Asymmetric Catalysis

DOI: 10.1002/ange.201304173

Catalytic Enantioselective Iodoetherification of Oximes**

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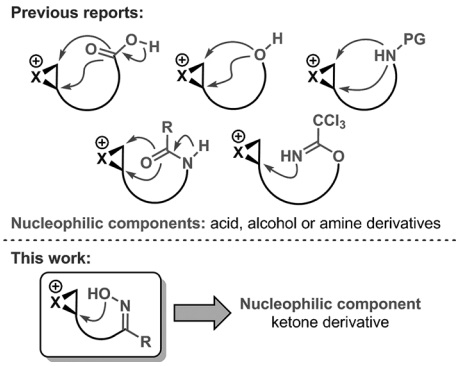
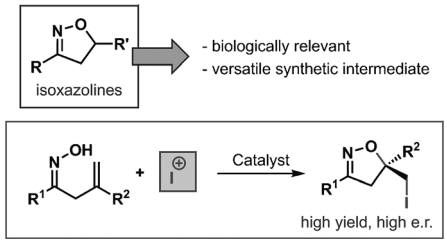
Dedicated to Professor E. J. Corey on the occasion of his 85th birthday

Heterodifunctionalization of unactivated olefins continues to be an attractive and widely utilized strategy for the generation of densely functionalized organic molecules. Electrophilic halogen induced reactions of olefins are remarkably efficient and popular for olefin heterodifunctionalization, mostly because of the stereoselectivity associated with it.[1] Development of asymmetric versions of these reactions proved challenging despite numerous attempts.[2] However, the last few years have witnessed a tremendous advancement in this area.[3] Since the initial breakthroughs in 2010,[4] numerous examples concerning catalytic asymmetric halolactonization,[5] haloaminocyclization,[6] haloetherification,[7] and other halofunctionalization reactions[8] of olefins appeared using various activation concepts (Scheme 1).[3c]



Scheme 1. Catalytic asymmetric halocyclization reactions.

We disclose here a catalytic method for the highly enantioselective iodoetherification of β,γ-unsaturated oximes, a hitherto unprecedented asymmetric transformation (Scheme 1).[9] Isoxazolines are an important class of compounds found in several biologically active agents and versatile intermediates in organic synthesis.[10] In spite of their utility in chemistry and biology, there is no report on the enantioselective synthesis of isoxazolines containing a quaternary stereogenic center. Our method offers a straightforward access to enantioenriched Δ^2-isoxazolines containing a quaternary stereogenic center (Scheme 2).[11]



Scheme 2. Catalytic enantioselective iodoetherification of oximes and its relevance to isoxazolines.

We have recently reported an *N*-bromosuccinimide (NBS)-mediated alcohol oxidation catalyzed by thiourea derivatives, which presumably proceeds through a halogen bonding interaction between the Lewis-basic sulfur center of thiourea and the electrophilic bromine atom.[12] We reasoned that a similar interaction might prove pivotal for electrophilic halogen induced olefin heterodifunctionalization. In fact, the same Lewis base catalysis[13] has been extensively studied by Denmark and Burk for halocyclization reactions[14] and also proposed as the key by Yeung et al. for the bromocyclization reactions catalyzed by aminothiocarbamate derivatives.[3e]

Iodoetherification of β,γ-unsaturated oxime **1a** using commercially available *N*-iodosuccinimide (NIS, **2**) as the electrophilic iodine source was chosen as the model reaction for catalyst screening and optimization of reaction conditions (Table 1). At the outset of our investigation it became apparent that the efficient uncatalyzed reaction (80% yield within 2 h at 25 °C; Table 1, entry 1) is the first hurdle, which needs to be surmounted for achieving any useful level of enantioselectivity. Fortunately, the background reaction was completely suppressed at −78 °C (Table 1, entry 2), allowing for the assessment of potential catalyst candidates **I**–**VII**.[15] The bisthiourea derivative **I** did not catalyze the reaction (Table 1, entry 3), thus indicating that the Lewis-basic sulfur center alone is not sufficient to bring about this transformation and points out the requirement of a Brønsted-basic functionality in the catalyst. Consequently, we turned our attention to the bifunctional chiral compounds (**II**–**VII**) derived from cinchona alkaloids.[16] When the reaction was

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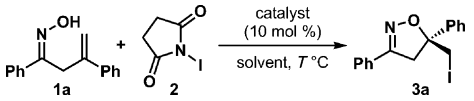
[**] Generous financial support from the Indian Institute of Science, Bangalore in the form of a start-up grant is gratefully acknowledged. This research program is funded by the Department of Science and Technology (DST), New Delhi (Grant No. SR/FT/CS-90/2010) and the Council of Scientific and Industrial Research (CSIR), New Delhi (Grant No. 01 (2505)/11/EMR-II). C.B.T. thanks CSIR for a doctoral fellowship. We thank Pavan M.S. and Vijith Shetty (Solid State and Structural Chemistry Unit, IISc, Bangalore) for their help with the X-ray diffraction analysis. We thank Soumya Jyoti Singha Roy for helpful discussion.

