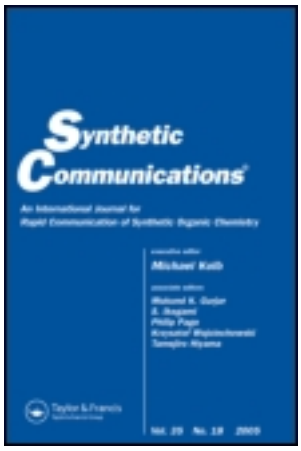

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Supported 3,5-Disubstituted Chiral Hydantoin: A Practical Catalyst for the Asymmetric Hydrocyanation of 3-Phenoxybenzaldehyde

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ABSTRACT

A novel synthesis of six (*R*)-3,5-disubstituted chiral hydantoins in mixed solvent is reported. The catalysts were supported on a new polymeric resin afterwards and their enantioselectivities are examined via the asymmetric hydrocyanation of 3-phenoxybenzaldehyde.

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Key Words: Chiral hydantoin; Catalyst; 3-Phenoxybenzaldehyde; Polymeric resin; Hydrocyanation; Enantioselectivity.

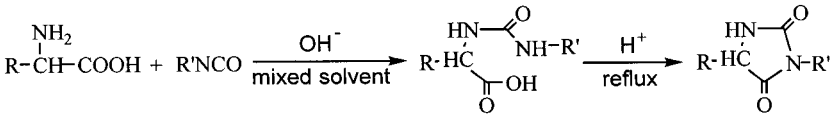
Chiral hydantoin (**1**) is a highly efficient catalyst for the asymmetric synthesis of optically active cyanohydrins. (*S*)-2-Hydroxy-2-(3-phenoxyphenyl)acetonitrile ((*S*)-**2**), being one of them, is an important alcohol moiety of optically active pyrethroid insecticides.[1] With respect to the enantioselective addition of hydrogen cyanide to 3-phenoxybenzaldehyde (*m*-PBA), there have been few literatures concerning the enantioselectivity in the presence of a chiral catalyst. Mori et al. have reported that the chiral cyclic dipeptide containing a (*S*)-histidine residue, demonstrated high enantioselectivities in the asymmetric hydrocyanation of aldehydes.[2] Danda has prepared several kinds of (*R*)-chiral hydantoins, which possess a structure similar to that of cyclo[(*S*)-phenylalanyl-(*S*)-histidyl], and reported that the highest enantiomeric excess (ee) of (*S*)-**2** was 37% in hydrocyanation of *m*-PBA.[3] In a published UK patent, a chiral cyclic dipeptide, adsorbed on a solid support comprising a non-ionic polymeric resin, XAD-4, was made for asymmetric synthesis of (*S*)-**2**.[4] All these methods, however, suffer from different drawbacks, and they are somewhat impractical from the industrial point of view.

It is therefore an object of the present study to provide an easily-made catalyst via reaction of (*R*)-histidine and aromatic isocyanate, in which mixed solvent was used instead of water. In our research, six kinds of 3,5-disubstituted chiral hydantoins have been prepared and supported on NDA-99, one of our newly-developed hypercrosslinked polymeric adsorption resins, which has better adsorption capacity compared with Amberlite XAD-4 (Rohm and Haas Company). In addition, the catalytic activities of the supported catalysts were investigated by means of asymmetric hydrocyanation of *m*-PBA on a similar industrial scale.

In mixed solvent, the chiral catalysts were prepared firstly by coupling of the specific amino acid with a series of isocyanates, some of which were obtained from reaction of the corresponding amine with phosgene, and then followed by cyclization under acidic condition to give **1** (Sch. 1).

The mixed solvent is a mixture of water and 1,4-dioxane, THF or acetonitrile, in which 1,4-dioxane being the best choice for the coupling reaction. We found that the by-product, diphenylurea, derived from hydrolysis of isocyanate, could be easily separated after the reaction, pure product thus being obtained.

