Organocatalysis

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Asymmetric One-Pot Four-Component Coupling Reaction: Synthesis of Substituted Tetrahydropyrans Catalyzed by Diphenylprolinol Silyl Ether

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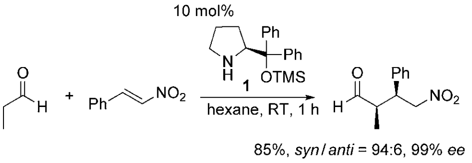
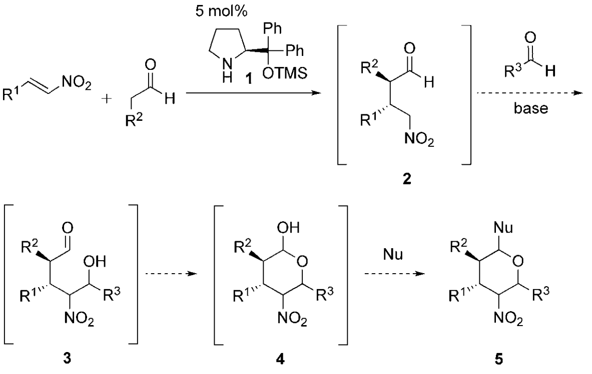
Multicomponent coupling reactions are one of the most powerful methods for assembling a single molecule from multiple starting materials and for forming several bonds in a one-pot process.[1] This uninterrupted sequence of reactions in a single flask eliminates several purifications, minimizes the generation of chemical waste, and saves time. Many successful examples of four-component reactions have been reported, such as the Ugi reaction,[2] and the anion relay chemistry reported by Smith et al.[3] The field of organocatalysis has developed rapidly in recent years,[4] and some organocatalyst-mediated four-component coupling reactions have been established.[5]

Tetrahydropyran is a synthetically important structural unit that is found in many natural products. Many methods have been developed for the preparation of the chiral tetrahydropyran structure,[6] including the hetero-Diels–Alder reaction,[7] intramolecular epoxide opening,[8] Ferrier rearrangement,[9] and the Prins reaction.[10]

We have previously reported the asymmetric direct Michael reaction of an aldehyde and a nitroalkene,[11] catalyzed by diphenylprolinol silyl ether **1**,[12] which was independently developed by our group[11] and the group of Jørgensen.[13] This synthetically important reaction[14] yields a chiral γ-nitroaldehyde with excellent enantioselectivity [Eq. (1); TMS = trimethylsilyl]; such an aldehyde is a useful intermediate that can be utilized in subsequent transformations. For instance, Enders and co-workers reported the domino reaction[1d,e] for the synthesis of chiral cyclohexenecarbaldehyde based on this reaction,[15] and Krause, Alexakis, and co-workers developed a domino reaction that involved the combination of the Michael reaction and a gold-catalyzed acetalization.[16] Our group reported the domino Michael/Henry reaction for the formation of chiral cyclohexane derivatives,[17] and recently we reported the synthesis of (−)-oseltamivir in two steps with a four-component coupling reaction as a key step.[18] We hypothesized that tetrahydropyran derivatives could be produced if the Michael adduct **2** [Eq. (2)] reacted with the aldehyde through the Henry reaction to produce the alcohol **3**, the hydroxy group of which would readily react intramolecularly with the aldehyde moiety to form the acetal, and thus generate the tetrahydropyranol **4**. Recently a similar reaction sequence was reported for an asymmetric three-component reaction, in which the conjugate addition of an aldehyde to a Michael acceptor was catalyzed by diphenylprolinol silyl ether, with a subsequent base-catalyzed addition/cyclization.[19] We thought that tetrahydropyranol **4** would react with a nucleophile to provide a tetrahydropyran, in which all the carbon atoms on the pyran ring are substituted with different groups. We report herein the results of the experiments performed to demonstrate this hypothesized process.



