Umpolung

DOI: 10.1002/anie.201400405

Flexible Stereoselective Functionalizations of Ketones through Umpolung with Hypervalent Iodine Reagents**

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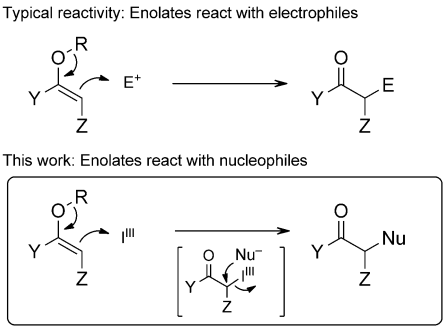
Abstract: *The functionalization of carbonyl compounds in the α-position has gathered much attention as a synthetic route because of the wide biological importance of such products. Through polarity reversal, or "umpolung", we show here that typical nucleophiles, such as oxygen, nitrogen, and even carbon nucleophiles, can be used for addition reactions after tethering them to enol ethers. Our findings allow novel retrosynthetic planning and rapid assembly of structures previously accessible only by multistep sequences.*

Reactions of carbonyl compounds are among the most exploited transformations in chemistry. Apart from direct reactions of the C=O moiety, their facile deprotonation at the adjacent carbon atom (α-position) makes enolates and their derivatives such as silyl enol ethers easily accessible. They are used almost exclusively as versatile nucleophiles for reactions with alkyl, aryl, or heteroatom electrophiles to achieve functionalizations in the α-position.[1] Polarity inversions are alternative, much less developed, approaches for the synthesis of otherwise difficult to access target molecules. The development of a flexible method for the α-functionalization of ketones with a range of nucleophilic coupling partners would provide a very useful alternative. We make use of the high electrophilicity as well as the high nucleofugality of hypervalent iodine reagents for the umpolung[2] of silyl enol ethers, thereby allowing a range of nucleophiles to react in a clean transformation (Scheme 1).[3] The ability to generate novel stereogenic centers in such a process is also highly promising. The synthetic advantage of adding nucleophiles to the α-position of carbonyl compounds through umpolung reactions has also been utilized in various other strategies.[4] This is exemplified by organocatalytic formation of enamines with aldehydes[5] and ketones[6] through activation with phosphates[7] or by electrochemical reactions.[8] Stepwise methods by initial introduction of a leaving group in the α-position followed by nucleophilic displacement have also been used to access the substituted derivatives.[9]



Scheme 1. Nucleophilic addition to enolates with reversed polarity. E^+ = electrophile; Nu^- = nucleophile; I^{III} = iodine(III) reagent; Y, Z = substituents.

Synthetic transformations mediated by hypervalent iodine have received growing attention in recent years.[10,11] This is not surprising, considering that these reagents are polyvalent electrophiles[12] and mild oxidants. They are a good alternative to the toxic transition metals often used to effect similar transformations and have already been used to perform α-functionalizations of ketones.[13,14] Hypervalent iodine moieties are sometimes referred to as hypernucleofuges, because of their high dissociation rates compared to standard leaving groups such as triflates.[15] To facilitate such reactions further, we have introduced tethers between the nucleophile and the enol ether. Temporary tethers have long been used to switch intermolecular reactions to intramolecular ones and thereby take advantage of the high degrees of regio- and stereocontrol arising from the less flexible transition states.

By using this strategy it is also possible to synthesize acyclic molecules by tethering the reactants and removing the linker group after the intramolecular reaction. Silicon is a popular choice when considering temporary tethers to link two reaction components.[16] This popularity is due to several factors, mainly because the acyclic silicon derivatives are facile to synthesize through the formation of either silyl ethers or acetals containing a wide range of functionalities. Additionally, the silicon tether remains inert in most reactions and can be easily and selectively removed after the reaction by either aqueous work-up or treatment with tetrabutylammonium fluoride. Thus, it is often referred to as being a "traceless silicon tether".[17]

For initial studies, compound **1a** (R = Ph, Nu = NEt_2) was treated with different hypervalent iodine reagents in the presence or absence of activating Lewis acids to yield the corresponding α-aminated product **2a**, with the tethered silyl moiety cleaved during the work-up. As shown in Table 1

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[**] This project was supported by an EU Marie Curie fellowship to P.M. (DIALMEC, No. 298642). Support from the School of Chemistry, Cardiff University is also gratefully acknowledged. We thank the EPSRC National Mass Spectrometry Facility, Swansea, for mass spectrometric data.

