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Alkyl Ethers as Traceless Hydride Donors in Brønsted Acid-Catalyzed Intramolecular Hydrogen Atom Transfer

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Dedicated to Professor Samir Z. Zard in celebration of his 63th birthday

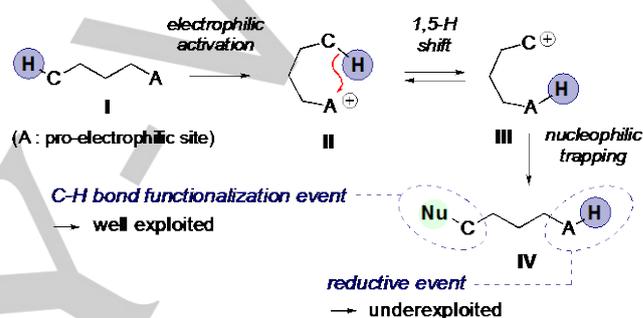
Abstract: A new protocol for the deoxygenation of alcohols and the hydrogenation of alkenes under Brønsted acid catalysis has been developed. The method is based on the use of a benzyl or an isopropyl ether as a traceless hydrogen atom donor and involves an intramolecular hydride transfer as a key step that can be achieved in regio- and stereoselective manners.

Intramolecular hydride shift has been shown over the years to be an efficient synthetic tool for the atom-economical functionalization of aliphatic C-H bonds under redox-neutral conditions (Scheme 1A).^[1] Proper electrophilic activation of the substrate (I→II) triggers such a process, whereby a hydrogen atom of a relatively electron-rich C-H bond is transferred onto a hydride acceptor (A) (II→III). 1,5-Hydride shift, which proceeds via a 6-membered ring transition state, is the most common mode of the process. Subsequent nucleophilic trapping of the transient carbocation III, that typically takes place in an intramolecular manner, completes the process (III→IV). Most of the chemistry developed so far on the basis of this concept has capitalized on the functionalization of aliphatic C-H bonds,^[1] whereas relatively less attention has been paid to exploiting the reductive event on the hydride acceptor. One major exception is the Evans–Tishchenko reaction that allows the diastereoselective reduction of β -hydroxy ketones in the presence of SmI_2 and an aldehyde (Scheme 1B).^[2]

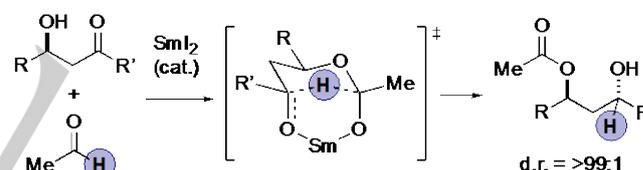
In this context and following our ongoing interest in hydrogen atom transfer reactions,^[3] we wondered if alkyl ethers could be used as traceless hydride donors in the reduction of a transiently generated carbocation V (Scheme 1C).^[4,5] In this process, the hydrogen atom α to the ethereal oxygen in V would migrate to the carbocation to produce a relatively stable oxocarbenium ion VI. Subsequent hydrolysis would ultimately deliver alcohol VII along with a ketone co-product derived from the hydride donor moiety. We report herein the realization of this concept, which has led to the regio- and stereoselective deoxygenation of alcohols and hydrogenation of alkenes under

Brønsted acid catalysis (Scheme 1D). It is worth noting that the majority of the processes involving intramolecular hydride shift reported so far employ electron-deficient alkene/alkyne moieties as hydride acceptors, whereas utilization of other types of hydride acceptors remain elusive.^[6]

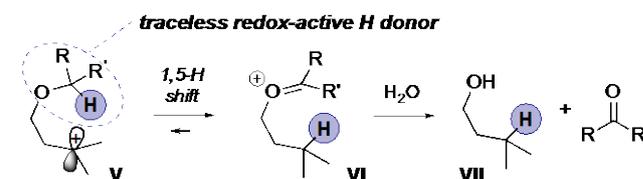
A- 1,5-Hydride transfer processes



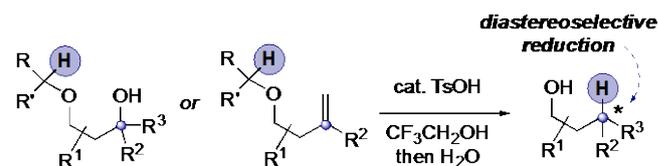
B- Evans-Tishchenko reaction



C- Alkyl ethers as hydride donors



D- Deoxygenation of alcohols and hydrogenation of alkenes using stereoselective 1,5-hydride transfers (this work)



