

# Amide Synthesis from Esters with Nitriles under Solvent-free Conditions Using Molecular lodine as a Catalyst

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Abstract: The reaction of esters with nitriles, using iodine as a catalyst under solvent-free conditions, was investigated. For example, 1-phenylethyl acetate reacted with benzonitrile in the presence of iodine to afford the amide, *N*-(1-phenylethyl)benzamide. Addition of water was effective in promoting amidation. The most suitable conditions were investigated, and determined as follows: temperature =  $80^{\circ}$ C, molar ratio of nitrile:alcohol:iodine:water = 1:3:0.2:1.0, and reaction time = 18 h. The amidation reactivity depended on the stability of the cationic intermediate formed from the ester. Only the reaction of 2-phenylpropan-2-yl acetate with benzonitrile gave no amide compound; rather, the cyclic compound, 1,1,3-trimethyl-3-phenyl-2,3-dihydro-1*H*-indene was obtained in 90% yield. The reaction of (-)-bornyl acetate with benzonitrile produced the racemic amide compound, (±)-*exo-N*-isobornylbenzamide, in 82% yield.

Key words: iodine, solvent-free, Ritter reaction, borneol

# **1 INTRODUCTION**

Compounds having an amide linkage, such as capsaicin and N-ethyl-p-menthane-3-carboxamide, are important in the perfume industry. One of the methods for obtaining amide compounds is known as the "Ritter reaction," which involves the reaction of alcohols with nitriles<sup>1)</sup>. Lin<sup>2)</sup> and Theerthagiri<sup>3)</sup> separately reported that iodine was an effective catalyst for the solution reaction of alcohols with nitriles to produce amide compounds. In addition, iodine was known to be an efficient catalyst in solvent-free reactions  $^{4-7)}$ . We previously reported that the amidation of alcohols with nitriles proceeded smoothly under solvent-free conditions using iodine as the catalyst<sup>8)</sup>. In this study, we investigated the amidation of esters with nitriles. Amidation with a nitrile was expected to proceed more smoothly when an ester was used instead of an alcohol. Reports on the amidation of esters with nitriles are sparse in comparison to the amidation of alcohols with nitriles. However, the catalysts used in these reports were conc. sulfuric  $\operatorname{acid}^{9,10}$ ,  $\operatorname{FeCl}_3^{11}$ , and ZnCl<sub>2</sub>/SiO<sub>2</sub><sup>12)</sup>. These are strong acids or heavy metal compounds, which are very expensive and/or toxic. In addition, solvent-free reactions are important in green chemistry. Accordingly, we investigated the amidation of esters

with nitriles using iodine as the catalyst under solvent-free conditions.

# 2 EXPERIMENTAL

# 2.1 General

Melting points uncorrected were measured on a Shibata micro melting point apparatus. NMR spectra were obtained using a 300 MHz FT-NMR spectrometer (Bruker DPX-300) with Me<sub>4</sub>Si as an internal standard and CDCl<sub>3</sub> as a solvent. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. Mass spectra were recorded on a JEOL JMS-HX110A, a SHIMADZU GCMS-QP5050A, or a Thermo Fisher Exactive-type spectrometer. Optical rotations were measured on a JASCO P2000. X-ray measurements were made on a Bruker AXS SMART APEX II at  $-100^{\circ}$ C.

# 2.2 Materials

All nitriles, 1-phenylethyl acetate (2), and benzyl acetate were obtained from Tokyo Chemical Industry CO., LTD. or Sigma-Aldrich, and used as received.