The asymmetric hydrocyanation of *m*-PBA was carried out in the presence of 1.0–2.5 mol% of **1** (based on *m*-PBA), supported on a resin



1

Scheme 1. **1a** (R = 5-imidazolylmethyl, R' = Ph); **1b** (5-imidazolylmethyl, R' = benzyl); **1c** (5-imidazolylmethyl, R' = 4-fluorobenzyl); **1d** (R = benzyl, R' = Ph); **1e** (R = benzyl, R' = benzyl); **1f** (R = benzyl, R' = 4-fluorobenzyl).

2

Scheme 2.

adsorbent, to give (*S*)-**2** with reasonable optical yield, as well as high conversion of *m*-PBA (Sch. 2).

In an attempt to examine the catalytic activities of different chiral hydantoins, addition of HCN to *m*-PBA, catalyzed by **1** directly and supported ones, was carried out in a similar procedure respectively. Some properties of the catalysts, conversions and ee values are listed in Table 1.

As can be seen from Table 1, the suspended catalysts resulted in a low ee value in the reaction compared with the supported ones, attributed to their poor solubility in the reaction mixture. Moreover, it was surprisingly found that catalyst supported on NDA-99 resulted in higher conversion and ee value than that on XAD-4. This may be due to its higher surface area and partial polarity of the novel structure with the residual chloromethyl, carbonyl, and hydroxyl groups. Table 2 lists some characteristics of the two polymeric adsorbents. It is believed that the catalyst adsorbed on NDA-99, provides an activated monomolecular layer of the chiral catalyst, which is responsible for the high efficiency and selectivity of the supported catalyst. Among all the catalysts, **1b** and **1c** immobilized on NDA-99 exhibited satisfactory catalytic activities with conversion of 96.1%, 94.8%, and ee of 49.7%, 64.0%, respectively.

The most important factor to practically use the supported catalysts, on the other hand, is the stability of them. In an attempt to test the stabilities of the catalysts on polymeric adsorbents, the procedure for asymmetric hydrocyanation of *m*-PBA was thus repeated consecutively,

Table 1. Experimental results of asymmetric addition of hydrogen cyanide to *m*-PBA catalyzed by suspended and supported chiral catalysts.

Chiral hydantoin	Solid support	Catalyst adsorbed/ solid support (%)	Conversion (%)	ee (%)
1a			89.2	9.3
1b			96.1	12.7
1c			94.8	17.6
1d			90.0	10.4
1e			91.5	8.3
1f			88.3	13.0
1a	XAD-4	4.12	86.0	21.8
1b	XAD-4	4.50	92.4	35.3
1c	XAD-4	5.06	95.5	42.1
1d	XAD-4	4.52	80.9	17.3
1e	XAD-4	5.30	86.0	20.4
1a	NDA-99	4.64	87.2	35.5
1b	NDA-99	5.38	96.1	49.7
1c	NDA-99	6.31	94.8	64.0
1d	NDA-99	6.05	86.5	21.7
1e	NDA-99	5.10	90.2	45.8
1f	NDA-99	5.42	86.4	32.1

Table 2. Typical characteristics of XAD-4 and NDA-99 adsorbents.

Property	XAD-4	NDA-99
Structure	Polystyrene, aromatic	Amine modified polystyrene
Polarity	Nonpolar	Moderate polar
BET surface area (m^2/g)	750[a]	950
Porosity (cm^3/g)	1.02	0.52
Average pore diameter (nm)	4.0	2.5
Average particle size (mm)	0.5	0.3–0.4
Residual chloride content (%)		3.5
Oxygen content (%)		5.95

[a]Value according to reference.[5]

using **1c** supported both on XAD-4 and NDA-99. The results of 6 runs for each solid support are detailed in Table 3.

As shown in Table 3, the catalytic activity of **1c** on XAD-4 substantially reduces with time, and the column thus needs to be recharged

Table 3. Repeated reactions of asymmetric hydrocyanation of *m*-PBA catalyzed by **1c** on different solids.