Scheme 1. Exploiting 1,5-hydride transfers in reductive processes

We started our investigations with model substrate **1a-Bn**, a tertiary alcohol having a benzyl ether moiety as a potential hydride donor, and attempted to find suitable reaction conditions

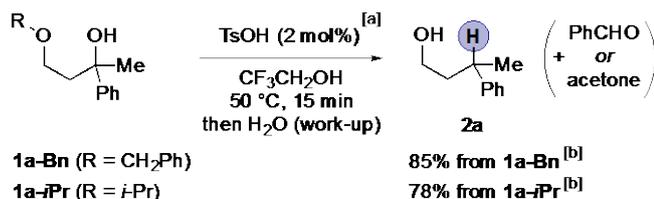
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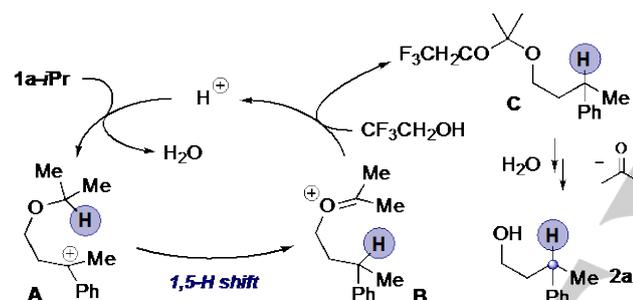
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for its deoxygenation (Scheme 2A). An extensive screening of the reaction settings (see the SI for details) revealed that the desired transformation could be optimally performed in trifluoroethanol at 50 °C using TsOH as a catalyst (2 mol%). Under these reaction conditions, the deoxygenated alcohol **2a** was rapidly produced in 85% isolated yield after aqueous work-up of the reaction mixture. Among other alkyl ethers examined,^[7] isopropyl ether **1a-*i*Pr** was found to perform with a similar efficiency, affording **2a** in 78% yield.

A- Optimized reaction conditions for the deoxygenation



B- Mechanistic proposal for the deoxygenation of 1a-*i*Pr

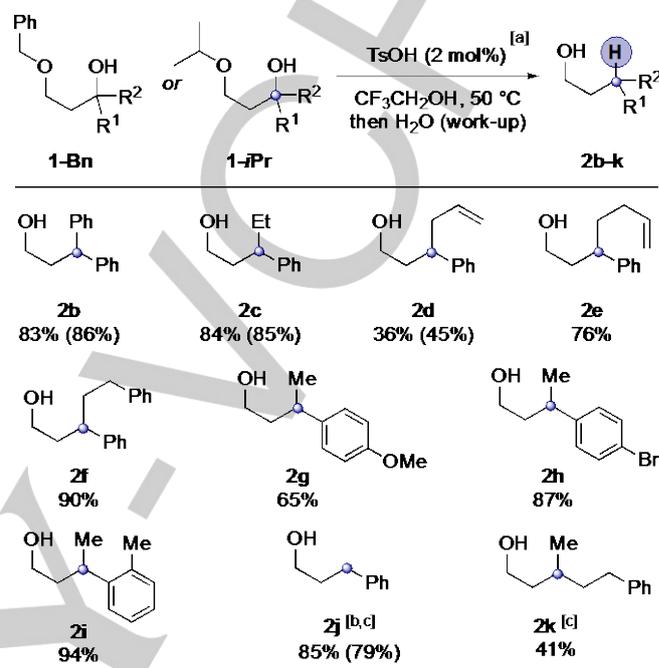


Scheme 2. TsOH-catalyzed deoxygenation of alcohols **1a**. [a] The reactions were conducted using 0.3–0.5 mmol of **1a** and 2 mol% of TsOH in CF₃CH₂OH (0.1 M) at 50 °C. [b] Isolated yields.

A mechanistic proposal for the formation of **2a** from **1a-*i*Pr** is depicted in Scheme 2B.^[8] The reaction of **1a-*i*Pr** with TsOH promotes its dehydration to afford the carbocation intermediate **A**.^[9] A subsequent 1,5-hydride transfer can then lead to the formation of the oxocarbenium ion **B**,^[10] which is then trapped by trifluoroethanol to deliver ketal **C**. This last step is accompanied by the regeneration of a proton that maintains the catalytic turnover. Ketal **C** is finally hydrolyzed under aqueous work-up to afford **2a** with concomitant elimination of acetone.