(1)



(2)

Ethyl glyoxylate was chosen as an electrophilic aldehyde because the anticipated 6-carboxy tetrahydropyran product is a synthetically important building block. At the outset propanal, nitrostyrene, and ethyl glyoxylate[20] were selected as model substrates. Thus, the γ-nitroaldehyde **2a** (Table 1), generated from the Michael addition of propanal to nitrostyrene by our established method,[11] was treated with ethyl glyoxylate in the presence of a base to produce a substituted tetrahydropyranol derivative. The effect of the base (Table 1) was studied using this one-pot reaction. The first Michael reaction proceeded in the presence of 5 mol% of catalyst **1** in toluene at room temperature for 7 hours. A small quantity of

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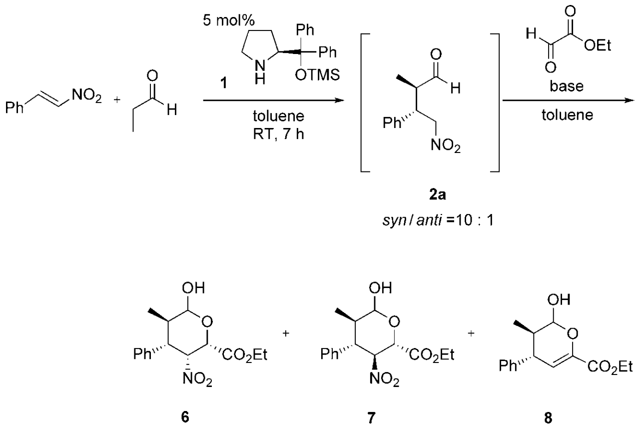
Table 1: The effect of base in the one-pot synthesis of tetrahydropyranol derivatives.[a]



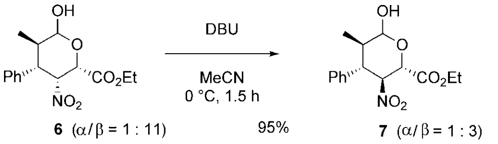
Entry	Base	Base [equiv]	T [°C]	t [h]	Yield [%][b] 6	7	8
1	DBU	2	23	17	<5	56	10
2	DBU	0.1	23	10	73	22[c]	<5
3	Et_3N	2	0	1	71 (98)[d]	24[c]	<5
4	Et_3N	2	−50	21	76 (>99)[d]	15[c]	<5
5	K_2CO_3	2	23	1	76 (98)[d]	18[c]	<5

[a] Reaction conditions: nitrostyrene (1.0 mmol), propanal (1.2 mmol), catalyst **1** (0.05 mmol), ethyl glyoxylate (261 μL, 1.2 mmol; used in the polymer form as a 47% toluene solution), toluene (1.0 mL). See the Supporting Information for detail. [b] Yield of the isolated product. [c] Isolated as an anomeric mixture. [d] Enantiomeric excess of **6** that was determined by HPLC analysis on a chiral stationary phase. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

the reaction mixture was analyzed using ^1H NMR spectroscopy, which indicated that complete conversion had occurred with a 10:1 diastereoselectivity. A toluene solution of the polymeric form of ethyl glyoxylate and base was added to the toluene solution of the first Michael adduct. When two equivalents of DBU were used, the reaction produced a 56% yield of tetrahydropyranol **7** and a 10% yield of dihydropyranol **8** (Table 1, entry 1); the latter is formed by the elimination of nitrous acid. When the quantity of the base was decreased another isomer (**6**) having the nitro moiety in the axial position was obtained (73% yield) along with a mixture of other diastereomers (22% yield; Table 1, entry 2). Compound **6** is the kinetic product obtained with excellent enantioselectivity, whereas compound **7** is the thermodynamic product (see below). Further investigation revealed that compound **6** is the predominant product when Et_3N and K_2CO_3 are used as the base, and is obtained in good yield (Table 1, entries 3–5). However, when all the reagents are mixed together initially, instead of adding the ethyl glyoxylate and base after the generation of the Michael product **2a**, only traces of the desired product were obtained.

