Orthogonally protected 1,2-diols from electron rich alkenes using metal-free olefin syn-dihydroxylation

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ABSTRACT: A new method for the stereoselective metal-free syn dihydroxylation of electron rich alkenes is reported, involving reaction with TEMPO/IBX in trifluoroethanol (TFE) or hexafluoroisopropanol (HFIP), and the addition of a suitable nucleophile. Orthogonally protected syn 1,2-diols were obtained with high levels of diastereoselectivity; and these products were selectively deprotected and selectively functionalized into synthetically useful compounds.

Olefin dihydroxylation is one of the most powerful tools in organic chemistry. The functionalization of vicinal carbons via double C-O bond formation can be achieved in a single step and established dihydroxylation methods give high levels of stereoselectivity. In particular, OsO₄ has been used extensively in organic synthesis for the syn dihydroxylation of alkenes, although its toxic nature is well recognized.

The development of new methods to overcome the use of toxic reagents is of great interest and many groups have been devoted to finding new metal-free dihydroxylation procedures. Peroxides, hydroxamic acids and hypervalent iodine reagents used in stoichiometric amounts give good yields of syn-dioxygenation products, with modest to good diastereoselectivity. Chiral hypervalent iodine reagents have also been used in dioxygenation and lactonization reactions. In addition, the use of sub-stoichiometric amounts of hypervalent iodine reagents has been developed recently. Alternatively the use of stable persistent radicals such as nitroxy radicals, in particular (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), has allowed a breakthrough in this area. Although great advances have been made in the functionalization of alkenes using TEMPO, with an emphasis on stereoselective intermolecular aminoxygenation, azidoxygenation, oxyarylation and trifluoroxygenation, the dioxygenation reaction itself remains under-explored.

Following our recent research on the stereoselective synthesis of cyclobutanes via oxidation of styrenes to a radical cation, we became intrigued with the idea of trapping this radical cation intermediate (Scheme 1). The use of TEMPO has led to the discovery of a new metal-free dihydroxylation process with the incorporation of both TEMPO and an external nucleophile (or the solvent in its absence).

Scheme 1. Metal-free dihydroxylation using hypervalent iodine and TEMPO in fluorinated solvents.
using a 1:1 mixture of TFE/AcOH gave 3a in 93% yield and with high diastereocontrol (Table 1 entry 13 vs. entry 8).

**Table 1. Optimization of the dioxygenation of 1a.**

| entry | solvent | oxidant | yield of 2 or 3 (%) | dr |
|-------|---------|---------|-------------------|----|
| 1     | HFIP    | 10 mol % PIDA | 2a (37) | ≥95:5 |
| 2     | HFIP    | 10 mol % DMP | 2a (66) | ≥95:5 |
| 3     | HFIP    | 10 mol % IBX | 2a (76) | ≥95:5 |
| 4     | TFE     | 10 mol % PIDA | 0 | - |
| 5     | TFE     | 10 mol % DMP | 0 | - |
| 6     | TFE     | 10 mol % IBX | 0 | - |
| 7     | HFIP    | 20 mol % IBX | 2a (85) | ≥95:5 |
| 8     | AcOH    | 20 mol % IBX | 3a (70) | 60:40 |
| 9     | EtOH    | 20 mol % IBX | 0 | - |
| 10    | TFE     | - | 0 | - |
| 11    | HFIP    | - | 2a (45) | ≥95:5 |
| 12    | AcOH    | - | 3a (42) | 60:40 |
| 13    | TFE/AcOH | 20 mol % IBX | 3a (93) | ≥95:5 |

* a traces of the corresponding cyclobutane were observed, however almost all starting material was recovered. b 50% of starting material was recovered.

