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Asymmetric Catalysis via Cyclic, Aliphatic Oxocarbenium Ions

Sunggi Lee, Philip S. J. Kaib, and Benjamin List*

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany

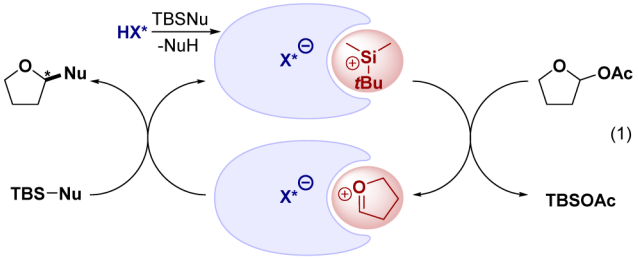
Supporting Information

ABSTRACT: A direct enantioselective synthesis of substituted oxygen heterocycles from lactol acetates and enolsilanes has been realized using a highly reactive and confined imidodiphosphorimidate (IDPi) catalyst. Various chiral oxygen heterocycles, including tetrahydrofurans, tetrahydropyrans, oxepanes, chromans, and dihydrobenzofurans, were obtained in excellent enantioselectivities by reacting the corresponding lactol acetates with diverse enol silanes. Mechanistic studies suggest the reaction to proceed via a nonstabilized, aliphatic, cyclic oxocarbenium ion intermediate paired with the confined chiral counteranion.

Oxocarbenium ions are key intermediates in enzymatic glycosidations but also in a variety of synthetic transformations.[1] The stereocontrol of such reactions is challenging, and catalytic enantioselective approaches have only recently been described.[2] Asymmetric nucleophilic substitutions via non-aromatic, cyclic oxocarbenium ions are particularly difficult to control, as these cations display neither Lewis basic sites nor large π-surfaces for substrate−catalyst interactions. We show here that silylium-based asymmetric counteranion-directed Lewis acid catalysis provides a general solution to this challenge; various lactol acetates react with enol silanes in the presence of a highly active and confined pre-Lewis acid organocatalyst to furnish substituted oxygen heterocycles with high enantioselectivity.

Despite the frequent appearance of saturated oxygen heterocycles in drugs and natural products,[3] general methods for their enantioselective synthesis are relatively rare.[4−11] One straightforward approach is the direct addition of nucleophiles to in situ-generated cyclic oxocarbenium ions. In pioneering studies, Braun and Kotter[2a] showed that a chiral titanium complex enables the dynamic kinetic asymmetric nucleophilic substitution of allyltrimethylsilane with silyl ethers and acetals. However, high enantioselectivity was achieved only with aromatic substrates. Recently the Jacobsen group reported enantioselective substitution reactions of silyl ketene acetals with aromatic glycosyl chlorides using anion binding catalysis.[2b,r−t] Chiral 1-substituted isochromanes and related products were also obtained via oxidative enamine catalysis, via alkynylation using a chiral copper catalyst combined with stoichiometric Lewis acids, via chiral silver-salt-catalyzed reductions, and via nucleophilic addition reactions to pyrylium salts using different catalysts.[2c−o] Most recently, the Mattson group developed a silandiol-catalyzed chromenone functionalization,[2p] and the Toste group utilized anionic phase transfer catalysis for the formation of 2,4-diarylbenzopyrans.[2q]

All of these examples are limited to the use of resonance-stabilized oxocarbenium ions within six-membered ring systems. In contrast, the enantioselective formation of tetrahydrofurans or tetrahydropyrans via nucleophilic addition reactions to aliphatic, cyclic oxocarbenium ions remained as a long-standing challenge. Their high electrophilicity often leads to catalyst degradation, and their small size and the absence of further functionalization makes enantiodifferentiation difficult to accomplish. We have recently introduced confined imidodiphosphoric acid catalysts (IDPs) that catalyze cyclization reactions via aliphatic oxocarbenium ions.[12] However, intermolecular reactions proceeding via unmodified, aliphatic, cyclic oxocarbenium ions could not be accomplished with these catalysts. We envisioned that our newly developed imidodiphosphorimidates (IDPi) could perhaps provide a solution to this significant problem.[13] Their acidity is higher than that of IDPs and even of disulfonimides (DSIs), enabling silylium-based asymmetric counteranion-directed catalysis (Si-ACDC).[14,15] In addition, their highly stabilized counteranions should support the generation of ion pairs with strongly electrophilic cations. Finally, the confined active site should allow efficient enantiodiscrimination of sterically and electronically unbiased cationic intermediates. On the basis of these considerations, a plausible catalytic cycle can be envisioned (eq 1), which is initiated with the in situ generation of the silylium



- *asymmetric catalysis via cyclic, aliphatic oxocarbenium ion*
- *enantiocontrol challenging: absence of Lewis basic or aromatic sites*

ion pair catalyst from the strongly Brønsted acidic precatalyst HX* and a silylated nucleophile (TBS-Nu). The cyclic oxocarbenium ion is subsequently generated via acetate abstraction from a lactol acetate by the silicon Lewis acid.[16] In the following nucleophilic addition of the silylated nucleophile to the oxocarbenium ion, the counteranion directs the enantiodifferentiation, leading to formation of the product and regeneration of the silylium Lewis acid catalyst.

