2,6-Bis(amido)benzoic Acid with Internal Hydrogen Bond as Brønsted Acid Catalyst for Friedel–Crafts Reaction of Indoles

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Abstract: Benzoic acid catalysts bearing two amide groups that increase the Brønsted acidity of the carboxylic acid moiety by internal hydrogen-bonding interactions were designed as a novel class of carboxylic acid catalysts for the Friedel–Crafts reaction of indoles with β -nitrostyrenes and 3,3-disubstituted *3H*-indoles to obtain the corresponding Friedel– Crafts adducts in high yields. The internal hydrogen-bonding benzoic acid catalysts have a relatively high Brønsted acidity compared with benzoic acid based on the p K_a measurements in DMSO by UV spectrophotometric titration.

Keywords: Brønsted acids; carboxylic acids; Friedel–Crafts reaction; hydrogen bonds; indoles

Brønsted acids are widely utilized as an organocatalyst for the advanced and practical transformation of organic molecules.^[1] Following the development of chiral binaphthyl phosphoric acids by Akiyama et al.^[2] and Terada et al.^[3] for the enantioselective Mannich reaction, various chiral Brønsted acid catalysts have been contrived for the corresponding enantioselective reactions.^[1,4] Strong acids, such as phosphoric acid, sulfonic acid, and their derivatives, are essential to promote the acid-catalyzed transformations. However, carboxylic acid has a lower Brønsted acidity than these strong acids. Accordingly, improving the acidity of a carboxylic acid by non-covalent interactions is a very attractive topic. On the other hand, Brønsted acid catalysts characterized by internal interactions of the functional groups have gathered attention because the internal interactions enhance the Brønsted acidity of the catalyst (Figure 1). Indeed, Brønsted acid catalysts activated by another Brønsted acid group have now emerged, including the chiral 2-



Figure 1. Designed organocatalysts with internal interactions of functional groups.

bis(triflyl)methyl-2'-hydroxy-1,1'-binaphthyl catalyst reported by Ishihara and Yamamoto et al.,^[5] the chiral binaphthyl bis-phosphoric acid catalyst described by Terada et al.,^[6] and the chiral binaphthyl bis-carboxylic acid catalyst developed by Maruoka et al.^[7] Furthermore, organocatalysts activated by a Lewis acid have been developed, examples of which are the chiral boronate carboxylic acid catalyst that is composed of an achiral borono-carboxylic acid and a chiral diol reported by Maruoka et al.^[8] as well as a boronate urea catalyst^[9] and an achiral boronate carboxylic acid catalyst^[10] published by Mattson et al. However, the activation of carboxylic acids by the internal hydrogen-bonding interaction with a neutral hydrogen of an amide has not been established so far. The hydrogen bond formed between the hydrogen of the amide and the oxygen of the carbonyl group is essential for the highly ordered architecture of peptides, and this construction opens the door to new possibili-



increase of Brønsted acidity by internal hydrogen bonding effect



Figure 2. Design of benzoic acid with internal hydrogen bonding as organocatalyst.

ties in the catalytic transformations of organic molecules. $^{\left[11\right] }$

Regarding the relationship between the internal hydrogen-bonding interaction and the Brønsted acidity of organic molecules, salicylic acid bearing a hydroxy group at the ortho position of the aromatic ring has higher acidity (p K_a =16.7, in MeCN) than benzoic acid ($pK_a = 21.5$, in MeCN) due to the formation of an internal hydrogen bond, and the acidity of 2,6-dihydroxybenzoic acid having two hydroxy groups at the ortho positions of benzoic acid is drastically increased by the two internal hydrogen bonds ($pK_a =$ 12.6, in MeCN) (Figure 2, upper part).^[12] Therefore, the internal hydrogen bond formed by the carbonyl group of benzoic acid and the neighboring hydrogen bond donors can create a new scaffold on the benzoic acid unit and at the same time increase the acidity of the Brønsted acid group. However, hydroxybenzoic acid derivatives may be inappropriate for the design of organocatalysts because they cannot form bonds with various functional groups while retaining the internal hydrogen bond, i.e., O-H, and are poorly soluble in organic solvents. The introduction of amide groups at the ortho positions of the benzoic acid unit, in contrast, would allow attachment of various functional groups and at the same time retain the internal hydrogen bonds (Figure 2, *lower part*). The C_2 -symmetrical bis(amido)benzoic acid and its calcium(II) complex with the internal hydrogen bonds between the two amide N–H groups and carboxylate oxygen atoms were reported by Crane et al.^[13] However, they have never been utilized as a Brønsted acid catalyst for organic reactions.