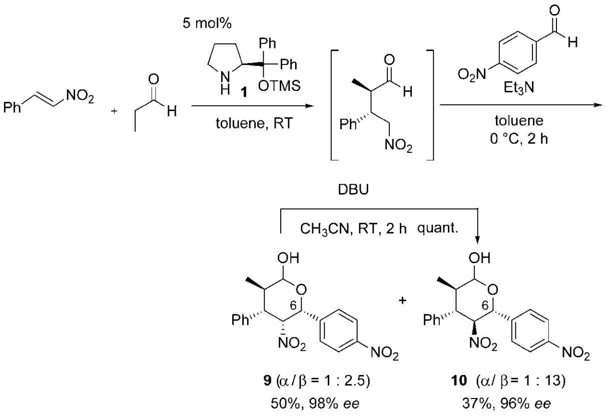
Having determined the best reaction conditions, the general nature of the reaction could be investigated (Table 2). In addition to nitrostyrene, β-aryl-substituted nitroethenes were also found to be suitable substrates. Phenyl groups that have electron-rich and electron-deficient substituents at the *para* position were successfully used to produce the tetrahydropyran derivatives with good yield and excellent enantioselectivity (Table 2, entries 2 and 3). In addition to aromatic groups heteroaromatic groups including pyridine and furan were also suitable (Table 2, entries 4 and 5). A tetrahydropyranol that contains two different ester moieties can be successfully synthesized from *tert*-butyl 3-nitropropenoate (Table 2, entry 6). The reaction can also be applied to β-alkyl-substituted nitroethene, which produces substituted tetrahydropyranols with excellent enantioselectivity (Table 2, entries 7 and 8). With respect to the nucleophilic aldehyde, butanal, isovaleraldehyde, and 3-phenylpropanal were suitable aldehydes in addition to propanal, and the tetrahydropyranol derivatives were obtained with excellent enantioselectivity (Table 2, entries 9–11). A highly substituted tetrahydropyranol having an alkoxy and two ester moieties was prepared with excellent enantioselectivity (Table 2, entry 12).

The kinetic product **6** has the nitro group in the axial position, whereas the thermodynamic compound **7** has the nitro moiety in the equatorial position. Therefore, the isomerization of **6** into **7** was investigated. When **6** was treated with DBU (1.0 equiv) at 0 °C for 1.5 hours, isomerization into **7** occurred with a 95% yield [Eq. (3)]. This indicates that good yields of both isomers **6** and **7** can be obtained.



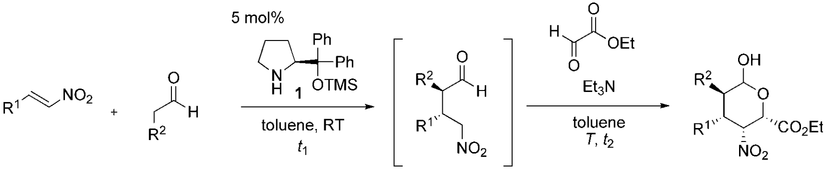
(3)

