011, **353**, 855.

30 (*a*) H. Newman, *Synthesis*, 1972, 692; (*b*) E. B. Merkushev, N. D. Simakhina and G. M. Koveshnikova, *Synthesis*, 1980, 486; (*c*) V. R. Reichert and L. J. Mathias, *Macromolecules*, 1994, **27**, 7015; (*d*) L. J. Mathias, V. R. Reichert and A. V. G. Muir, *Chem. Mater.*, 1993, **5**, 4.