2-Phenylpropan-2-yl acetate was prepared from 2-phe-

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2-Phenyl-2-propanol (2.720 g, 20 mmol), N,N -dimethyl-4-aminopyridine (0.121 g, 1.0 mmol), and triethylamine (6.060 g, 60 mmol) were placed in a 200 mL flask, and stirred at room temperature for 30 min. Then, while chilling in an ice bath, acetic anhydride (4.084 g, 40 mmol) was added dropwise over 15 min. The reaction mixture was stirred at room temperature for 24 h. Then, 6 M HCl(10 ml) was added, and the mixture was extracted three times with diethyl ether (40 mL). The organic layer was dried with anhydrous sodium sulfate, and evaporated. The product was purified by column chromatography with hexane/ethyl acetate (4/1) eluant. 2-Phenylpropan-2-yl acetate (2.327 g, 13.1 mmol; 65% yield) was obtained as a colorless oil.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$ : 1.76 (s, 6H), 2.04 (s, 3H), 7.22-7.37 (m, 5H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$ : 22.3, 28.6, 81.5, 124.2, 126.9, 128.2, 145.9, 169.7; IR (neat): 2981, 1736, 1244 cm<sup>-1</sup>; EI-MS *m/z* (rel intensity): 178 (M<sup>+</sup>, 18).

### 2.3 Amidation

A typical procedure is as follows:

Iodine (50.8 mg, 0.20 mmol), benzonitrile (1) (0.103 g, 1.0 mmol), and 1-phenylethyl acetate (2) were placed in a reaction tube. The mixture was stirred at 80°C for 9 h. A 20% aqueous solution of sodium thiosulfate (5 mL) was added to the reaction mixture to remove iodine. The reaction mixture was then extracted three times with chloroform (20 mL). The organic layer was washed with saturated aqueous sodium chloride solution (20 mL), and then dried with anhydrous sodium sulfate. After concentration, the product was purified by silica-gel column chromatography, eluting with hexane/ethyl acetate (4/1). A total of 185 mg (0.82 mmol; 82% yield) of N-(1-phenylethyl) propanamide (3) was obtained. GC-MS purities of all products were above 98%.

The spectroscopic data for N-(1-phenylethyl) benzamide (3), 4-chloro-N-(1-phenylethyl) benzamide(4a), 4-methoxy-N-(1-phenylethyl) benzamide(4b), N-(1-phenylethyl) propanamide(5a), N-benzylbenzamide(6a), and( $\pm$ ) -exo-N-isobornylbenzamide were previously reported, and these products were assigned by their spectroscopic data.

The spectroscopic data of the other products are as follows.

2-Chloro-N-(1-phenylethyl) benzamide(4c)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) &: 1.61 (d, J = 6.9 Hz, 3H), 5.34 (qd, J = 7.1 and 7.2 Hz, 1H), 6.47 (bs, 1H), 7.26-7.42 (m, 8H), 7.65-7.66 (m, 1H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$  : 21.7, 49.6, 126.2, 127.1, 127.4, 128.7, 130.1, 130.2, 130.6, 131.2, 135.1, 142.7, 165.5; IR (KBr,); 3271, 2970, 1647 cm<sup>-1</sup>; HRMS (FAB-MS) m/z calcd for C<sub>15</sub>H<sub>14</sub>ONCl + Na: 282.0656, found 282.0649; m.p. 106-107°C.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) &: 1.64 (d, J = 6.9 Hz, 3H), 5.44 (qd, J = 7.0 and 7.3 Hz, 1H), 6.27 (bs, 1H), 7.25-7.58 (m, 9H), 7.82-7.91 (m, 2H), 8.25-8.28 (m, 1H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) &: 21.9, 49.3, 124.7, 124.8, 125.3, 126.2, 126.4, 127.1, 127.5, 128.3, 128.8, 130.1, 130.5, 133.6, 134.5, 143.0, 168.6; IR (KBr): 3231, 3028, 1633 cm<sup>-1</sup>; HRMS (ESI-MS) m/z calcd for C<sub>19</sub>H<sub>17</sub>ON + Na: 298.1202, found 298.1197; m.p. 145-147°C.