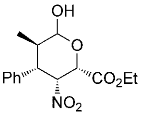
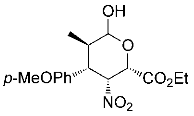
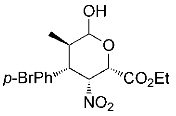
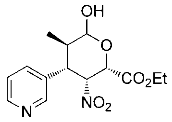
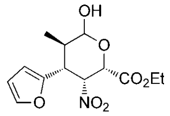
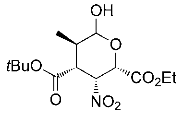
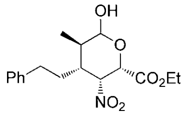
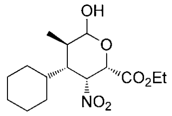
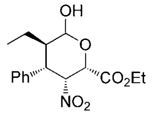
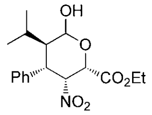
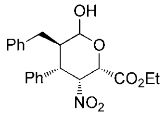
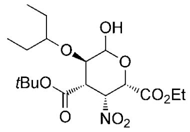
Next we investigated the reaction using *p*-nitrobenzaldehyde as an electrophilic aldehyde. It was found that the one-pot reaction also proceeded smoothly to produce good yields of the 6-*p*-nitrophenyl-substituted tetrahydropyranols **9** and **10** with excellent enantioselectivity; in this reaction the stereochemistry at the C6 position was completely controlled [Eq. (4)]. The tetrahydropyranol **9** was successfully converted quantitatively into the thermodynamically more stable **10** by treatment with DBU in CH_3CN. By adding DBU to the reaction of a nitroalkane and an aldehyde, the Henry reaction



(4)

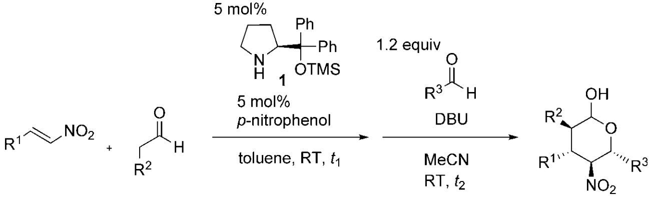
Table 2: The general reaction of nitroalkene, aldehyde and ethyl glyoxylate in the one-pot synthesis of tetrahydropyranols.[a]

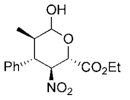
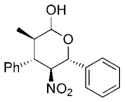
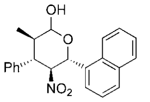
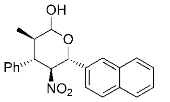
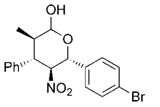
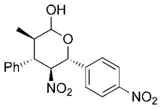
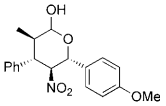
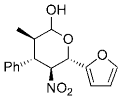
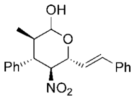
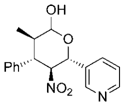
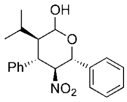
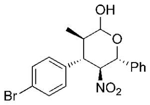
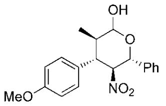


Entry	R^1	R^2	t_1 [h]	T [°C]	t_2 [h]	Product	Yield [%][b,c]	*ee* [%][d]
1	Ph	Me	6	−50	21		76 (1:11)	>99
2	*p*-MeOC$_6$H$_4$	Me	10	−50	55		75 (1:7)	96
3	*p*-BrC$_6$H$_4$	Me	8	−50	9		67 (1:10)	98
4	3-pyridyl	Me	12	−50	12		49 (1:16)	98
5	2-furyl	Me	12	−30	9		74 (1:>20)	>99
6	*t*BuO$_2$C	Me	4	−50	24		50 (1:6)	98
7	PhCH$_2$CH$_2$	Me	12	−30→−10	16		64 (1:1.4)	98
8	cyclohexyl	Me	120	−20→0	42		51 (1:3.5)	91
9	Ph	Et	26	−20	7		74 (1:9)	91
10	Ph	*i*Pr	156	−20	8		81 (1:7)	99
11	Ph	PhCH$_2$	67	−20	4		70 (1:7)	95
12	*t*BuO$_2$C	Et$_2$CHO	3	−50→−20	6		44 (1:2.9)	92

[a] Reaction conditions: nitroalkene (1.0 mmol), aldehyde (1.2 mmol), catalyst **1** (0.05 mmol), ethyl glyoxylate (261 μL, 1.2 mmol; used in the polymer form as a 47% toluene solution), toluene (1.0 mL). See the Supporting Information for details. [b] Yield of the isolated product. [c] The figure in the brackets is the diastereomeric ratio of α and β isomers. [d] Determined by HPLC analysis on a chiral stationary phase.