We report herein the preparation of 2,6-bis(amido)benzoic acid as the design of a powerful carboxylic acid catalyst and the designed benzoic acid-catalyzed Friedel–Crafts reaction of indoles with β -nitrostyrenes and 3,3-disubstituted 3*H*-indoles.

First, we screened for benzoic acid derivatives as Brønsted acid catalysts and solvents for the Friedel– Crafts reaction of indole (1a) with β -nitrostyrene (2a) (Table 1).^[14] When 1a (1.5 equiv.) was treated with 2a using bis(pivalamido)benzoic acid (A) as the designed benzoic acid catalyst in CHCl₃ at room temperature, Friedel–Crafts adduct (3aa) was obtained in 88% yield (entry 1). Whereas the reactions in CH₂Cl₂ and toluene showed similar reactivity to that in CHCl₃ (entries 2 and 3), the reactions in THF, EtOAc, and MeCN gave rise to decreases in the yield of 3aa (entries 4–6).

Table 1. Screening of benzoic acid and solvent for Friedel–Crafts reactions of indole (1a) with β -nitrostyrene (2a).



^[a] The reaction was carried out at 40 °C.

Table 2. The effect of the functional group on the benzoic acid catalyst.



In a control experiment of benzoic acid catalysts, the use of benzoic acid and salicylic acid was much less effective than that of A for the Friedel-Crafts reaction (entries 7 and 8). It is noteworthy that use of the highly acidic 2,6-dihydroxybenzoic acid and ophthalic acid led to a drastic decrease in the yield of **3aa** because these acids have low solubility in CHCl₃ (entries 9 and 10). When bis[3,5-bis(trifluoromethyl) phenyl]thiourea, a previously used catalyst for the Friedel-Crafts reaction,^[13a] was used to compare its catalytic activity with that of 2,6-bis(amido)benzoic acid, the product was obtained in 63% yield (entry 11). Whereas the absence of catalyst A the Friedel-Crafts reaction gave a trace of product, elevation of the reaction temperature afforded a similar yield to that obtained at room temperature (entries 12 and 13). Furthermore, we investigated the effect of the functional groups on the aromatic ring or the amide groups on the benzoic acid catalysts for this reaction (Table 2). The use of 4-bromo-2,6-bis(pivaloylamido)benzoic acid (B), 2,6-bis(acetamido)benzoic acid (C), 2,6-bis(benzamido)benzoic acid (D), 2,6bis(benzensulfonamido)benzoic acid (E), and N-pivaloyl-anthranilic acid (F) gave the Friedel-Crafts adduct (3aa) in 83%, 40%, 78%, 75%, and 91% yields, respectively. The significant decrease in the yield of 3aa with catalysts C-E is attributable to their low solubilities in CHCl₃ for the present reaction.

To explore the scope of the benzoic acid-catalyzed Friedel–Crafts reaction, various indoles (1) and β -ni-trostyrenes (2) were examined under the optimum conditions (Table 3). The reaction of indole 1a with β -nitrostyrenes bearing 4-Me (2b), 3-Me (2c), 2-Me (2d), 4-Br (2e), 4-Cl (2f), 4-CF₃ (2g), 4-MeO (2h),

Table 3. Friedel–Crafts reactions of indoles and pyrroles (1) with β -nitrostyrenes (2) using the designed benzoic acid catalyst.

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^[a] The reaction was carried out for 48 h.

and 3-NO₂ (2i) gave the corresponding products (3ab-3ai) in high yields (75–99%), respectively. When 1a was treated with aliphatic nitropentene (2j), the desired adduct (3aj) was obtained in 78% yield. The Friedel–Crafts reaction of indoles with β , β -disubstituted nitroalkenes, which produces synthetically useful indole derivatives bearing a quaternary carbon center, is extremely difficult because the intrinsic steric hindrance at the β -carbon of nitrostyrene decreases the reactivity.^[14] The reaction of α -methoxycarbonyl- β styrene (2k) with indole (1a) was also effective to give the desired product (3ak) in 75% yield.