Based on the above experiments our mechanistic proposal is shown in Scheme 2. Observing a strong backbon reaction in the absence of hypervalent iodine reagent (Table 1, entries 11-12), and being aware of the ability of TEMPO to disproportionate in acidic solvents, we propose the generation of hydroxylamine III and oxoammonium cation IV. Electron rich olefin 1a may react with oxoammonium cation IV to form benzylic cation intermediate V, which will then be trapped by a nucleophile (either an external carboxylic acid or HFIP). The beneficial role of IBX in this reaction may then be to generate oxoammonium cation IV in situ, therefore improving the yield. The stereochemical outcome of the cation trapping can be rationalized using intermediate V, with the external nucleophile approaching antiperiplanar to the R1 group, in a conformation that minimises allylic strain, thus rendering a net syn dihydroxylation. At this point we do not rule out the possibility of the OTEMP nitrogen atom in the intermediate cation playing a role in directing the nucleophile. The high levels of diastereocntrol displayed when using fluorinated solvents may be related to their larger dielectric constant (ε = 26 for TFE and ε = 18 for HFIP) compared to AcOH (ε = 6.2), which may influence the conformation and reactivity of a cationic intermediate. At this point we cannot comment on the role that ion-pairing plays in controlling the cation reactivity and this factor may well differ between the two solvent regimes. Control experiments which involved resubjecting mixtures or single diastereoisomers of 3a to the reaction conditions in HFIP or AcOH solvents led to no change in product composition, thus ruling out equilibration at the benzylic centre.

**Scheme 2. Proposed reaction pathway.**

Next, we decided to explore the reaction scope for both the addition of HFIP leading to products 2 (Scheme 3) and the incorporation of AcOH to give orthogonally protected 1,2-diols 3 (Scheme 4). The scope for the dioxygenation of alkenes via HFIP addition was explored using styrenes with different electron-rich aromatic rings; therefore starting from E-asarone (Ar = 2,4,5-trimethoxyphenyl) or from the 3,4-dimethoxy derivative, products 2b and 2c were obtained. The incorporation of an ortho-Br substituent in the aromatic ring is tolerated, without diminishing the reactivity (2d) (Scheme 3). Moreover, substituents on the allylic position, such as ethyl, i-Pr or cyclopentyl were all compatible (2e-g) (Scheme 3). When (Z)-1f styrene was used under these conditions, the same syn diastereoisomer 2f was observed; this stereoconvergence is supporting evidence for the proposed mechanistic pathway proceeding via a free cation. When the regiochemistry and syn relative stereochemistry was proved based on an X-Ray crystal structure of 2c, and the remaining products in Scheme 3 were assigned by analogy.

**Scheme 3. Scope of the metal-free dioxygenation with hexafluoroisopropanol incorporation.**

We then focused our efforts on studying the scope of carboxylic acid incorporation because of the easy and selective deprotection protocols that exist. We also decided to concentrate on 1,2-disubstituted alkenes in order to study the diastereocntrol of the process. Keeping the p-methoxyphenyl ring (PMP) constant we first investigated the compatibility of the allylic substitution. Aliphatic linear (3b), branched (3c) (Scheme 4) or alicyclic (3d) substitution resulted in good yields of the corresponding TEMPO/acetate products (Scheme 4). Furthermore, different functional groups such as protected alcohol (3e) (Scheme 4), halide (3f) (Scheme 4) or ester (3g) (Scheme 4) were examined, all with very good results. For all of the examples above only the syn diastereoisomer was observed by NMR spectroscopy. However, when an alkene sub-

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**Notes:**
- Entry 4 used TFE as the solvent.
- Entry 6 used TFE as the solvent.
- Entry 7 used HFIP as the solvent.
- Entry 8 used AcOH as the solvent.
- Entry 9 used EtOH as the solvent.
- Entry 11 used HFIP as the solvent.
- Entry 12 used AcOH as the solvent.
- Entry 13 used TFE/AcOH as the solvent.