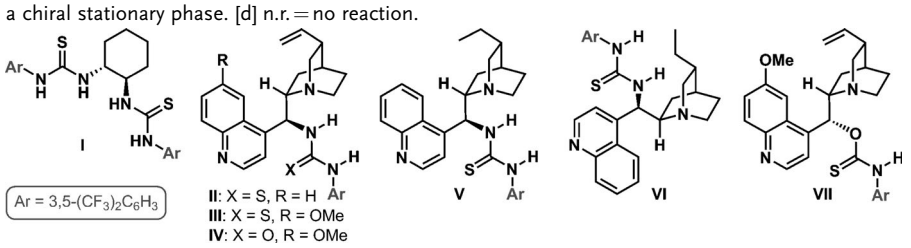
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201304173.

Table 1: Catalyst screening and reaction conditions optimization for the enantioselective iodoetherification of oxime **1a**.[a]



Entry	Catalyst	Solvent	Conc. [M]	I_2 [mol%]	T [°]	t [h]	Yield [%][b]	e.r.[c]
1	none	toluene	0.25	–	25	2	80	–
2	none	toluene	0.25	–	−78	48	n.r.[d]	–
3	**I**	toluene	0.25	–	−78	48	n.r.[d]	–
4	**II**	toluene	0.25	–	−78	18	60	82:18
5	**II**	CH_2Cl_2	0.25	–	−78	2	92	68:32
6	**II**	toluene/CH_2Cl_2 (4:1)	0.1	–	−78	14	72	92:8
7	**II**	toluene/$(CH_2Cl)_2$ (4:1)	0.1	–	−78	46	79	92:8
8	**II**	toluene/$CHCl_3$ (4:1)	0.1	–	−78	22	95	93.5:6.5
9	**II**	toluene/CH_2Cl_2 (4:1)	0.1	5	−78	14	72	93:7
10	**III**	toluene/CH_2Cl_2 (4:1)	0.1	–	−78	24	85	89:11
11	**IV**	toluene/CH_2Cl_2 (4:1)	0.1	–	−78	48	n.r.[d]	–
12	**IV**	CH_2Cl_2	0.1	–	−78	24	90	54:46
13	**V**	toluene/$CHCl_3$ (4:1)	0.1	–	−78	48	74	94:6
14	**V**	toluene/$CHCl_3$ (4:1)	0.1	5	−78	38	82	94.5:5.5
15	**V**	toluene/$CHCl_3$ (4:1)	0.1	2	−78	68	88	95:5
16	**V**	toluene/$CHCl_3$ (4:1)	0.1	2	−60	24	91	92:8
17	**VI**	toluene/$CHCl_3$ (4:1)	0.1	5	−78	58	83	6:94
18	**VII**	toluene/CH_2Cl_2 (4:1)	0.1	–	−78	66	n.r.[d]	–

[a] Reactions were carried out using 1.0 equiv of **1a** and 1.2 equiv of NIS (**2**). [b] Yield of isolated product after column chromatography. [c] Enantiomeric ratio (e.r.) was determined by HPLC analysis using a chiral stationary phase. [d] n.r. = no reaction.