Table 3: One-pot synthesis of tetrahydropyranols by an asymmetric Michael/Henry/acetalization/isomerization reaction sequence.[a]



Entry	R^1	R^2	R^3	t_1 [min]	t_2 [h]	Product	Yield [%][b,c]	*ee* [%][d]
1[e, f]	Ph	Me	CO_2Et	15	38		79 (1:2.9)	99
2	Ph	Me	Ph	15	5		79 (1:1)	99
3	Ph	Me	1-naphthyl	15	5		71 (1:1.3)	94
4	Ph	Me	2-naphthyl	15	7		75 (1:4.7)	99
5[e]	Ph	Me	p-BrC_6H_4	15	21		89 (1:1.6)	95
6	Ph	Me	p-$NO_2C_6H_4$	15	10		89 (1:13)	96
7	Ph	Me	p-$MeOC_6H_4$	15	21		74 (1:1.3)	98
8[e]	Ph	Me	2-furyl	15	8		84 (1:2.2)	97
9	Ph	Me	styryl	15	7		50 (1:1.5)	98
10	Ph	Me	3-pyridyl	15	3		91 (1:2.1)	99
11	Ph	*i*Pr	Ph	1140	6		85 (1:2)	96
12	p-BrC_6H_4	Me	Ph	15	5		86 (1:1.3)	96
13	p-$MeOC_6H_4$	Me	Ph	15	23		78 (1:1.5)	95

[a] Reaction conditions: nitroalkene (1.0 mmol), nucleophilic aldehyde (1.2 mmol), electrophilic aldehyde (1.2 mmol), *p*-nitrophenol (0.05 mmol), and catalyst **1** (0.05 mmol). Unless otherwise shown, the reaction was performed at room temperature. Toluene was employed in the Michael reaction and CH_3CN was used in the subsequent reaction. See the Supporting Information for details. [b] Yield of the isolated product. [c] The figure in the parenthesis is the diastereomer ratio of α and β isomers. [d] Determined by HPLC analysis on a chiral stationary phase. [e] Toluene was employed in the Henry/acetalization/isomerization reaction. [f] The reaction was performed at −20°C.

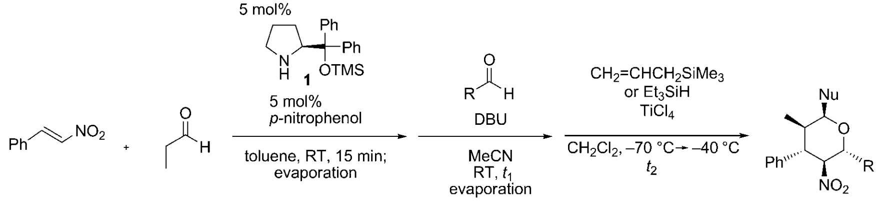
and acetalization, with subsequent isomerization proceeded in one pot to afford **10** in good yield (89 %; Table 3, entry 5).

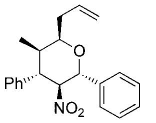
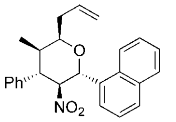
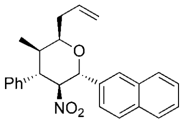
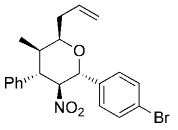
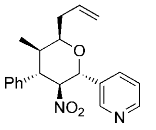
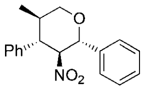
The scope of the selective synthesis of the thermodynamically stable tetrahydropyranol, from the nitroalkene and two different aldehydes, by a one-pot sequence involving the asymmetric Michael/Henry/acetalization/isomerization reactions was investigated (Table 3). As we found that the first Michael reaction was accelerated by acid, this reaction was performed in the presence of 5 mol % of *p*-nitrophenol, and was completed within 15 minutes. Not only ethyl glyoxylate, but also aromatic aldehydes, such as benzaldehyde, reacted efficiently to afford the tetrahydropyranol in good yield and with excellent diastereo- and enantioselectivities. Both electron-deficient aromatic aldehydes such as *p*-bromobenzaldehyde and *p*-nitrobenzaldehyde (Table 3, entries 5 and 6, respectively) and electron-rich aromatic aldehydes such as *p*-anisaldehyde (Table 3, entry 7) afforded the corresponding tetrahydropyranols with excellent enantioselectivity. Heteroaromatic aldehydes such as furfural (Table 3, entry 8) were also successfully employed.