The designed benzoic acid **A**-catalyzed transformation was applied to the reaction of various indoles and pyrrole (1) with β -nitrostyrene **2a**. Reactions of indoles bearing 5-MeO (1b), 5-Br (1c), 6-Cl (1d), 7-Me (1e), and 2-Me (1f) with **2a** gave the corresponding products (**3ba–3fa**) in high yields (74–99%), respectively. *N*-Methyl-protected indole (1e) was also converted into Friedel–Crafts adduct (**3ga**) in 98% yield. Treatment of 2-methylpyrrole (1h) with **2a** gave the 5-position adduct (**3ha**) in 85% yield.

The time course of the Friedel–Crafts reaction of indole (1a) with β -nitrostyrene (2a) using catalyst **A** or benzoic acid was monitored, and the efficiencies of the two catalysts were compared (Figure 3). The reac-



Figure 3. Plot of percentage conversion for the Friedel– Crafts reaction of indole (1a) with β -nitrostyrene (2a) using a catalytic amount of A (\bullet) or benzoic acid (\blacktriangle) *versus* time (min).

tion with catalyst \mathbf{A} proceeded more rapidly than that with benzoic acid.

To elucidate the high Brønsted acidity of the internal hydrogen-bonding activated catalyst compared with that of the simple carboxylic acid, we measured the pK_a values of benzoic acid and catalysts (**A** and **C**-**F**) in DMSO by UV/Vis spectrophotometry following Berkessel and O'Donoghue's method,^[16] and the final pK_a values are summarized in Table 4.

The p K_a value of benzoic acid against 4-nitrophenol (NP) as indicator was 10.6 in DMSO. Predictably, the p K_a values of 2,6-bis(amido)benzoic acids **A** and **C–D** were decreased to 4.28–5.17 against 4-chloro-2,6-dinitrophenol (CDNP), and that of catalyst **F** was 7.56 against 9-cyanofluorene (CN-FH) in DMSO. In particular, the acidity of 2,6-bis(benzensulfonyl)benzoic acid (**E**) is higher than that of 2,6-bis(amido)benzoic acid (p K_a =2.72). It is interesting to note that the acidities of 2,6-bis(amido)benzoic acids **A**, **D**, and **E** are similar to those of the phosphoric acid catalysts (p K_a =2.42–4.22) in DMSO (see ref.^[16]).

The results suggest that the two amide groups at the 2,6-positions of benzoic acid increase the Brønsted acidity of the carboxylic acid group on an identical molecule by the internal hydrogen bond (Table 4 and Figure 4a), especially, the pivaloyl group has high solubility in organic solvents due to its hydrophobic property (Figure 4b).

Next, we investigated the Friedel–Crafts reaction of indoles with 3,3-disubstituted 3*H*-indoles using the designed internal hydrogen-bonding benzoic acid catalyst. Marchelli et al. reported this reaction under acidic conditions, that is, in acetic acid solution.^[19] However, the catalytic reaction was never achieved. Interestingly, treatment of indole (**1a**) with spiro[cyclohexane-1,3-[3*H*]indole] (**4a**) using catalyst **A** in CH₂Cl₂ at 0°C provided the desired 2-(3-indolyl)-spiro[cyclohexane-1,3-[3*H*]indole] (**5aa**) in 92% yield, whereas use of benzoic acid and catalyst **F** as Brønsted acid catalysts, aswell as the thiourea catalyst drasti-

Table 4. The pK_a values of benzoic acid and catalysts (**A** and **C-F**) in DMSO solution at 20 °C based on Berkessel and O'Donoghue's method.

HA	Indicator ^[a]	$pK_a [HIn]^{[b]}$	pK_a [HA]
benzoic acid	NP	10.8	10.6 [11.0] ^[c]
Α	CDNP	3.56	4.60
С	CDNP	3.56	5.17
D	CDNP	3.56	4.28
Е	CDNP	3.56	2.72
F	CN-FH	8.3	7.56

^[a] NP=4-nitrophenol, CDNP=4-chloro-2,6-dinitrophenol, CN-FH=9-cyanofluorene.