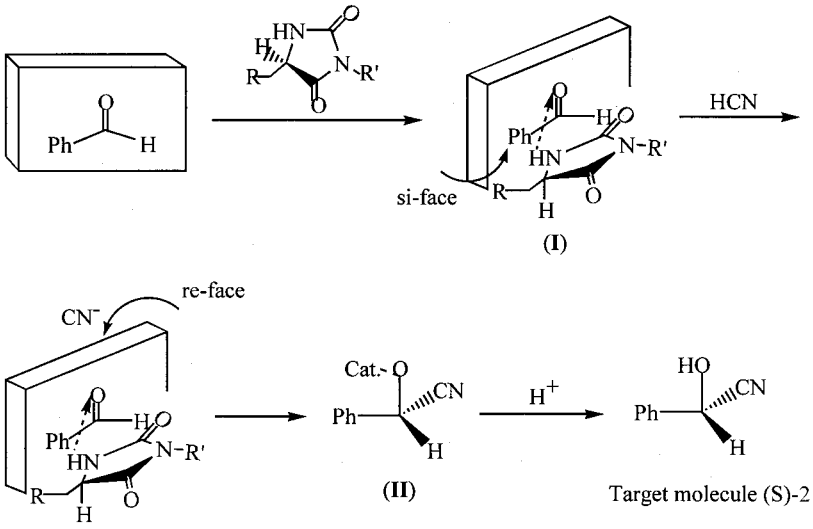
Entry	Support	Cat./*m*-PBA (mole %)[a]	*m*-PBA conc. (%)[b]	Reaction temp. (°C)	Reaction time (h)	Conversion (%)	ee (%)[c]
1	XAD-4	2.0	21.75	5	3.0	94.1	39.4
2	XAD-4	1.04	21.75	5	3.0	85.4	33.5
3	XAD-4	0.79	21.75	5	3.0	87.0	18.2
4	XAD-4	0.36	25.8	5	3.5	74.9	12.2
5	XAD-4	0.40	25.8	5	4.0	82.9	10.3
6	XAD-4	0.38	25.8	5	4.0	78.1	12.7
7	NDA-99	2.0	21.75	5	3.0	95.0	66.3
8	NDA-99	1.85	21.75	5	3.0	96.3	62.4
9	NDA-99	1.68	21.75	5	3.0	94.1	61.2
10	NDA-99	1.53	21.75	5	3.5	97.0	63.9
11	NDA-99	1.50	25.8	5	4.0	93.6	57.0
12	NDA-99	1.46	25.8	5	4.0	94.7	59.4

[a]The ratio is calculated according to the initial concentration and the amount recycled.
[b]The *m*-PBA concentration is defined as: (*m*-PBA volume/total volume of solution) × 100.
[c]All reactions are carried out under similar conditions.

before each performance, which is in correspondence with the literature reported.[4] In contrast, **1c** on NDA-99 provides a consistent performance with favorable conversions of 94–96% and ee of around 62%, and does not undergo appreciable physical changes after 5 runs. It is attributed to the fine pore structures of the latter and interactions of polar groups between the catalyst and the adsorbent, resulting in a tight immobilization of the chiral hydantoin. Therefore, the process introduced herein is practical.

When carrying out asymmetric synthesis, it is generally believed that the enantioselectivity results from the spatial blocking effect of the chiral catalyst.[6] We may discuss the catalytic mechanism of asymmetric hydrocyanation of aldehyde catalyzed by the chiral hydantoin, **1c** for example, based on the postulation which Tanaka et al. made for the asymmetric hydrocyanation by a cyclic dipeptide.[7] It is postulated, according to Prelog rule,[8] that the molecule of the aldehyde forms a stereo structure with si-face and re-face (Sch. 3).

As illustrated in Sch. 3, the carbonyl oxygen in the substrate is considered firstly to combine with the catalyst **1c** ($R =$ 5-imidazolylmethyl,



Scheme 3.