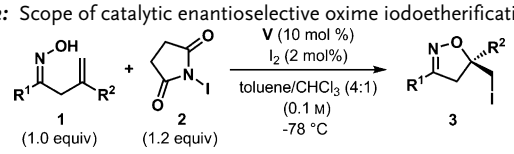


conducted with the cinchonidine-derived thiourea **II** (10 mol%) in toluene, the desired Δ^2-isoxazoline **3a** was produced in 60% yield with modest enantioselectivity (82:18 e.r.) within 18 h (Table 1, entry 4). A dramatic rate enhancement was observed in the more polar solvent dichloromethane, but the product was obtained with significantly inferior e.r. (Table 1, entry 5). A balance between the reaction rate and the product enantioselectivity was reached by using a mixture of toluene and chlorinated solvents (Table 1, entries 6–8), with toluene/$CHCl_3$ (4:1) emerging as the optimum (entry 8). A small amount (5 mol%) of iodine marginally improved the enantioselectivity (Table 1, entry 9). The methoxy substitution on the quinoline moiety showed a deleterious effect on the enantioselectivity as evident from the quinine-derived thiourea **III** (Table 1, entry 10). Curiously, the corresponding urea derivative **IV**, under the same reaction conditions, completely failed to catalyze the reaction (Table 1, entry 11). Even though **IV** showed sufficient catalytic activity in CH_2Cl_2, the product could be obtained only with very poor e.r. (Table 1, entry 12). These results are in sharp contrast to the enantioselective iodolactonization reported by Jacobsen and Veitch using a tertiary aminourea catalyst[4b] and clearly point towards a different activation principle. Product enantioselectivity was slightly improved when dihydrocinchonidine-derived thiourea **V** was employed as the catalyst (Table 1, entry 13). Further enhancement in enantioselectivity was achieved when the reaction was conducted in the presence of a catalytic amount (2 mol%) of molecular iodine (Table 1, entry 15). The reaction could be accelerated by increasing the temperature to −60 °C, though with a slight decrease of enantioselectivity (Table 1, entry 16). The other antipode of the product could be obtained with similar enantioselectivity by using the pseudoenantiomeric catalyst **VI** (Table 1, entry 17). The thiocarbamate derivative **VII**, similar to the catalysts developed by Yeung et al. for a number of olefin bromocyclization reactions,[3e] surprisingly turned out to be completely ineffective towards this iodoetherification reaction (Table 1, entry 18), thereby highlighting the importance of dual hydrogen bonding from thiourea. Overall, almost every structural component present in compound **V** also seems functionally essential for both catalytic activity and enantioselectivity.

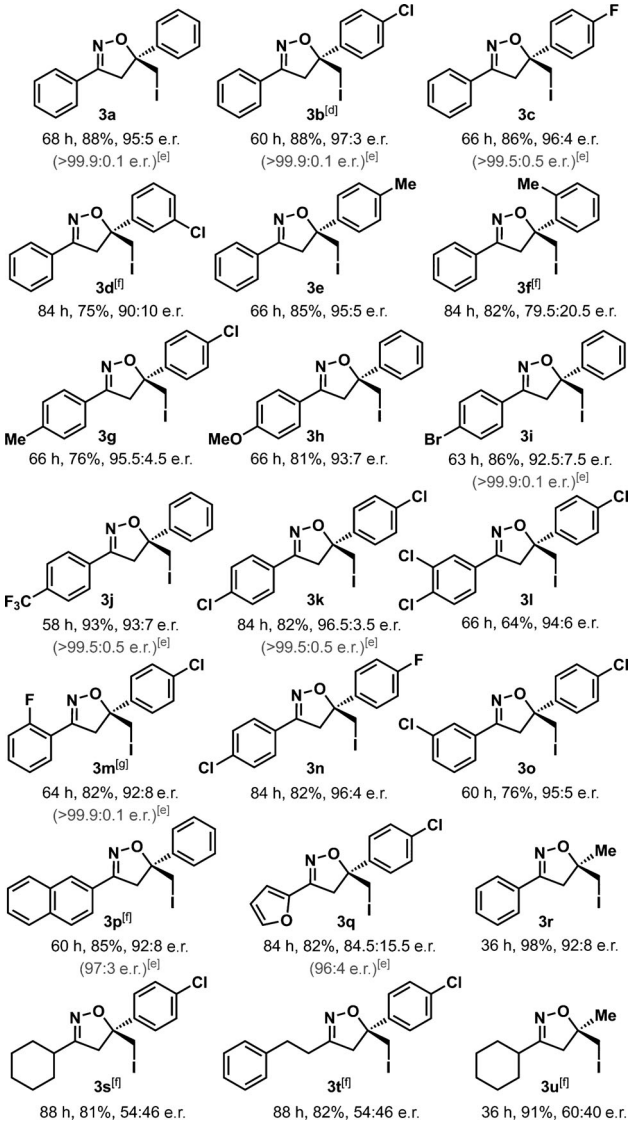
With the optimal catalyst and the reaction conditions identified (Table 1, entry 15), the substrate scope of this oxime iodoetherification reaction was explored. A broad range of β,γ-unsaturated oximes containing aromatic substituents on olefin and oxime could be converted to the corresponding Δ^2-isoxazolines **3a–q** in high yield with good to excellent enantioselectivity (Table 2). Both electron-rich and electron-deficient substituents on the aryl rings were generally tolerated. However, lower enantiomeric ratios were obtained in the cases of *ortho*-tolyl-substituted olefin **3f** and 2-furyl-substituted oxime **3q**. In most of these cases a single recrystallization furnished essentially enantiopure products. An oxime having an aliphatic substitution on the olefin was found to be an active substrate for this reaction, and the product **3r** could be obtained with good enantioselectivity (92:8 e.r.). In contrast, aromatic substitution on the oxime carbon atom appears to be essential for achieving a good level of enantioselectivity, since products from aliphatic oximes (**3s,t**) were formed with very poor e.r. Therefore it is not surprising that the product **3u** with aliphatic substitution on both sites was obtained with low e.r.

