The Zinc(II)-Catalyzed Henkel Reaction of Dipotassium 1,8-Naphthalenedicarboxylate in a Dispersion Medium

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The Henkel reaction of dipotassium 1,8-naphthalenedicarboxylate in naphthalene as a dispersion medium gave dipotassium 2,6-naphthalenedicarboxylate (**1**) in a higher yield and with a better reproducibility than the reaction without a dispersion medium . Catalysts, particularly zinc catalysts, were examined in detail. The anion moiety of zinc catalysts affected the reaction, and the halide anion was effective for the selective formation of **1**. The addition of potassium halide to the zinc catalysts also increased the yield of **1**. The catalytic activity of the halide anion increased in the order; $Cl^- < Br^- < I^-$. The activity of the zinc catalysts was also compared with that of cadmium catalysts.

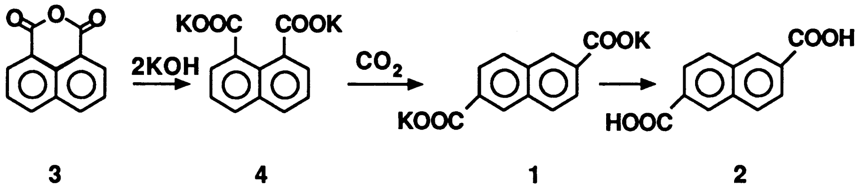
2,6-Naphthalenedicarboxylic acid (**2**) has attracted attention because it is often used as a component of high-performance polymers. For example, poly(ethylene naphthalenedicarboxylate) is known for its heat resistance and high modulus.[1] We have been studying the preparation of **2** from 1,8-naphthalenedicarboxylic anhydride (**3**) (Scheme 1). The transformation of dipotassium 1,8-naphthalenedicarboxylate (**4**) into the 2,6-isomer (**1**) is well-known as the Henkel reaction, which is usually carried out by heating **4** under a pressure of carbon dioxide at 350—450 °C in the presence of a catalytic amount of cadmium salts or sometimes zinc salts.[2—7] The activity of the cadmium catalysts is much higher than that of the zinc catalysts. In order to produce **1** industrially, however, some practical problems must be overcome: (1) It is difficult to transport the starting material **4** and the reaction mixture because both of them are in the solid state during this process. (2) The powders of the reaction mixture stick together during the reaction, which leads to inefficient mixing and local superheating, resulting in a poor reproducibility of the reaction along with a low yield of **1**. (3) Cadmium salts are very toxic, though their catalytic activity is very high. We have focused our efforts on overcoming these problems. We have found that the addition of a dispersion medium such as naphthalene to the starting material obviates the problems, and improves both the reproducibility of the reaction and the yield of **1**. We have also found that the cadmium catalysts can be replaced by a combination of zinc(II) and the halide anion X^-, whose activity is as same as that of the cadmium catalysts. The roles of zinc(II) and X^- during the reaction are discussed on the basis of the effects of the anionic moiety of the zinc catalyst on the reaction and on the basis of thermal gravimetric analyses.

Experimental

All high-performance liquid chromatographies (HPLC) were taken on a Shimadzu LC-4A apparatus. All melting-points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. The ^1H NMR spectra were taken on a JEOL JMN-FX90 spectrometer. The thermal gravimetric analyses were done with a Rigaku Denki TG-DTA apparatus.

Preparation of 4. According to the reported procedure,[2] **4** was prepared from 1,8-naphthalenedicarboxylic anhydride (**3**) and potassium hydroxide.

Henkel Reaction in a Dispersion Medium (General Procedure). The dipotassium salt **4** and the catalyst (1—12 mol% based on **4**) were mixed intimately in a glass ball mill. After drying in vacuo at 150 °C, 10 g of the mixed powder was put into a 200 cm^3 autoclave, which had been preheated at 100 °C, along with 30 g of a dispersion medium such as naphthalene. The autoclave was then filled with carbon dioxide to a pressure of 4.1 MPa. While the mixture in the autoclave was stirred at 100 °C, carbon dioxide was occasionally introduced into the autoclave until there was no pressure drop. The mixture was thereafter heated to 450 °C at the heating rate of 6 °C min^{-1} while being stirred; it was then maintained at 450 °C for 1 h. The pressure increased to 7.1 MPa. After the autoclave had been cooled, toluene (200 cm^3) and water (200 cm^3) was successively added to the reaction mixture; the mixture was then stirred at 60 °C for 0.5 h. The insoluble materials, which mainly consisted of carbonized materials, were separated by filtration. After the organic layer had been removed, the aqueous layer was washed with toluene (100 cm^3×2), and then subjected to the



Scheme 1. Henkel process.

following product analysis.