Having optimized the reaction conditions, we next investigated the scope and limitations of this deoxygenative reaction using a variety of β-benzyloxy alcohols **1-Bn** or β-isopropoxy alcohols **1-*i*Pr** (Scheme 3). The method could be applied to the formation of mono or bis-benzylic tertiary carbon centers as exemplified by the formation of benzhydryl derivative **2b** and benzyl derivatives **2c-2f**. In these cases, the yields were generally high (>80%) except for the formation of allyl derivative **2d**. No significant difference in reactivity was observed among isopropyl and benzyl ethers as hydride donors (see formation of **2b-d**). The process tolerated substitution of different electronic nature on the aromatic ring (see **2g-i**) and was not influenced by the presence of a sterically demanding *o*-tolyl group at the

carbinol center (see **2i**). The deoxygenation of secondary benzylic alcohols could also be achieved (see **1j**) but an increase of the reaction temperature to 80 °C was required in this case. We found that the reduction of a non-benzylic carbon center was possible (see **2k**) albeit with lower efficiency (41%).

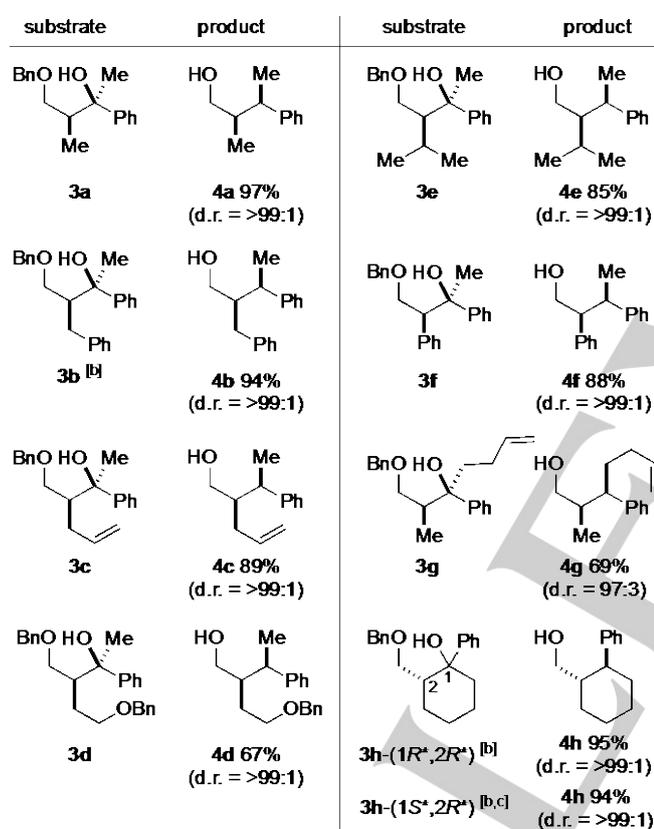


Scheme 3. Substrate scope: TsOH-catalyzed deoxygenation of alcohols **1-Bn** and **1-*i*Pr**. [a] Unless otherwise stated, the reactions were performed using 0.5 mmol of **1-Bn** or **1-*i*Pr** and 2 mol% of TsOH in CF₃CH₂OH (0.1 M) at 50 °C. Isolated yields are given. Yields in parentheses refer to the use of **1-Bn** as the substrates. Yields without parentheses refer to the use of **1-*i*Pr** as the substrates. [b] The reaction was conducted using 0.3 mmol of **1j**. [c] The reaction was conducted at 80 °C.