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**Scheme 4. Proposed reaction pathway.**

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**Table 2. Scope of the dioxygenation of alkenes with hexafluoroisopropanol incorporation.**

| Scheme 3 | Scope of the metal-free dioxygenation with hexafluoroisopropanol incorporation. | Scheme 4 | Scope of the dioxygenation of alkenes with hexafluoroisopropanol incorporation. |
strate containing a carboxylic acid was tested, δ-lactone 3h derived from intramolecular attack was obtained in excellent yield. In this case the anti-isomer was formed selectively; this change in stereochemistry is due to the intramolecular nature of the nucleophile and supports our mechanistic proposal (see attack of a nucleophile from within the R1 group in V, Scheme 2). Different carboxylic acid nucleophiles can be used; thus allyl TMS substrate in combination with propionic acid gives 3i with good results. Alternatively adding an acidic or pivalic acid offers the possibility of accessing syn 1,2-diols 3j and 3k with diverse protecting groups.

Scheme 4. Scope of the metal-free dioxygenation with carboxylic acid incorporation.

Moving to the aromatic ring we examined electron rich examples such as E-asarone (3l) (Scheme 4), 2-methyl (3m) (Scheme 4) or 3-methyl (3o) derivatives (Scheme 4) as well as those bearing other substituents, for example 2-fluoro (3n) (Scheme 4). The aryl olefin is not limited to p-methoxy styrenes and the method also works with less electron-donating substituents, for example 3,4-dimethyl (3p) or naphthalene substituents (3q) (Scheme 4), however in these cases the yield and diastereocotrol are compromised. Moreover, a representative group of terminal styrenes 3r-t (Scheme 4) and a
diene 3u (Scheme 4) were tested with the latter example showing regioselectivity in favour of oxidation of the terminal olefin. Although the reaction scope is quite broad, the olefin must remain electron-rich for the reaction to proceed. In Scheme 4, the spin relative stereochemistry was proven using the X-Ray crystal structure of 3a, and the remaining compounds were assigned by analogy or by correlation of derivatives to compounds that are known in the literature, vide infra.

Finally in order to demonstrate the utility of this new method we addressed the selective deprotection of both hydroxy groups. Firstly, treating acetates 3a-d with K2CO3 in MeOH gave mono-protected alcohols 4a-d in excellent yields (Scheme 5a). In order to deprotect the OTEMP functionality, hexafluoroisopropyl ether 2a and esters 3a and 3j were subjected to reductive cleavage under standard conditions using Zn/acetone to form alcohols 5a-c in very good yields (Scheme 5a). Note that when acetate 3a was used alcohol 5c was obtained together with the acetate migration product (not shown, see supporting information). Fully deprotected syn 1,2-diols 6a-d were prepared by reaction of a mono-deprotected product under the complementary set of conditions (see 4a-d→6a-d via N-O bond cleavage and 5c→6a by acetate cleavage).

Scheme 5. Functionalization of the OTEMP adducts.

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The spectroscopic data for syn 1,2-diols 6a/6c was in agreement with that previously reported in the literature, and the 1H/13C NMR spectroscopic data of diols 6b and 6d
matched that of authentic syn diols made by OsO₄ catalysed dihydroxylation of the corresponding E-alkene (see supporting information). In addition, ketones 7a-b were obtained by oxidative cleavage of the N-O bond with m-CPBA from 2e or 3a (Scheme 5a). The deprotection of lactone 3b under reductive conditions resulted in the formation of transisterified product 8 in good yield and the NMR data for this anti-compound matched that in the literature (Scheme 5b). Alternatively the electron rich aromatic PMF ring can be oxidized to a carboxylic acid using catalytic RuCl₃, forming orthogonally protected α,β-dihydroxy acids 9. Deprotection of 2d via reductive N-O bond cleavage and subsequent Pd catalysed intramolecular O-arylation furnished dihydrobenzofuran 10 (Scheme 5d). Furthermore, nOe experiments on 10 supported its cis-stereochemistry and therefore the syn stereochemistry of 2d.

A new method for the syn-selective metal-free dioxygenation of electron rich olefins in fluorinated solvents has been presented; the procedure involves a proposed reaction with an in-situ generated oxygeno ammonium cation, followed by the addition of a suitable nucleophile.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website.
Full experimental details, copies of spectral data (PDF) and crystallographic data (CIF)

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Notes
The authors declare no competing financial interest.

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