$R' =$ 4-fluorobenzyl), via hydrogen bond, to form the intermediate **I**. It is also believed that hydrogen cyanide interacts with the imidazolyl moiety of the histidine residue to form a cyanide ion, which subsequently attacks the re-face of the activated carbonyl group to form the intermediate **II**, while the si-face is blocked by the aromatic ring of 4-fluorobenzyl isocyanate residual group (R'), in which the substituted fluoro-group reinforces the blocking effect to some extent. However, the blocking caused by the aromatic ring would be too loose to give (*S*)-**2** with a satisfactory enantioselectivity.[9]

For addition of hydrocyanic acid to aldehyde, some important factors which should be considered are: (a) the molar ratio of the catalyst to *m*-PBA, (b) the concentration of *m*-PBA, and (c) the temperature at which the reaction takes place.

The quantity of the catalyst should be in the range of 1.0–2.5%. The molar ratio below 1.0% does not afford high ee value, but high conversions are obtained both at low and high catalyst concentrations. Higher catalyst concentration, on the other hand, may adversely affect ee value, due to competing racemization.

The concentration of *m*-PBA in the reaction mixture affects the rate of reaction, as well as conversion and ee. With concentrations of *m*-PBA between 20–25%, high conversions of 92–96% and ee of 60–65% are obtained.

The reaction temperature is usually around 0°C. From −5°C to 25°C, conversion proceeds in the reaction. However, the lower the temperature, the higher the ee, the temperature of 5°C is thus suitable for the reaction.

Other factors of importance are the excess of HCN and solvent of the reaction. In our study, two molar times of HCN relative to *m*-PBA were used. With respect to the solvent, toluene is recommended. However, other solvents can be employed as well, such as benzene, disopropyl ether, and hydrocarbon solvents. But they mostly result in unsatisfactory conversions and ee.

In conclusion, chiral hydantoin **1c** was found to be an excellent optically active catalyst for asymmetric synthesis of (*S*)-cyanohydrins, owing to its catalytic groups in the structure. While the hypercrosslinked polymeric adsorbent NDA-99, which possesses a favorable pore structure and functional groups, demonstrated fine properties for supporting the catalyst **1c**. The supported chiral hydantoin, **1c** on NDA-99, therefore, has been evaluated as a suitable catalyst for asymmetric synthesis of (*S*)-**2**.

EXPERIMENTAL

General

X-4 Microscopic melting point meter and WXG-4 polarimeter (Shanghai Optic Instrument Plant, Shanghai, China), were used to detect the data of m.p. and optical rotations of **1** respectively. ^{1}H NMR spectra were obtained at 300 MHz on a Bruker AM-300; IR spectra were obtained on a Neclet FTR-360; Carleerbea EA-1106 was used for elementary analysis; Waters HPLC-660 was employed, YWG-18 being used as column for determination of the conversion of *m*-PBA, Sumipax OA-4100 (Sumitomo Chemical Co. Ltd., Japan) as chiral column for determination of the optical yield of (*S*)-**2**.

Preparation of (5R)-5-(5-Imidazolylmethyl)-3-phenyl-2,4-imidazolidinedione (**1a**)

To a mixture of 3.1 g (20 mmol) of (*R*)-histidine in 150 mL of mixed solvent (H_2O/1,4-dioxane = 1/3, V/V), was added 30% aqueous NaOH under mechanical stirring, until the solution showed pH 9 and the solid disappeared. Three point six grams (30 mmol) of phenyl isocyanate was

then added to the solution at 35–40°C, meanwhile, 30% aqueous NaOH was added drop-wise to adjust pH 8.5–9. After the pH was unchangeable, the reaction mixture was stirred at 40°C for 1.5 h, and distilled under vacuum to remove 1,4-dioxane. After being cooled to ambient temperature, the mixture was filtered as to separate the by-product derived from hydrolysis of isocyanate.