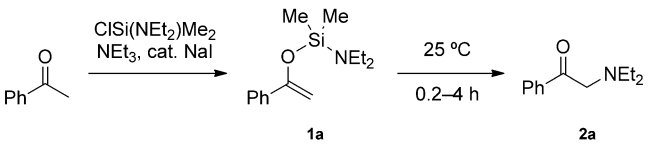
Supporting information for this article (all synthetic methods including spectroscopic and analytical data) is available on the WWW under http://dx.doi.org/10.1002/anie.201400405.

(entries 2–6), the reaction proceeds much faster in the presence of a Lewis acid through activation of the iodine reagent, but the yields decreased substantially. The use of iodine triacetate[18] (Table 1, entry 7) allows a fast work-up without the necessity to remove iodobenzene, but using this highly reactive reagent results in the acetate also reacting as a nucleophile to produce **8a** as a side product. The reaction with (diacetoxyiodo)benzene [$PhI(OAc)_2$] as the reagent proceeds very smoothly at room temperature without the necessity of any Lewis acid to yield **2a** in up to 94% yield (Table 1, entry 8). A one-pot procedure for this sequence has also been developed.

We then examined the scope of the carbon–nitrogen bond formation under the established reaction conditions. As shown in Table 1, many nitrogen-containing dimethylsilyl enol ethers were prepared, which all participated in a straightforward manner in the amination reaction, thereby furnishing the corresponding amines with high efficiency. The method is very efficient with aromatic, aliphatic, and cyclic ketones, and the α-aminated products **2** are obtained in good yields. The nature of the substituents has almost no effect on the overall course of the reaction. Electron-rich aromatic substituents (**2f**) are tolerated as well as electron-poor substituents (**2r**). Although the thermodynamic control of enolate formation allows the selective synthesis of **2n**, a kinetic control of the enolate formation could deliver the amino functionality at the ring carbon atom.

The method was extended to the synthesis of secondary amines **3**, primary amines **4**, and also towards alcohols **5**, ethers **6** and **7**, and esters **8** by using other suitable nucleophiles on the tethered linker (Table 2). The yields in the synthesis of secondary amines **3** on using tosyl amide as the nucleophile were low but increased to good levels when the tosyl amide was protected with a trimethylsilyl moiety. A bis(trimethylsilyl)amine moiety tethered to the silicon atom was used as the nucleophile for the direct synthesis of primary amines **4**. The trimethylsilyl groups are cleaved during work-up, thereby leading directly to the unprotected α-aminoketones **4** as products. To ensure complete and fast cleavage, the work-up is carried out with one equivalent of tetrabutylammonium fluoride (TBAF). Aliphatic ketones also show good yields with various oxygen nucleophiles to furnish free alcohols **5**, ethers **6** and **7**, or with the oxygen atom protected as an ester (acetate) in **8**.

Table 1: Optimization of reaction conditions.

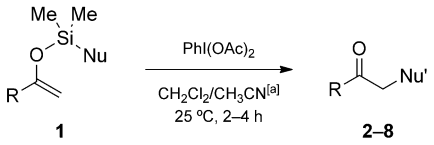


Entry	Reagent(s)	Solvent	**2a** yield [%]
1	$PhI(OCOCF_3)_2$	MeCN	69
2	$PhI(OCOCF_3)_2$, TMSOTf	MeCN	<10
3	$PhI(OCOCF_3)_2$, $BF_3{\cdot}OEt_2$	MeCN	<5
4	$PhI(OAc)_2$, $BF_3{\cdot}OEt_2$	MeCN[a]	20
5	$PhI(OAc)_2$, $BF_3{\cdot}OEt_2$	CH_2Cl_2[a]	70
6	$PhI(OAc)_2$, $BF_3{\cdot}OEt_2$	CH_2Cl_2	45
7	$I(OAc)_3$	CH_2Cl_2	57[b]
8	$PhI(OAc)_2$	CH_2Cl_2	94

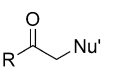
[a] Reaction performed at 0°C. [b] In addition to **2a**, compound **8a** is formed in 23% yield.

The method also allowed carbon–carbon coupling reactions by using an enolate as the nucleophile and as the electrophile in the same reaction, thus providing direct access

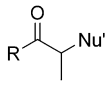
Table 2: Reaction of enol ethers **1** with nitrogen and oxygen nucleophiles.