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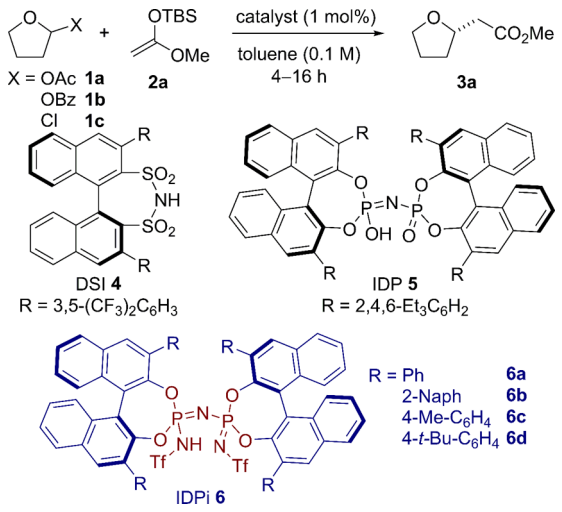
To test this design, we explored the reaction of different oxocarbenium ion precursors **1** with ketene acetal **2a** in the presence of a variety of acidic catalysts previously developed in our group (Table 1). Chiral disulfonimide catalyst **4** enabled

Table 1. Reaction Development[a]



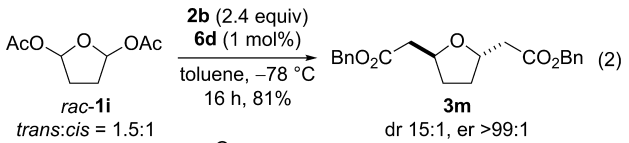
entry	substrate	catalyst	temp	conv.[b]	er
1[c,d]	**1a**	**4**	r.t.	>95	50:50
2[c,d]	**1a**	**5**	r.t.	<10	ND
3[c]	**1a**	**6a**	r.t.	>95	59.5:40.5
4	**1a**	**6a**	r.t.	>95	61.5:18.5
5	**1a**	**6b**	−20 °C	>95	60:40
6	**1a**	**6c**	−20 °C	>95	84:16
7	**1a**	**6d**	−20 °C	>95	94:6
8	**1b**	**6d**	−20 °C	>95	93:7
9	**1c**	**6d**	−20 °C	>95[e]	87:13
10	**1a**	**6d**	−78 °C	>95	97:3
11[f]	**1a**	**6d**	−78 °C	>95	98:2
12[f,g]	**1a**	**6d**	−78 °C	>95 (88[h])	98:2

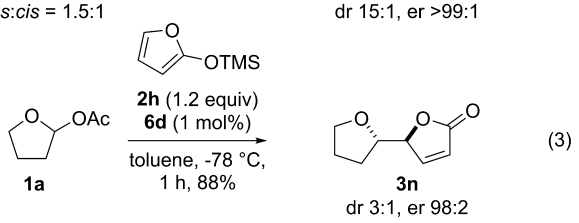
[a]Unless otherwise indicated, reactions were conducted on a 0.05 mmol scale with 3.0 equiv of **2a** and 1.0 mol% catalyst in 0.5 mL of toluene. The er was determined by GC. ND = not determined. [b]Determined by NMR analyses with an internal standard. [c]The reaction was carried out in CH_2Cl_2. [d]5 mol% catalyst. [e]A 19% yield of product was observed by crude NMR analysis. [f]1.2 equiv of nucleophile. [g]1.0 mmol scale, 0.1 mol% catalyst. [h]Isolated yield.