The filtrate was adjusted to pH 1 with 36% hydrochloric acid and kept under reflux for 3 h. Finally, the mixture was cooled to 5°C and neutralized to pH 6 with 30% aqueous NaOH. After being allowed to stand at 5°C for 2 h, the precipitate was filtered, washed with cold water and then recrystallized from anhydrous ethanol to give 3.9 g of **1a** as white crystals: yield (76%), m.p. 187–188°C. $[\alpha]_D^{25}$ 158.2° (MeOH). IR (KBr): 3192, 1765, 1711, 1595, 1500 (cm^{-1}). ^1H NMR (TMS, DMSO-d_6), δ: 3.0 (m, 2H, CH_2), 4.5 (t, 1H, CH), 6.9 (s, 1H, CONH), 7.2–7.5 (m, 5H, ArH), 7.6 (s, 1H, CH), 8.4 (s, 1H, NH). Calcd. for $C_{13}H_{12}N_4O_2$ (**1a**): C, 60.93; H, 4.72; N, 21.86. Found: C, 60.60; H, 4.84; N, 21.79%.

Preparation of (5R)-3-Benzyl-5-(5-imidazolylmethyl)-2,4-imidazolidinedione (**1b**)

To a solution of 5.32 g (40 mmol) of benzylamine in 40 mL of toluene was added 12 g (120 mmol) of phosgene at 100°C, stirring for 1 h. After removal of the solvent and surplus phosgene under vacuum, the residual crude oil of benzyl isocyanate was directly subjected to the following procedure.

The procedure given for **1a** was then carried out in the same way with benzyl isocyanate obtained above to give 4.43 g of **1b** as white crystals: yield (82%), m.p. 212–214°C. $[\alpha]_D^{25}$ 16.8° (MeOH). IR (KBr): 3245, 1762, 1709, 1599, 1500, 1425 (cm^{-1}). ^1H NMR (TMS, DMSO-d_6), δ: 3.0 (m, 2H, CH_2), 4.4 (m, 2H, CH_2), 4.5 (t, 1H, CH), 6.9 (s, 1H, CONH), 7.2–7.5 (m, 5H, ArH), 7.6 (s, 1H, CH), 8.4 (s, 1H, NH). Calcd. for $C_{14}H_{14}N_4O_2$ (**1b**): C, 62.21; H, 5.22; N, 20.73. Found: C, 62.21; H, 5.38; N, 19.67%.

Preparation of (5R)-3-(4-Fluorobenzyl)-5-(5-imidazolylmethyl)-2,4-imidazolidinedione (**1c**)

The procedure given for **1b** was performed on the same scale, using 4-fluorobenzylamine instead of benzylamine, to give 4.6 g of **1c** as white solids: yield (79%), m.p. 207–208°C. $[\alpha]_D^{25}$ 24.2° (MeOH). IR (KBr): 3300, 2924, 1752, 1695, 1571, 1502, 1430 (cm^{-1}). ^1H NMR (TMS, DMSO-d_6),

δ: 3.0 (m, 2H, CH_2), 4.4–4.44 (m, 2H, CH_2), 4.5 (t, 1H, CH), 6.9 (s, 1H, CONH), 7.2–7.4 (m, 4H, ArH), 7.5 (s, 1H, CH), 8.3 (s, 1H, NH). Calcd. for $C_{14}H_{13}FN_4O_2$ (**1c**): C, 58.33; H, 4.55; N, 19.43. Found: C, 58.10; H, 5.63; N, 19.31%.

Preparation of (5R)-5-Benzyl-3-phenyl-2,4-imidazolidinedione (**1d**)

With (*R*)-phenylalanine replacing (*R*)-histidine, the procedure given for **1a** was carried out on the same scale to give 3.35 g of **1d** as white crystals: yield (63%), m.p. 167–168°C. $[\alpha]_D^{25}$ 161.1° (MeOH). IR (KBr): 3245, 3110, 1774, 1715, 1600, 1500, 1428, 1348 (cm^{-1}). ^1H NMR (TMS, $CDCl_3$), δ: 3.0–3.1 (m, 2H, CH_2), 4.4 (m, 1H, CH), 6.5 (s, 1H, CONH), 7.2–7.5 (m, 10H, ArH). Calcd. for $C_{16}H_{14}N_2O_2$ (**1d**): C, 72.17; H, 5.30; N, 10.52. Found: C, 72.02; H, 5.31; N, 10.26%.