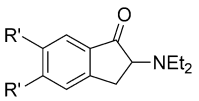
Nu	Nu'	Ph, Nu'	MeO, Nu'	Nu'	Nu'
NEt_2	NEt_2	**2a**: 94%	**2b**: 92%	**2h**: 82%	**2i**: 87%
NHTs	NHTs	**3a**: 67%	**3b**: 50%	-	-
$N(SiMe_3)Ts$	NHTs	**3a**: 92%	**3b**: 90%	-	**3c**: 85%
$N[(SiMe_3)_3]_2$	NH_2	**4a**: 86%	**4b**: 82%	-	**4c**: 80%
OH	OH	**5a**: 85%	**5b**: 80%	**5c**: 72%	**5d**: 65%
OMe	OMe	**6a**: 86%	**6b**: 81%	**6c**: 70%	**6d**: 66%
OEt	OEt	**7a**: 83%	**7b**: 81%	**7c**: 68%	**7d**: 60%
OAc	OAc	**8a**: 90%	**8b**: 92%	**8c**: 91%	**8d**: 82%



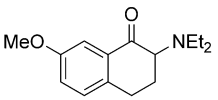
2c: (R = 2-MeO-C_6H_4, Nu' = NEt_2): 86%
2d: (R = 2-Br-C_6H_4, Nu' = NEt_2): 85%
2e: (R = 3-Br-C_6H_4, Nu' = NEt_2): 88%
2f: (R = 3,4-$(MeO)_2$-C_6H_3, Nu' = NEt_2): 88%
2g: (R = Me, Nu' = NEt_2): 80%
2r: (R = 4-F-C_6H_4, Nu' = NEt_2): 76%
3d: (R = Me, Nu' = NHTs): 70%
3e: (R = 2-Br-C_6H_4, Nu' = NHTs): 85%
4d: (R = Me, Nu' = NH_2): 80%
4e: (R = 2-Br-C_6H_4, Nu' = NH_2): 81%



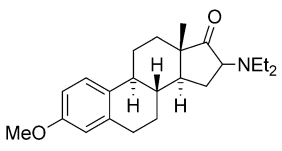
2o: (R = Ph, Nu' = NEt_2): 62%
4f: (R = Ph, Nu' = NH_2): 60%
2p: (R = 4-MeO-C_6H_4, Nu' = NEt_2): 60%
4g: (R = 4-MeO-C_6H_4, Nu' = NH_2): 56%
2q: (R = 2-Br-C_6H_4, Nu' = NEt_2): 59%
4h: (R = 2-Br-C_6H_4, Nu' = NH_2): 53%



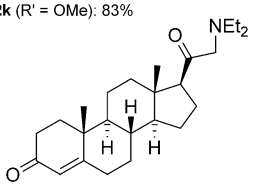
2j (R' = H): 83%
2k (R' = OMe): 83%



2l: 85%



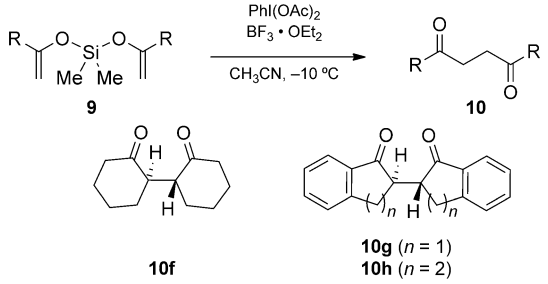
2m: 81%



2n: 80%

[a] Synthesis of compounds **2**, **7**, **8**: CH_2Cl_2; **3**–**6**: CH_2Cl_2/CH_3CN 1:1.

to highly versatile 1,4-dicarbonyl derivatives. This process was initially reported in 1935[19] and since that time also used frequently in stereoselective reactions,[20] but almost exclusively involving metal enolates. A major limitation lies with the lack of methods that allow for the selective and controlled coupling of enolates under metal-free conditions and only a few reactions describe the dimerization of trimethylsilyl enol ethers to form 1,4-diketones.[21–24] We have expanded the use of bis(silyl enol ethers) **9**[25,26] to coupling reactions for the easy synthesis of aliphatic and bicyclic 1,4-diketones (Scheme 2). The 1,4-diketones **10** are obtained in good



Scheme 2. Coupling of bis(enol ethers) **9** to 1,4-diketones **10**.

yields after the necessary activation of the hypervalent iodine reagent with boron trifluoride etherate. The reaction was sluggish when the reagent was not activated with boron trifluoride etherate. In the case of cyclic precursors, the coupled products (**10f–10h**) are produced as racemates with the *meso* isomers as minor side products (ca. 5%). New stereogenic centers can be generated in reactions with cyclic or substituted enol ethers.