The absolute configuration of the product **3b** was found to be *S* by single-crystal X-ray diffraction analysis (Figure 1).[17] The absolute configuration of the remaining examples can be expected to be the same, when considering that a similar catalytic mechanism is followed.

Table 2: Scope of catalytic enantioselective oxime iodoetherification.[a,b,c]



1 (1.0 equiv) + 2 (1.2 equiv) → 3



[a] All reactions were performed on a 0.1 mmol scale. [b] Yields correspond to the isolated product after column chromatography. [c] Enantiomeric ratio (e.r.) determined by HPLC analysis using a stationary phase chiral column (See the Supporting Information for details). [d] Reaction was carried out at 0.07 M conc. [e] Values in parenthesis indicate e.r. of the product after a single recrystallization. [f] Reaction was conducted at −60 °C. [g] Reaction was conducted at −65 °C.

The oxime iodoetherification products can be subjected to a number of synthetically useful transformations (Scheme 3). For example, reductive deiodination of **3a** led to Δ^2-isoxazolines **4**, a masked self-aldol product of acetophenone. Substitution of the iodine atom with thiophenol and sodium azide furnished the corresponding thioether **5** and azide derivative **6**, respectively. The azide **6** was further converted to the Boc-protected amine **7** and the triazole derivative **8**. All these transformations were achieved in outstanding efficiency

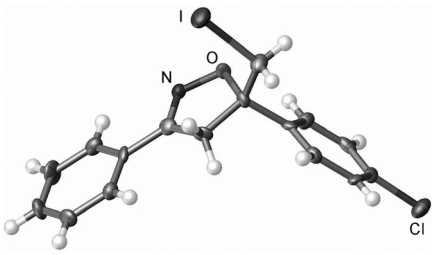
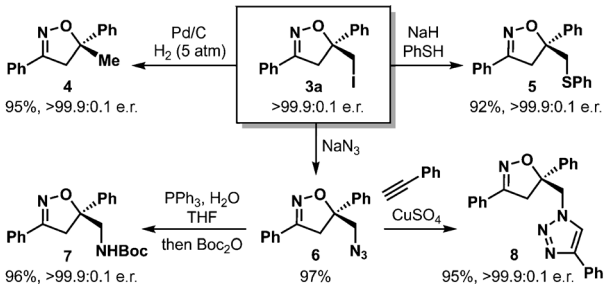


Figure 1. X-ray structure of **3b** showing its absolute configuration.



Scheme 3. Synthetic transformations involving **3a**.

and without any loss of enantiopurity, thereby highlighting the versatility and synthetic value of this enantioselective iodoetherification protocol and the resulting isoxazolines.

In conclusion, the first catalytic asymmetric iodoetherification of oximes has been accomplished with the help of a bifunctional thiourea catalyst. A variety of β,γ-unsaturated ketoximes were cyclized using commercially available NIS to furnish Δ^2-isoxazolines containing a quaternary stereogenic center in high yield with good to excellent enantioselectivity. To our knowledge, this is the first time that Δ^2-isoxazolines containing a quaternary stereogenic center were prepared in enantioenriched form. Considering the abundance of Δ^2-isoxazolines in biologically active agents and as synthetically useful chiral building blocks, our method should find application across various disciplines. Efforts towards elucidating the mechanism and expanding the scope of this reaction are currently underway and will be the subject of further reports.

Received: May 15, 2013
Revised: June 12, 2013
Published online: July 3, 2013

Keywords: asymmetric catalysis · bifunctional catalyst · organocatalysis · oximes · thioureas

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