The tetrahydropyranols had been prepared in a highly diastereo- and enantioselective manner. We next investigated the four-component coupling reaction to give access to tetrahydropyranes, which are synthetically useful chiral building blocks. The three-component coupling product, which was generated above, was directly treated with allyltrimethylsilane or triethylsilane in the presence of a Lewis acid. After optimization of the reaction conditions, $TiCl_4$ was found to be a suitable promoter to afford the highly substituted tetrahydropyran with excellent enantioselectivity (Table 4). Not only benzaldehyde (Table 4, entry 1), but also 1- and 2-naphthalenecarbaldehyde, and *p*-bromobenzaldehyde were successfully employed as electrophilic aldehydes (Table 4, entries 2–4). The heteroaromatic aldehyde 3-pyridinecarbaldehyde was also a suitable electrophilic aldehyde (Table 4, entry 5). In all cases, 2-allyltetrahydropyrans, in which all the carbon atoms are substituted with different substituents, were obtained with excellent diastereo- and enantioselectivity. When triethylsilane was used instead of allyltrimethylsilane, the reduction proceeded efficiently to afford the tetrahydropyran in 75 % yield with 99 % *ee* (Table 4, entry 6). All these reactions were performed in a single flask.

In summary, we have developed an asymmetric one-pot synthesis of substituted tetrahydropyranols with excellent diastereo- and enantioselectivity through the diphenylprolinol silyl ether mediated Michael reaction of aldehydes and nitroalkenes, with subsequent Henry and acetalization reactions. The one-pot four-component coupling reaction was also realized by using an asymmetric Michael/Henry reaction/acetalization/Lewis acid mediated allylation reaction to provide highly substituted tetrahydropyran derivatives with excellent diastereo- and enantioselectivity. All the carbon atoms on the tetrahydropyran ring are substituted with different groups, and the relative and absolute stereochemistry of the five contiguous carbon centers is completely controlled. As the allyl moiety can be easily transformed into other functional groups, the 2-allyl tetrahydropyran generated is a useful chiral building block.

Table 4: One-pot synthesis of tetrahydropyrans by the asymmetric Michael/Henry/acetalization/isomerization/nucleophilic addition reaction sequence.[a]



Entry	R	Nucleophile	t_1 [h]	t_2 [h]	Product	Yield [%][b]	*ee* [%][c]
1	Ph	$CH_2{=}CHCH_2TMS$	5	6		72	99
2	1-naphthyl	$CH_2{=}CHCH_2TMS$	12	4		60	94
3	2-naphthyl	$CH_2{=}CHCH_2TMS$	12	4		65	99
4	*p*-BrC_6H_4	$CH_2{=}CHCH_2TMS$	5	6		73	95
5	3-pyridyl	$CH_2{=}CHCH_2TMS$	3	8		57	99
6	Ph	Et_3SiH	5	10		75	99

[a] Reaction conditions: nitrostyrene (1.0 mmol), propanal (1.2 mmol), electrophilic aldehyde (1.1 mmol), *p*-nitrophenol (0.05 mmol), catalyst **1** (0.05 mmol), and allylsilane (3.5 mmol) or Et_3SiH (3.5 mmol), and $TiCl_4$ (3.5 mmol). See the Supporting Information for details. [b] Yield of the isolated product. [c] For the determination of the enantiomeric excess, see the Supporting Information.

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