Analysis of Products. Ten isomers of dipotassium naphthalenedicarboxylates can be obtained. Nine of them, potassium 2-naphthoate and tripotassium 2,3,6-naphthalenetricarboxylate were determined by HPLC using 1-naphthoic acid as the internal standard (column: Shimadzu Co.; Shimpack CLC ODS, and/or Japan Spectroscopic Co.; Finepak SIL C18S, eluent: a mixture of methanol and 0.2 wt% aqueous phosphoric acid solution). The yield of **1** is given by Eq. 1 (Eq. 2 is used in the case of a reaction using zinc naphthalate as the catalyst);

$$\text{Yield of } \mathbf{1}\,(\%) = 100A/R \tag{1}$$

$$\text{Yield of } \mathbf{1}\,(\%) = 100A/(R + C) \tag{2}$$

A/mol: Molar amount of **1** in the reaction mixture was determined by HPLC.
R/mol: Molar amount of **4**.
C/mol: Molar amount of zinc naphthalate.

Authentic Specimens. In order to analyze the products in the reaction mixture, a wide variety of naphthalenecarboxylic acids was prepared as follows. The 2,6-naphthalenedicarboxylic acid, 2,3-naphthalenedicarboxylic acid, 1,8-naphthalenedicarboxylic anhydride, 1-naphthoic acid, and 2-naphthoic acid were commercially available. Other dicarboxylic acids, such as the 1,2-, 1,3-, 1,4-, 1,5-, 1,6-, and 2,7-isomers, were prepared by the oxidation of the corresponding dimethylnaphthalenes with aqueous sodium dichromate.[9] The acid values were measured by titration in aqueous methanol with 0.1 mol dm^{-3} aqueous potassium hydroxide using 3,3-bis(4-hydroxyphenyl)phthalide as an indicator. The diacids prepared from dimethylnaphthalenes were esterified into the corresponding dimethyl esters by a usual procedure (catalyst: concd sulfuric acid) and were identified as follows.

1,2-Naphthalenedicarboxylic Acid: Acid value: 517.2. (Calcd for naphthalenedicarboxylic acid: 519.1). Dimethyl ester. Mp 83.5—84.8 °C (lit,[9] mp 84.0—85.0°C). ^{1}H NMR (CDCl$_3$) δ=3.96 (3H, s), 4.08 (3H, s), 7.5—7.7 (2H, m), 7.8—8.1 (4H, m).

1,3-Naphthalenedicarboxylic Acid: Acid value: 518.2. Dimethyl ester. Mp 101.5—102.5 °C (lit,[9] mp 104.5—105.0 °C. ^{1}H NMR (CDCl$_3$) δ=3.99 (3H, s), 4.08 (3H, s), 7.5—7.8 (2H, m), 7.9—8.0 (1H, m), 8.72 (2H, s), 8.93 (1H, d, J=8 Hz).

1,4-Naphthalenedicarboxylic Acid: Acid value: 517.5. Dimethyl ester. Mp 63.4—64.8 °C (lit,[9] mp 65.0—66.0 °C). ^{1}H NMR (CDCl$_3$) δ=4.00 (6H, s), 7.61 (2H, dd, J=10 Hz, 3 Hz), 8.05 (2H, s), 8.80 (2H, dd, J=10 Hz, 3 Hz).

1,5-Naphthalenedicarboxylic Acid: Acid value: 518.0. Dimethyl ester. Mp 119.0—119.5 °C (lit,[9] mp 119.0—120.0 °C). ^{1}H NMR (CDCl$_3$) δ=4.00 (6H, s), 7.61 (2H, t, J=8 Hz), 8.19 (2H, d, J=9 Hz), 9.11 (2H, d, J=9 Hz).