full conversion to the desired product **3a** within 4 h but without any enantioselectivity (entry 1). In contrast, imidodiphosphate catalyst **5** gave no conversion, likely because of its insufficient acidity. Remarkably, however, IDPi catalyst **6a** efficiently promoted the reaction with promising enantioselectivity (entries 3 and 4). The corresponding 2-naphthyl-substituted catalyst **6b**, previously used in the asymmetric Hosomi−Sakurai allylation of aldehydes, showed no improvement in the enantioselectivity (entry 5). We found that *para* substituents on the 3,3′-phenyl groups of the BINOL backbone strongly affect the enantioselectivity. A stepwise increase in enantioselectivity was observed by varying from small methyl to bulky *tert*-butyl groups, affording up to 94:6 er at −20 °C in toluene (entries 6 and 7). Switching from acetate **1a** to benzoate **1b** did not influence reactivity or selectivity (entry 8), and 2-chlorotetrahydrofuran (**1c**) gave only a 19% yield of the desired product with reduced enantioselectivity. The selectivity was further increased to 97:3 er by lowering the temperature to −78 °C (entry 10). Furthermore, the amount of nucleophile could be reduced to 1.2 equiv without affecting the enantioselectivity or conversion (entry 11). Under the optimal conditions, as little as 0.1 mol% catalyst **6d** was sufficient to furnish tetrahydrofuran **3a** in 88% yield after 16 h (entry 12). It is noteworthy that product **3a** is the starting material for several syntheses of biologically active molecules but there are only a few procedures for its synthesis, using enzymatic kinetic resolutions.[17]

With the optimal conditions in hand, we next investigated the reaction scope (Table 2). Various nucleophiles and electrophiles can be utilized in our reaction. The size of the nucleophile does not seem to influence the selectivity and reactivity much (entries 1−3). In addition to silyl ketene acetals, the silyl enol ether derived from acetophenone (**2d**) was also applicable, although with slightly lower enantioselectivity (entry 4). A conjugated silyl enol ether gave product **3e** with high enantioselectivity (entry 5). Extended nucleophiles such as vinylogous ketene acetal **2f** and dioxinone-derived silyloxydiene **2g** reacted at the γ-position, furnishing the corresponding heterocycles with >95:5 er in moderate to excellent yields (entries 6 and 7). Tetrahydropyran and oxepane products **3h** and **3i** could be obtained under identical conditions with high enantiomeric ratios from the corresponding six- and seven-membered lactol acetates (entries 8 and 9). In addition to simple aliphatic substrates, aromatic substrates possessing chroman and benzodihydrofuran moieties could also be converted under our reaction conditions but required longer reaction times and higher concentration. Full conversion to products **3j** and **3k** with excellent and good enantioselectivity was observed after 7 and 4 days, respectively (entries 10 and 11). In contrast, the reaction with 1-acetoxyisochroman **1h** was complete within 10 min and gave product **3l** in high yield but with only moderate enantioselectivity (entry 12).

Remarkably, when 2,4-bis(acetoxy)tetrahydrofuran (**1i**) was subjected to the reaction conditions using 2.4 equiv of nucleophile **2b**, the entire mixture of stereoisomers (*meso*-**1i**, (*S*,*S*)-**1i**, and (*R*,*R*)-**1i**) was converted into a single major product stereoisomer (eq 2). The initial 1.5:1 racemic *trans*:*cis*





ratio of substrate **1i** gave a 15:1 *trans*:*cis* ratio in product **3m**, which was obtained with superb enantiomeric ratio (>99:1) in a diasteroconvergent and enantioconvergent kinetic resolution. We were also able to utilize α-branched nuclophiles. For example, 2-(trimethylsiloxy)furan (**2h**) reacted with lactol acetate **1a** to give lactone product *syn*-**3n** with excellent er and moderate dr (eq 3).[18]

Toward elucidating the mechanism of our reaction, we monitored the enantiomeric excesses of substrate **1a** and product **3a** during the course of the reaction (Figure 1). While the enantiomeric excess of the product was constantly high

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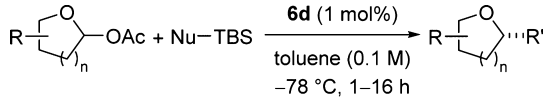
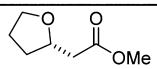
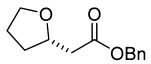
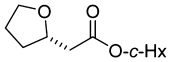
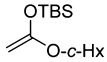
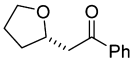
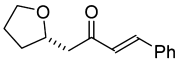
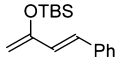
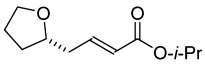
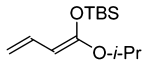
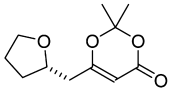
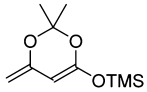
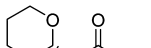
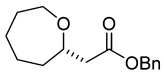
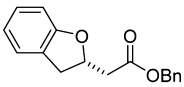
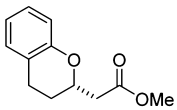
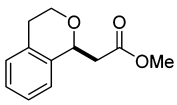
Table 2. Substrate Scope[a]



entry	product	Nu-TBS	yield (%)	er
1[b]	 **3a**	 **2a**	88	98:2
2	 **3b**	 **2b**	94	97:3
3	 **3c**	 **2c**	95	96:4
4[c]	 **3d**	 **2d**	97	89.5:10.5
5	 **3e**	 **2e**	74	95:5
6	 **3f**	 **2f**	70	96.5:3.5
7	 **3g**	 **2g**	90	96.5:3.5
8[c]	 **3h**	**2b**	80	96.5:3.5
9	 **3i**	**2b**	91	97:3
10[d,e]	 **3j**	**2b**	43	98.5:1.5
11[d,f]	 **3k**	**2b**	96	94.5:5.5
12[g]	 **3l**	**2a**	73	67:33