Preparation of (5R)-3,5-Dibenzyl-2,4-imidazolidinedione (**1e**)

Using phenylalanine, the procedure for **1b** was performed on the same scale resulting in 4.1 g of **1e** as white solids: yield (74%), m.p. 141–142°C. $[\alpha]_D^{25}$ 41.8° (MeOH). IR (KBr): 3260, 1765, 1694, 1598, 1500, 1425 (cm^{-1}). ^1H NMR (TMS, $CDCl_3$), δ: 3.0 (m, 2H, CH_2), 4.2–4.5 (m, 2H, CH_2), 4.6 (m, 1H, CH), 6.7–7.3 (m, 10H, ArH), 8.3 (s, 1H, CONH). Calcd. for $C_{17}H_{16}N_2O_2$ (**1e**): C, 72.84; H, 5.75; N, 9.99. Found: C, 72.56; H, 5.81; N, 9.87%.

Preparation of (5R)-5-Benzyl-3-(4-fluorobenzyl)-2,4-imidazolidinedione (**1f**)

With phenylalanine and 4-fluorobenzylamine, the procedure given for **1b** was repeated in a similar way to give 4.9 g of **1f** as white crystals: yield (82%), m.p. 152–153.5°C. $[\alpha]_D^{25}$ 18.6° (MeOH). IR (KBr): 3252, 1759, 1690, 1603, 1498, 1420, 1340 (cm^{-1}). ^1H NMR (TMS, $CDCl_3$), δ: 3.1 (m, 2H, CH_2), 4.3–4.5 (m, 2H, CH_2), 4.7 (m, 1H, CH), 7.0–7.4 (m, 9H, ArH), 8.4 (s, 1H, CONH). Calcd. for $C_{17}H_{15}FN_2O_2$ (**1f**): C, 68.45; H, 5.07; N, 9.39. Found: C, 68.29; H, 5.14; N, 9.14%.

Asymmetric Hydrocyanation of *m*-PBA

A reasonable amount of XAD-4 and NDA-99, after a pretreatment process of the resins,[10] were immobilized in the columns. The supported

catalysts were prepared by passing a solution of **1** in water (0.1–0.2%) through the column at a rate of 3BV/h. After the prescribed amount of **1** was charged onto the support, the column was washed with water to remove any traces of non-adsorbed material, and dried in vacuum oven at 50°C.

The column packed with 10 g of supported catalyst (about 0.6 g (2.5 mmol) of chiral hydantoin adsorbed), was connected to a three-neck flask containing 25 g (125 mmol) of *m*-PBA in 100 mL of toluene, and the mixture was circulated through the top of the column by a metering pump. After the system was cooled to 5°C in ice/water bath, 6.8 mL (250 mmol) of hydrogen cyanide was added drop-wise to the circulation from the top of the column over 1 h. The reaction mixture was recycled at a rate of 20 mL min^{-1} through the column at 5°C for 2 h. Finally, the mixture was extracted with 50 mL of dilute phosphoric acid to remove the damaged catalyst if necessary. After evaporation of toluene under vacuum, the residue gave (*S*)-**2** with an optimal conversion and ee value, of which ee was determined by HPLC analysis (column, Sumipax OA-4100; eluent, acetonitrile/petroleum ether=15/85(V/V); flow rate, 1.0 mL min^{-1}; detection, 254 nm) and the conversion of *m*-PBA was also determined by HPLC analysis (column, YWG-18; eluent, THF/petroleum ether =2/98(V/V); flow rate, 1.0 mL min^{-1}; detection, 254 nm). Found: $[\alpha]_D^{25}$ −22.3° (DMSO). IR (KBr): 3308 (OH), 3059 (ArH), 2931, 2874 (CH), 2242 (CN), 1582, 1497, 1448 (Ar) (cm^{-1}).

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