1,6-Naphthalenedicarboxylic Acid: Acid value: 518.4. Dimethyl ester. Mp 98.6—99.5 °C (lit,[9] mp 98.0—99.0 °C). ^{1}H NMR (CDCl$_3$) δ=3.98 (3H, s), 4.01 (3H, s), 7.54 (1H, dd, J=8 Hz, 8 Hz), 8.0—8.4 (3H, m), 8.61 (1H, d, J=2 Hz), 8.98 (1H, d, J=9 Hz).

2,7-Naphthalenedicarboxylic Acid: Acid value: 519.0. Dimethyl ester. Mp 136.5—137.3 °C (lit,[9] mp 136.5—137.0 °C). ^{1}H NMR (CDCl$_3$) δ=3.90 (6H, s), 7.7—8.2 (4H, m), 8.60 (2H, s).

2,3,6-Naphthalenetricarboxylic acid was isolated by sublimation from the reaction mixture as follows. The aqueous layer, which had been obtained from the reaction mixture as described in the general procedure, was concentrated in vacuo to give a slurry. The subsequent filtration of the slurry yielded **1** as colorless crystals. The filtrate was treated with active charcoal and acidified (pH less than 1) with concd hydrochloric acid to give precipitates of a mixture of naphthalenecarboxylic acids. The precipitates were filtered, washed with water, and dried. The esterification of the mixture of naphthalenecarboxylic acids with methanol was carried out in a usual procedure (catalyst; concd sulfuric acid, 130 °C, 0.61 MPa, 2 h). The esters were recrystalyzed from methanol to afford colorless crystals. The crystals were hydrolyzed with aqueous alkali, and then acidified with concd hydrochloric acid to give the corresponding acids. HPLC revealed that these acids were an isomeric mixture of naphthalenetricarboxylic acids and consisted mainly of the 2,3,6-isomer. The sublimation of the acids at 230 °C/133 Pa gave 2,3,6-naphthalenetricarboxylic acid 2,3-anhydride as colorless crystals. Found: C, 64.40; H, 2.41%. Calcd for $C_{13}H_6O_5$: C, 64.47; H, 2.50%. Trimethyl ester. Mp 123.0—125.0 °C (lit,[9] mp 125.0—126.0 °C). ^{1}H NMR (CDCl$_3$) δ=3.97 (6H, s), 4.00 (3H, s), 7.9—8.4 (4H, m), 8.64 (1H, s).

Thermal Gravimetric Analysis (TGA). A mixture (15 mg) of **4** and the catalyst was put into a platinum cell, and then heated to 520 °C at the rate of 10 °C min^{-1} in a stream of carbon dioxide.

Results and Discussion

Dispersion Mediums. The results of the Henkel reaction with and without a dispersion medium are summarized in Table 1. A mixture of zinc chloride and potassium iodide (8 mol% based on **4**, respectively) was used as the catalyst. Without a dispersion medium, the composition of the reaction mixture varied depending on the site in the autoclave. It was also found that **1** was obtained in a low yield and that the reproducibility of the reaction was very poor (Runs 1—3). On the other hand, the reaction in naphthalene as a dispersion medium gave **1** in a good yield (70 mol%), and the reproducibility was improved (Runs 4, 5). Using a specially designed autoclave equipped two windows in its wall, we were able to observe the reaction process and found that black powders of the crude products were dispersed uniformly in the liquid naphthalene. It should be also noted that the reaction gave almost the same products irrespective of whether or not **4** and the catalyst had been premixed before they were charged into liquid naphthalene. These results indicate that the liquid naphthalene promotes both heat and mass transfer in the reaction, so that the reproducibility of the reaction is improved along with the yield of **1**.

When biphenyl, a mixture of diphenyl ether and biphenyl, or phenanthrene was used as the dispersion medium, the yield of **1** was also improved (Runs 6—8).[10] On the other hand, the addition of methylnaphthalene or ethylbipenyl decreased the yield of **1** and gave more tarry materials (Runs 9, 10). Aromatic compounds with acidic hydrogens of the alkyl groups,

Table 1. Henkel Reaction in Various Dispersion Mediums

Run No.	Dispersion medium	Yields of products/mol%[a]			
		1	**5**	**6**	**7**
1	None	53.8	12.0	10.6	4.3
2	None	45.7	17.2	19.6	4.5
3	None	48.1	15.2	18.0	4.5
4	Naphthalene	69.1	2.5	3.0	2.4
5	Naphthalene	69.2	2.7	3.1	2.5
6	Biphenyl	62.6	3.3	2.5	2.5
7	Diphenyl ether+biphenyl[b]	60.4	2.8	2.5	3.3
8	Phenanthrene	61.3	4.8	9.0	3.3
9	Methylnaphthalene	44.6	1.1	10.5	0.4
10	Ethylbiphenyl[c]	21.3	21.3	34.0	0.8