[a]Unless otherwise indicated, reactions were conducted with 1.0 equiv of substrate, 1.2 equiv of nucleophile, and 1.0 mol% catalyst in toluene (0.1 M). The er was determined by HPLC or GC. [b]1.0 mmol scale, 0.1 mol% catalyst. [c]0.3 mol% catalyst. [d]0.5 M. [e]7 days. [f]4 days. [g]10 min.

from the beginning of the reaction, not unexpectedly, one enantiomer of substrate **1a** reacted faster than the other, affording a gradual enrichment of the enantiomeric excess of the substrate. This phenomenon corresponds well to a theoretical graph using the equation of Kagan[19] with a

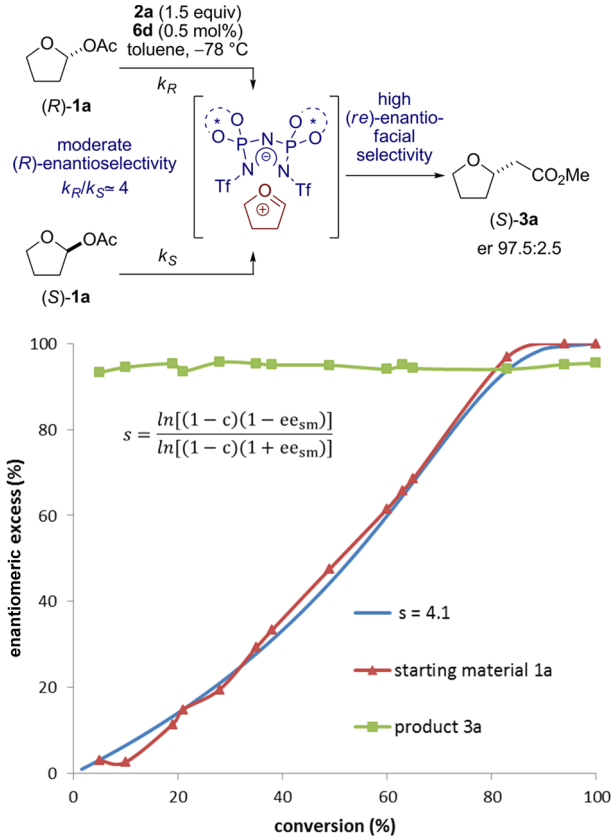


Figure 1. Proposed mechanism and enantiomeric excess vs conversion. s = selectivity factor, c = conversion, ee = enantiomeric excess, sm = starting material.

selectivity factor (s) of ca. 4. Both the decrement of the reaction rate by electron deficiency on oxygen (Table 2, entries 10 and 11) and the fact that both enantiomers are converted into the same enantiopure product are consistent with an S_N1 mechanism involving a cyclic oxocarbenium ion intermediate paired with the chiral counteranion.

In conclusion, we have developed a catalytic enantioselective synthesis of oxygen-containing heterocycles from readily accessible lactol acetate precursors and silylated nucleophiles. We suggest the reaction to proceed via an ACDC-type S_N1 mechanism involving a nonstabilized, aliphatic, cyclic oxocarbenium ion paired with the confined IDPi counteranion. The scope of our reaction is broad, and five-, six-, and seven-membered-ring lactol acetates react with various nucleophiles. Moreover, our catalyst system also tolerates aromatic substrates, furnishing chroman and dihydrobenzofuran products. Finally, a highly diastereo- and enantioconvergent catalytic asymmetric transformation has been realized with substrate **1h**, providing a C_2-symmetric tetrahydrofuran product.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b11993.

Experimental procedures, characterizations and analytical data of products, and NMR and HPLC spectra (PDF)

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AUTHOR INFORMATION

Corresponding Author

*list@kofo.mpg.de

ORCID

Benjamin List: 0000-0002-9804-599X

Notes

The authors declare no competing financial interest.

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NOTE ADDED AFTER ASAP PUBLICATION

The chemical scheme above Figure 1 was missing, it was added February 9, 2017.

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