^[b] Numbers were taken from ref.^[17]

^[c] Number in brackets indicates pK_a value based on Bordwell's method taken from ref.^[18]

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(a) The effect of amide group for increacing of Brønsted acidity.



(b) The effect of functional group for solubility in organic solvent. low solubility in solvent high solubility in solvent



Figure 4. Effect of functional groups on the increase of Brønsted acidity of the catalyst.



Scheme 1. Friedel–Crafts reaction of indole (1a) with 3,3disubstituted 3*H*-indole (4a).

cally decreased the yield of **5aa** (6%, 33%, and 14%, respectively) for the present reaction (Scheme 1). As a result, this reaction depends dramatically on the Brønsted acidity of the catalyst to activate 3,3-disubstituted 3H-indole (4). Moreover, the substrate scope of the internal hydrogen-bonding Brønsted acid-catalyzed Friedel-Crafts reaction was investigated with various indoles and pyrroles (1), and 3,3-disubstituted 3H-indoles (4) (Table 5). Reacting 3,3-disubstituted 3H-indoles bearing 5-Br-3,3-cyclohexyl (4b) and 3,3dimethyl (4c) groups with indole (1a) provided the corresponding products (5ab and 5ac) in quantitative yields. The diastereomeric reaction of 3-Ph-3-Me-3Hindole (4d) with 1a furnished Friedel-Crafts adduct (5ad) in quantitative yield with a moderate diastereoselectivity (dr = 77:23). The reaction of various indoles bearing 5-MeO (1b), 5-Br (1c), 6-Cl (1d), 7-Me (1e),



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^[a] The reaction was carried out in CH_2Cl_2 (1.0 M).

^{b]} The reaction was carried out for 48 h.

and 2-Me (1f) with 4a also occurred to provide the desired products (1ba-1fa) in high yields (90-94%), respectively. Moreover, 2-methylpyrrole (1h) reacted with 4a at the 5-position selectively to give product (5ha) in 88% yield.

In conclusion, we have developed 2,6-bis(amido)benzoic acid as a powerful carboxylic acid catalyst that activates the Brønsted acidity of the carboxylic acid by internal hydrogen-bonding interactions. The designed catalyst was more active than benzoic acid for the Friedel–Crafts reaction of indoles (1) with β nitrostyrenes (2) and 3,3-disubstituted 3*H*-indoles (4), and showed a relatively high Brønsted acidity as compared with benzoic acid based on pK_a measurements in DMSO by UV spectrophotometric titration.

Experimental Section

Synthesis &

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Catalysis

Friedel–Crafts Reaction of Indoles (1) with β-Nitrostyrenes (2) using 2,6-Bis(amido)benzoic Acid Catalyst

To a solution of **2a** (37.3 mg, 0.25 mmol) and **A** (16.0 mg, 0.050 mmol) in CHCl₃ (125 μ L) was added **1a** (43.9 mg, 0.375 mmol) at room temperature, and the reaction mixture was stirred at 40 °C for 24 h. Saturated aqueous NaHCO₃ solution (5 mL) was added to the reaction mixture, and the product was extracted with AcOEt (10 mL×3). The combined extracts were washed with brine (10 mL) and dried over Na₂SO₄. The organic phase was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt=4/1) to give desired product **3aa**; yield: 57.2 mg (86%).

Friedel–Crafts Reactions of Indoles (1) with 3,3-Disubstituted 3*H*-Indoles (4) using 2,6-Bis(amido)benzoic Acid Catalyst

To a solution of **4a** (69.5 mg, 0.375 mmol) and **A** (8.0 mg, 0.025 mmol) in CH₂Cl₂ (750 μ L) was added **1a** (29.3 mg, 0.25 mmol) at 0 °C, and the reaction mixture was stirred for 24 h. Saturated aqueous NaHCO₃ solution (5 mL) was added to the reaction mixture, and the product was extracted with AcOEt (10 mL×3). The combined extracts were washed with brine (10 mL) and dried over Na₂SO₄. The organic phase was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt=9/2) to give desired product **5aa**; yield: 69.6 mg (92%).

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