4 was heated at 45 °C (c; 410 °C) for 1 h in the presence of $ZnCl_2$ (8 mol%) and KI (8 mol%). The initial pressure of CO_2 was 4.1 MPa at 100 °C. Thirty grams of the dispersion medium were used for each 10 g of the starting materials (**4** and the catalyst). a) **1**: dipotassium 2,6-naphthalenedicarboxylate, **5**: dipotassium naphthalenedicarboxylate except for **1**, **6**: potassium 2-naphthoate, **7**: tripotassium 2,3,6-naphthalenetricarboxylate. b) The molar ratio of diphenyl ether to biphenyl was 74/26.

Table 2. Zinc(II)-Catalyzed Henkel Reaction

Run No.	Catalyst	Yields of products/mol%[a]			
		1	**5**	**6**	**7**
11	ZnO	41.1	17.5	22.4	5.7
12	$ZnCO_3$	55.1	7.8	11.5	2.6
13	Zinc naphthalate[b]	57.1	4.6	8.2	4.5
14	$ZnCl_2$	62.3	4.0	7.7	4.7
15	ZnI_2	69.6	2.6	4.1	2.7
16	$ZnCl_2$+KCl	62.5	4.2	8.2	4.5
17	$ZnCl_2$+KBr	64.8	3.7	6.1	4.4
4	$ZnCl_2$+KI	69.1	2.5	3.0	2.4
18	Zinc naphthalate+KI[b]	70.3	2.4	5.1	2.4
19	ZnO+KI	45.8	20.7	16.1	3.7
20	$ZnCO_3$+KI	58.1	4.9	9.6	1.3

The reactions were carried out at 45 °C for 1 h in the presence of 8 mol% (b) 8.7 mol%) of the catalyst. The initial pressure of CO_2 was 4.1 MPa. Thirty grams of naphthalene were used for each 10 g of the starting materials (**4** and the catalyst). a) **1**: dipotassium 2,6-naphthalenedicarboxylate, **5**: dipotassium naphthalenedicarboxylate except for **1**, **6**: potassium 2-naphthoate, **7**: tripotassium 2,3,6-naphthalenetricarboxylate.

such as methylnaphthalene and ethylbiphenyl, seem to bring about the decarboxylation of both the starting material **4** and the products to lower the yield of **1**.

Catalysts. Zinc catalysts have rarely been used for the Henkel reaction because their catalytic activity was lower than that of cadmium catalysts.[2—6] From the standpoint of industrial production, however, it is desired to replace cadmium catalysts with zinc catalysts because of their toxicity and high price. Therefore, a wide variety of zinc compounds was examined as catalysts on this Henkel reaction.

Effects of the Anionic Moiety of the Zinc Catalysts: The results of the reactions with a wide variety of zinc compounds are shown in Table 2. The influence of the anionic moiety of the zinc catalysts on the yields of products was unexpecctedly large. Zinc halides were the most effective catalysts to yield **1** predominantly (Runs 14, 15), while zinc oxide (Run 11) or zinc carbonate (Run 12) gave **1** in a low yield. The addition of potassium halides to zinc chloride or zinc naphthalate catalyst (Runs 16—18, 4) was also effective in increasing the yield of **1**. The catalytic activity increased in the order;

$$Cl^- < Br^- < I^-$$

On the other hand, the addition of potassium iodide to zinc oxide (Run 19) or zinc carbonate (Run 20) hardly improved the yield of **1** at all.