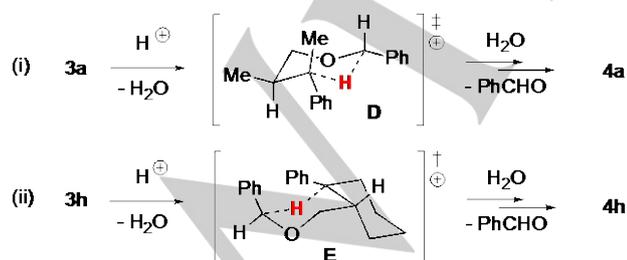
We next investigated the substituent effect on the stereoselectivity of the transformation (Scheme 4A).^[11] We wondered if the presence of a substituent at the position adjacent to the hydroxyl group would allow 1,2-dia stereoselection during the 1,5-hydride transfer step. Interestingly, the reaction of **3a**^[12] under the optimized reaction conditions proceeded smoothly to afford **4a**^[13] as a single diastereomer (Me groups in a relative *syn* configuration) in an excellent yield. High efficiencies and perfect 1,2-*syn* diastereoselectivity were also attained when structurally related substrates bearing a benzyl (for **4b**), an allyl (for **4c**), a benzyloxyethyl (for **4d**), an isopropyl (for **4e**) and a phenyl group (for **4f**) at the position adjacent to the hydroxyl group were employed. Interestingly, the reaction of **3d** having two benzyloxy groups as potential hydride donors proceeded selectively via a 1,5-shift (not via a 1,6-shift). The installation of a butenyl group at the carbinol position (**3g**) resulted in a slightly lower yield of **4g** (67%) but the diastereoselectivity remained high (97:3). Cyclohexanol derivative **3h** was also shown to be a suitable substrate for this transformation. It is worth noting that different diastereomers **3h-(1*R**,2*R**)** and **3h-(1*S**,2*R**)** furnished the

identical single diastereomer of **4h** in excellent yields. These results attest of the stereoconvergence of the process, which is not affected by the stereochemistry at the carbinol centre. The present 1,2-*syn* diastereoselection could be rationalized by invoking a 6-membered ring chair-like transition state in the key 1,5-hydride transfer step. In this model, represented for substrate **3a** in Scheme 4B-i, the more sterically demanding phenyl group^[14] on the carbocation and the methyl group at the adjacent position would both adopt a pseudo-equatorial position (TS **D**). For the formation of cyclohexane derivative **4h**, the selectivity could be explained by a transfer of the hydride onto a pseudo-axial position of the cyclohexyl moiety *via* a *cis* decaline type transition state **E**, in which the benzyloxymethyl tether would be lying in the pseudo-equatorial position.

A- 1,2-Diastereoselection: substrate scope^[a]

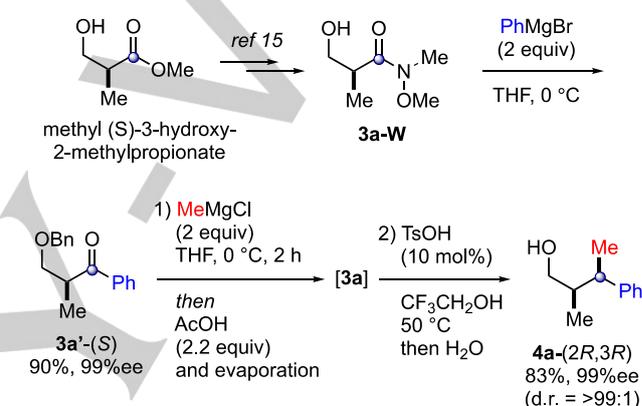


B- Origin of the diastereoselectivity



Scheme 4. 1,2-Diastereoselection in the deoxygenation of alcohols. [a] The reactions were conducted using 0.5 mmol of alcohol **3** as a single diastereomer and 2 mol% of TsOH in CF₃CH₂OH (0.1M) at 50 °C. Isolated yields and diastereomeric ratio of **4** are given. [b] The reaction was conducted using 5 mol% of TsOH at 80 °C. [c] 0.39 mmol of **3h**-(1*S**,2*R**) was used.

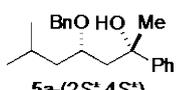
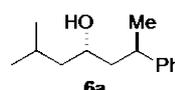
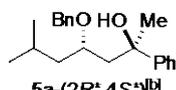
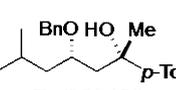
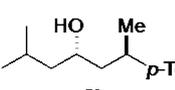
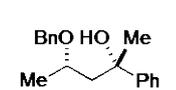
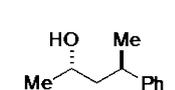
We also demonstrated construction of a new chiral centre by taking advantage of the diastereoselective nature of the present 1,5-hydride transfer (Scheme 5). The literature-known optically active Weinreb amide **3a-W** (prepared from commercially available methyl (*S*)-3-hydroxy-2-methylpropionate)^[15] was first treated with PhMgBr to afford the enantio-enriched β-benzyloxy phenyl ketone **3a'-(*S*)** (99% ee). Its subsequent treatment with MeMgCl followed by an acidic work-up with a slight excess amount of AcOH delivered the crude methyl phenyl carbinol **3a**. The reaction of **3a** in the presence of TsOH (10 mol%) in trifluoroethanol at 50 °C furnished **4a**-(2*R*,3*R*) in 83% yield as a single diastereomer with a high degree of enantiopurity (99% ee). Overall the one-pot conversion of **3a'-(*S*)** into **4a**-(2*R*,3*R*) can be regarded as a stereoselective deoxygenative methylation of the ketone moiety.