Chiral lactate-based hypervalent iodine reagents developed by the research groups of Fujita[27] and Ishihara[28] have recently been used for highly efficient diaminations,[29,30] aminofluorinations,[31] aminohydroxylations,[32] and rearrangement reactions.[33] Although methods exist for stereoselective α-hydroxylations,[34] the direct and stereoselective introduction of a simple amino moiety next to ketones would allow novel synthetic strategies to build up important structural features. We show that the chiral reagent **14**, which has been used for the stereoselective functionalization of double bonds,[28–33] can be used for highly enantioselective C–O and C–N bond formations when cyclic enol ethers **1** are used as substrates. The stereoselective coupling of bisenol ethers to form diketones **10** by employing chiral hypervalent iodine reagents was also carried out (Table 3). However, the enantiomers could not be separated.[35]

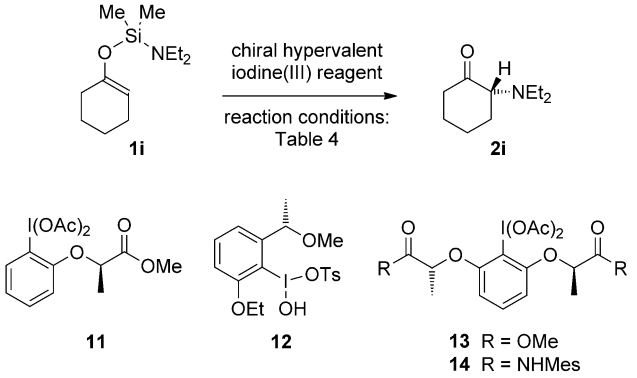
The direct and stereoselective synthesis of unprotected α-hydroxyketones or α-aminoketones from enol ethers is highly valuable as it allows the rapid generation of chiral building blocks. Different chiral hypervalent iodine compounds and various reaction conditions have been investigated in the synthesis of **2i** (Table 4). The screen of different reagents **11**–**14** established **14** to be the most efficient chiral iodine(III) compound. The highest selectivity was obtained when Ishihara amide **14** was used at room temperature in the absence of

Table 3: Synthesis of 1,4-diketones **10**.

Entry	Product	R	Yield [%]
1	**10a**	Me	75
2	**10b**	*t*Bu	79
3	**10c**	Ph	89
4	**10d**	4-$MeOC_6H_4$	82
5	**10e**	2-BrC_6H_4	78
6	**10f**	–	85[a]
7	**10g**	–	82[a]
8	**10h**	–	80[a]

[a] The *meso* isomer is formed in about 5% yield.

Table 4: Optimization of the enantioselective reaction to **2i**.

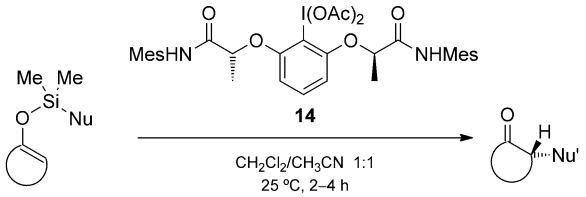


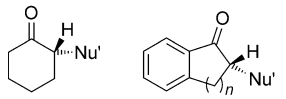
Entry	Reagent	Solvent/additives	*T* [°C]	**2i** yield [%]	**2i** *ee* [%]
1	**11**[28]	CH_3CN	25	21	32
2	**12**[36]	CH_3CN	25	35	45
3	**13**[27]	CH_3CN	25	30	60
4	**14**[28]	CH_3CN	25	45	69
5	**14**	CH_3CN, $BF_3{\cdot}OEt_2$	−48	24	7
6	**14**	CH_2Cl_2, $BF_3{\cdot}OEt_2$	25	40	35
7	**14**	CH_3CN, TMSOTf	−48	trace	–
8	**14**	CH_2Cl_2/CH_3CN 1:1	0	65	68
9	**14**	CH_2Cl_2/CH_3CN 1:1	25	81	79
10	**14**	CH_2Cl_2/CH_3CN 1:1	50	60	41

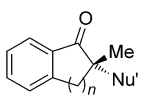
an additive in CH_3CN/CH_2Cl_2 (1:1; Table 4, entry 9). Higher or lower temperatures led to lower selectivities; the use of a Lewis acid as an additive for the activation of the reagent also strongly affected the selectivity (Table 4, entries 5–7). Interestingly, carrying out the reaction at reaction temperatures between 0 °C and 50 °C (Table 4, entries 8–10) showed the highest enantioselectivity to be obtained at room temperature. The chiral reagent was used in stoichiometric amounts, but the reduced aryl iodide can be recovered after the reaction without loss of optical purity and can be reused.