Effects of the Amount of the Catalyst: The effects of the amounts of zinc naphthalate and potassium iodide are summarized in Table 3. It was found that the yield of **1** depended on both the amount of the zinc naphthalate and the molar ratio of the potassium iodide to the zinc naphthalate. When the amount of the zinc naphthalate was 1 mol%, regardless of the amount of potassium iodide, the reaction gave **1** in a low yield (Runs 21, 22). When the amount of the zinc naphthalate was over 4 mol%, the yield of **1** increased, whereas the yields of the isomers of **1** (**5**) and potas-

Table 3. Effects of the Amount of the Catalyst

Run No.	Amount of catalyst/mol%[a]		Yields of products/mol%[b]			
	Zinc naphthalate	KI	**1**	**5**	**6**	**7**
21	1.0	1.0	55.7	10.1	15.1	5.5
22	1.0	8.0	56.9	12.7	12.5	3.2
23	4.3	4.3	67.5	3.8	7.3	3.6
24	8.7	4.3	64.5	4.5	6.1	4.3
18	8.7	8.7	70.3	2.4	5.1	2.4
25	8.7	12.0	69.5	2.5	5.2	3.1

The reactions were carried out at 45 °C for 1 h. The initial pressure of CO_2 was 4.1 MPa. Thirty grams of naphthalene were used for each 10 g of the starting materals (**4** and the catalyst). a) The amounts of the catalyst were based on **4**. b) **1**: dipotassium 2,6-naphthalenedicarboxylate, **5**: dipotassium naphthalenedicarboxylate except for **1**, **6**: potassium 2-naphthoate, **7**: tripotassium 2,3,6-naphthalenetricarboxylate.

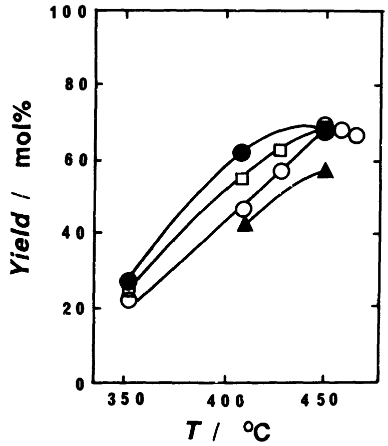


Fig. 1. Yields of **1** at different temperatures: **4** was heated at different temperatures for 1 h. The initial pressure of CO_2 was 4.1 MPa at 100 °C. Thirty grams of naphthalene were used for each 10 g of the starting materials (**4** and the catalyst). ○: zinc naphthalate (8.7 mol%)+KI (8.7 mol%), □: $ZnCl_2$ (8 mol%)+KI (8 mol%), ●: CdI_2 (8 mol%), ▲: CdO (8 mol%).

sium 2-naphthoate (**6**) decreased. When the amount of the potassium iodide was used more than that of the zinc naphthalate, **1** was obtained in a satisfactory yield, i.e., 67—70 mol% (Runs 18, 23, and 25).

Comparison between Zinc and Cadmium Catalyst: The reaction using the zinc catalyst was carried out at different temperatures in order to compare the activity with that of the cadmium catalyst. The results are shown in Fig. 1. The activities of zinc catalysts having iodide anion (plots ○, □) were lower than that of the cadmium iodide (plot ●) below of the reaction temperature 430 °C, but almost the same as that at 450 °C.

The activity of the cadmium oxide (plot ▲) was lower than that of the cadmium iodide (plot ●), so the anionic moiety of the cadmium catalyst seems to play the same role as that of the zinc catalyst. Ogata et al. reported a similar observation that the increasing order of the catalytic activity was $CdCl_2 < CdBr_2 < CdI_2$ in the preparation of dipotassium terephthalate from dipotassium phthalate.[11]