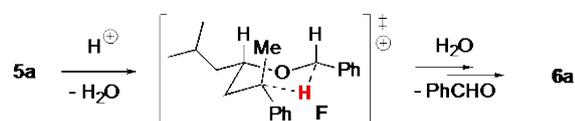
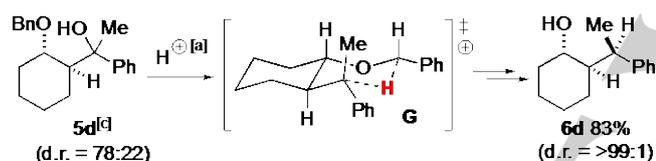


Scheme 5. Synthesis of enantio-enriched **4a**-(2*R*,3*R*).

We next examined the effect of a substituent located at the γ position to the hydroxyl group (Scheme 6). The reaction of **5a**-(2*S**,4*S**)^[16] under the optimized reaction conditions afforded alcohol **6a** in 91% yield with a good 1,3-*anti* diastereoselectivity (86:14). It should be noted that the reaction of another diastereomer **5a**-(2*R**,4*S**) afforded identical outcomes in terms of yield and the diastereoselectivity. Installation of a *p*-tolyl group at the carbinol position in **5b** allowed for the synthesis of dihydro-*arturmerol* **6b**, which was reported to exhibit acetylcholinesterase (AChE) inhibitory activity.^[17] Replacement of the isobutyl substituent with a smaller methyl group did not affect the diastereoselectivity (for **5c**). The origin of the 1,3-*anti* diastereoselection could be explained by the involvement of a 6-membered ring chair-like transition state such as **F**, in which the most sterically demanding groups occupy a pseudo-equatorial position (exemplified with **5a** in Scheme 6B). Interestingly, the reaction of **5d**, which possesses two adjacent stereocenters in an *anti* relationship on the cyclohexane fragment, afforded the deoxygenated compound **6d**^[18] in high yield (83%) as a single diastereomer (Scheme 6C). This transformation might proceed *via* the rigid chair-like 6-membered ring transition state **G** shown in Scheme 6C.

A- 1,3-Diastereoselection: substrate scope^[a]

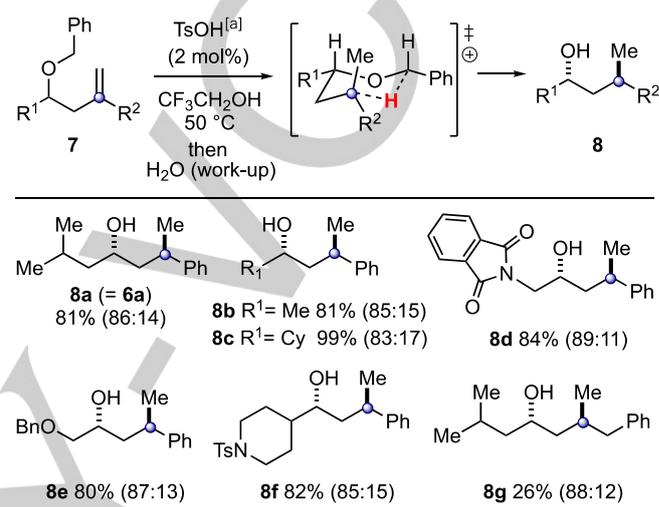
substrate	product	yield (d.r.)
		91% (86:14)
		92% (89:11)
		82% (88:12)
		89% (88:12)

B- Origin of the diastereoselectivity**C- 1,2,3-Diastereoselection**

Scheme 6. 1,3- and 1,2,3-Diastereoselection in the deoxygenation of alcohols. [a] The reactions were conducted using 0.5 mmol of alcohol **5** and 2 mol% of TsOH in CF₃CH₂OH (0.1M) at 50 °C. Isolated yields and diastereomeric ratio (d.r.) of **6** are given. [b] The reaction was conducted using 0.36 mmol of **5a**-(2*R**,4*S**). [c] The reaction was conducted using 0.36 mmol of **5d**.