The examples in Table 5 demonstrate that this approach is superior to the classical substitution of α-halo ketones,[37] as high stereoselectivities have not been reported in such multistep approaches. A recent report used α-oxytosyl ketones as oxyallyl cation precursors for reactions with nucleophiles.[9] We show that not only secondary alcohols and amines, but also chiral tertiary alcohol derivatives (**5g**, **5h**, **8e**, **8f**) and tertiary amines (**4k**, **4l**) are accessible and

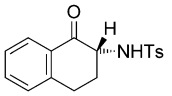
Table 5: Stereoselective reactions of cyclic enol ethers **1** introducing nitrogen and oxygen nucleophiles by using lactate-based hypervalent iodine reagent **14**. Yields are given in brackets.



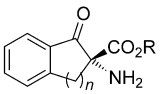




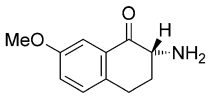
Nu'	*ee*	*ee* (*n*=1)	*ee* (*n*=2)	*ee* (*n*=1)	*ee* (*n*=2)
NEt_2	**2i**: 79% (81%)	**2j**: 92% (45%)			
NH_2	**4c**: 82% (87%)	**4i**: 94% (60%)	**4j**: 78% (72%)	**4k**: 77% (76%)	**4l**: 76% (73%)
OH	**5d**: 85% (71%)	**5e**: 90% (76%)	**5f**: 91% (79%)	**5g**: 88% (79%)	**5h**: 89% (82%)
OAc	**8d**: 89% (79%)			**8e**: 90% (81%)	**8f**: 89% (80%)
OMe	**6d**: 92% (78%)				



3f: 90% *ee* (62%)



Nu'	R	*ee* (*n*=1)	*ee* (*n*=2)
NEt_2	Me	**4m**: 92% (54%)	**4n**: 91% (50%)
NH_2	*t*Bu	**4o**: 91% (53%)	**4p**: 90% (49%)



4q: 90% *ee* (80%)

obtained in good stereoselectivities (77–90% *ee*). Under the same reaction conditions, β-keto esters permitted the synthesis of cyclic amino acid derivatives **4m**–**4p** in enantioselectivities above 90%. Traditionally, such compounds are synthesized by multistep sequences.[38] The absolute configuration of the reaction products was confirmed to be *R* in every case by comparison with known compounds.[39] It is therefore assumed that the chiral reagent **14** (Ishihara amide) reacts preferentially from the *Re* face of the cyclic silyl enol ether, thereby resulting in the *R* stereochemistry in all reaction products shown in Table 5.

The method is very convenient for the synthesis of 2-amino ketones under benign and extremely simple reaction conditions. The hypervalent iodine reagent is added to a solution of the substrate at room temperature. After a short reaction time (2–4 h), the cleavage of the silyl linker and protecting group proceeds during the work-up at room temperature under almost neutral reaction conditions. The removal of nitrogen protecting groups usually involves the use of drastic reaction conditions or transition-metal catalysts.[40,41] The products obtained with the method presented herein are stable and can be obtained efficiently with or without subsequent purification steps. Under the reaction conditions shown here, it seems that a catalytic procedure using a stoichiometric oxidant and catalytic amounts of a chiral iodine(I) precursor is not feasible as it is known that oxidants such as *m*CPBA will directly react with silyl enol ethers.[34]

In summary, we present a novel and broadly applicable strategy for the α-functionalization of carbonyl derivatives using hypervalent iodine reagents. This provides rapid access to nitrogen- and oxygen-substituted ketones in a simple operation. Products, including amino acid derivatives, are obtained with high stereoselectivities by using chiral hypervalent iodine reagents for the α-functionalization of ketones in a transition-metal-free protocol.

Received: January 14, 2014
Revised: March 18, 2014
Published online: May 20, 2014

Keywords: amination · hydroxylation · hypervalent iodine · stereoselective synthesis · umpolung

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