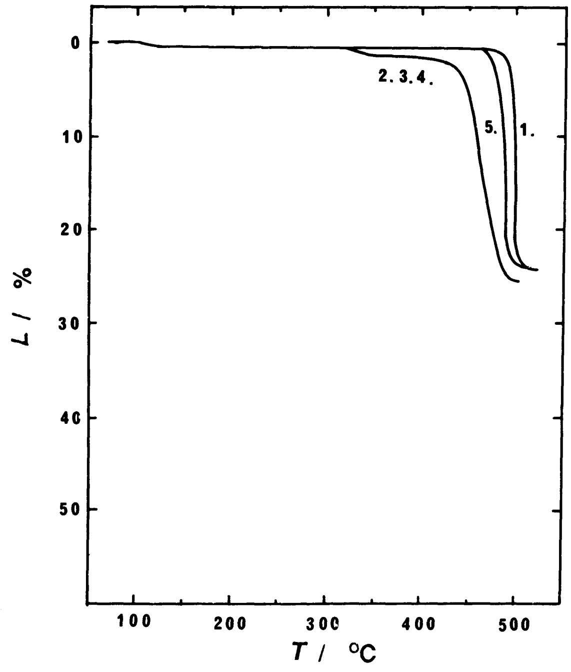
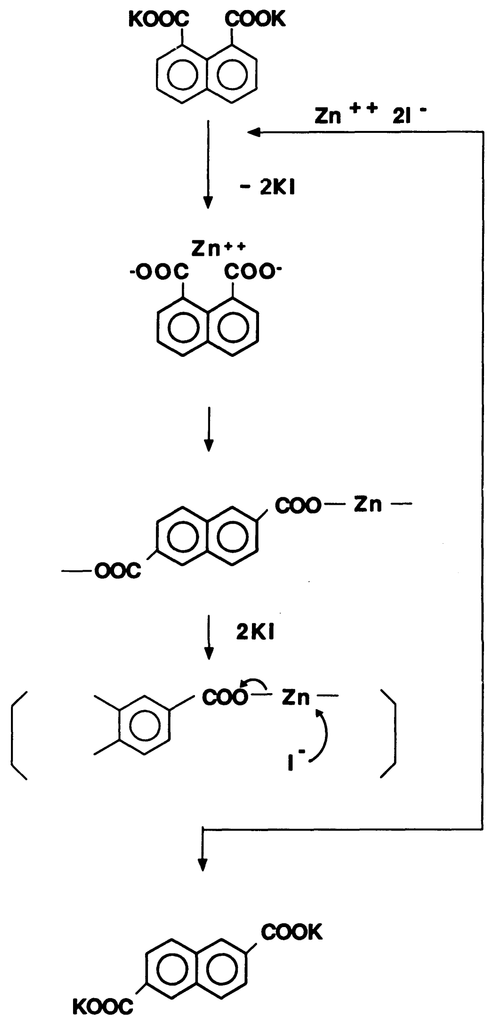


Fig. 2. Thermal gravimetric analyses for the starting materials in carbon dioxide stream: *L* is the weight loss of the starting material. 1: **4**, 2: **4**+$ZnCl_2$ (8 mol%)+KI (8 mol%), 3: **4**+zinc naphthalate (8.7 mol%)+KI (8.7 mol%), 4: **4**+zinc naphthalate (8.7 mol%), 5: **4**+ZnO (8 mol%)+KI (8 mol%).

We found that the cadmium catalyst could be replaced by a combination of zinc(II) and I^- catalyst whose activity was the same as that of the cadmium catalyst.

Thermal Gravimetric Analyses (TGA). TGA of **4** in the presence of various catalysts were carried out in order to examine the thermal behavior of **4** in its dependence on the kinds of the zinc catalysts. The results of TGA in a steam of carbon dioxide at an atmospheric pressure are shown in Fig. 2. In the presence of a catalytic amount of zinc chloride or zinc naphthalate (Line 2—4), **4** started to lose weight from 320 °C with foaming. The weight loss observed from 320 °C in TGA may be due to the decarboxylation of **4**.



Scheme 2. Roles of the catalysts.

It should be noted that the Henkel reaction began to proceed at almost the same temperature. On the other hand, **4** without the catalyst (Line 1) or **4** with the catalytic amount of zinc oxide and potassium iodide (Line 5) started to lose weight over 450 °C. These results indicate that the zinc cation of zinc halide or zinc naphthalate can react with **4** and bring about the cleavage of the C–C bond between the carboxyl group and the naphthalene nucleus of **4**. In the case of zinc oxide, however, the affinity of the oxygen to the zinc is so strong that a little zinc oxide reacts with **4**.

Role of Catalysts: On the basis of our experimental findings, we propose the roles of the catalysts as shown in Scheme 2. The potassium cation of **4** is replaced by the zinc cation to form a zinc compound such as zinc naphthalate. The zinc cation of the zinc naphthalate loosens the C–C bond between the carboxyl group and the naphthalene nucleus and allows **4** to rearrange to give 2,6-isomer; then, the zinc cation is exchanged for the potassium cation. In this exchange reaction, the halide anion promotes the exchange rate.

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10) The reason why the reaction in naphthalene gave the best yield of **1** seems to be that some carboxylic groups of **4** are introduced into naphthalene as a dispersion medium to give naphthalenecarboxylic acid. We will discuss the transcarboxylation between carboxylic acid and naphthalene in the future.

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