Finally, we examined the use of alkenes as an alternative source of carbocations under the Brønsted acid catalysis.^[19] The optimized reaction conditions for the deoxygenation of alcohols were applicable to the hydrogenation of alkenes (Scheme 7). For instance, the reaction of homoallylic alcohol *O*-benzyl ether **7a**^[20] proceeded smoothly to produce **8a** (= **6a**) in 81% yield with a good 1,3-*anti* diastereoselectivity (d.r. = 86:14). This result is very similar to that obtained for the deoxygenation of **5a** (Scheme 6A), indicating that both reactions proceed *via* the formation of a common carbocation intermediate. The investigation of the substrate scope revealed that various primary and secondary alkyl groups could be installed as R¹ to generate products (**8b-f**) in good yields and diastereoselectivity. Notably, nitrogen-containing substituents such as a phthalimide (**8d**)^[21] or a piperidine (**8f**) were tolerated. The transformation also exhibited selective 1,5-hydride shift over 1,6-shift in the case of **7e** having two benzyloxy groups. The reduction process could also be applied to benzyl substituted alkene **7g**, but, while the diastereoselectivity was similarly high, a noticeable drop in the yield was observed.

This work demonstrates the use of alkyl ethers as traceless hydride donors for the deoxygenation of alcohols and the hydrogenation of alkenes under Brønsted acid catalysis. The reductive process described herein, which is based on an intramolecular 1,5-hydride shift onto a transient carbocation, exhibits high degree of efficiency and stereoselectivity. The present concept will be extended and exploited in the development of other types of reductive processes, especially asymmetric variants.



Scheme 7. TsOH-catalyzed hydrogenation of alkenes **7**. [a] The reactions were conducted using 0.3-0.5 mmol of alkenes **7** and 2 mol% of TsOH in CF₃CH₂OH (0.1M) at 50 °C. Isolated yields and diastereomeric ratio (d.r.) of the products are given. Cy = cyclohexyl

Acknowledgements

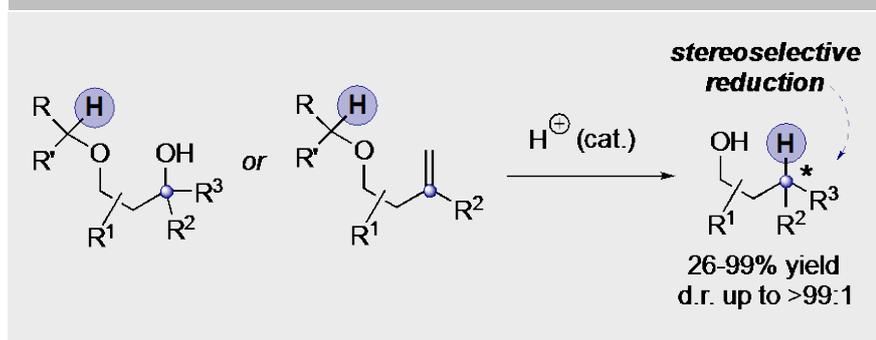
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Keywords: Hydrogen atom transfer • Brønsted acid • alcohols • alkenes • reduction

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- [16] Substrates **5** were prepared by addition of Grignard reagents to the corresponding β -benzyloxyketones. These reactions proceeded in a diastereoselective manner (d.r. = 74:26-70:30) according to a chelation model. The diastereomers except for **5d** could be separated by the column chromatography (see the SI for details).
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- [21] The stereochemistry of the major isomer of **8d** was determined by X-ray crystallographic analysis. See the SI for details.

COMMUNICATION



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Page No. – Page No.

Use of Alkyl Ethers as Traceless Hydride Donors in Brønsted Acid-Catalyzed Intramolecular Hydrogen Atom Transfer

A new protocol for the deoxygenation of alcohols and the hydrogenation of alkenes under Brønsted acid catalysis has been developed. The method is based on the use of a benzyl or an isopropyl ether as a traceless hydrogen atom donor and involves an intramolecular hydride transfer as a key step that can be achieved in regio- and stereoselective manners.