N-(1-Phenylethyl) furan-2-carboxamide (4e)

 $^{\rm 1}\rm H\text{-}NMR\,(\rm CDCl_3)\,\delta\text{:}\,1.60\,(d,\,J\!=\!6.9$  Hz, 3H), 5.31 (qd,  $J\!=\!7.0$  and 7.3 Hz, 1H), 6.48-6.50 (m, 1H), 6.56 (bs, 1H), 7.11-7.12 (m, 1H), 7.26-7.42 (m, 6H);  $^{\rm 13}\rm C\text{-}NMR\,(\rm CDCl_3)\,\delta\text{:}\,21.8,$  48.4, 112.2, 114.3, 126.2, 127.5, 128.7, 142.9, 143.7, 148.0, 157.5; IR (KBr): 3254, 2973, 1637 cm  $^{-1}$ ; HRMS (FAB-MS) m/z calcd for  $\rm C_{13}H_{13}O_2N$  + H: 216.1019, found 216.1011; m.p. 85-87°C .

#### N-(1-Phenylethyl) isobutyramide (5b)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>)δ: 1.15 (dd, J = 6.8 and 6.9 Hz, 6H), 1.48 (d, J = 6.8 Hz, 3H), 2.34 (s, J = 6.9 Hz, 1H), 5.13 (qd, J = 7.0 and 7.2 Hz, 1H), 5.69 (bs, 1H), 7.23-7.37 (m, 5H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)δ: 19.5, 19.6, 21.7, 35.7, 48.3, 126.1, 127.3, 128.6, 143.3, 175.9; IR (KBr): 3293, 2966, 1640 cm<sup>-1</sup>; HRMS (FAB-MS)m/z calcd for C<sub>12</sub>H<sub>17</sub>ON + H: 192.1383, found 192.1380; m.p. 105-106°C.

## N-(1-Phenylethyl) pivalamide (5c)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$ : 1.20 (s, 9H), 1.48 (d, J = 7.0 Hz, 3H), 5.11 (qd, J = 7.0 and 7.1 Hz, 1H), 5.81 (bs, 1H), 7.23-7.37 (m, 5H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$ : 21.7, 27.5, 27.5, 38.6, 48.4, 126.0, 127.2, 128.6, 143.5, 177.4; IR (KBr): 3316, 2979, 1621 cm<sup>-1</sup>; HRMS (FAB-MS) m/z calcd for C<sub>13</sub>H<sub>19</sub>ON + H: 206.1539, found 206.1533; m.p. 120-121°C.

#### N-(1-Phenylethyl) acrylamide (5d)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) &: 1.53 (d, J = 7.0 Hz, 3H), 5.21 (qd, J = 6.9 and 7.2 Hz, 1H), 5.61-5,65 (m, 1H), 5.98 (bs, 1H), 6.05-6.13 (m, 1H), 6.26-6.32 (m, 1H), 7.25-7.34 (m, 5H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) &: 21.6, 48.8, 126.2, 126.6, 127.4, 128.7, 130.8, 142.9, 164.6; IR (KBr): 3258, 3059, 2972, 1654 cm<sup>-1</sup>; HRMS (FAB-MS) m/z calcd for C<sub>11</sub>H<sub>13</sub>ON + H: 176.1070, found 176.1067; m.p. 64-65°C.

#### N-(1-Phenylethyl) methacrylamide (5e)

 $^{\rm H}\mbox{-NMR}\ (\rm CDCl_3)\ \delta:\ 1.53\ (d,\ J=6.8\ Hz,\ 3H),\ 1.96\ (s,\ 3H),\ 5.18\ (qd,\ J=7.0\ and\ 7.1\ Hz,\ 1H),\ 5.33\ (s,\ 1H),\ 5.68\ (s,\ 1H),\ 6.02\ (bs,\ 1H),\ 7.24\mbox{-}7.38\ (m,\ 5H)\ ;\ ^{13}\mbox{C-NMR}\ (\rm CDCl_3)\ \delta:\ 18.7,\ 21.6,\ 48.8,\ 119.4,\ 126.2,\ 127.4,\ 128.7,\ 140.1,\ 143.1,\ 167.5;\ IR\ (KBr)\ :\ 3368,\ 3027,\ 2969,\ 1609\ cm^{-1};\ HRMS\ (FAB-MS)\ m/\ z\ calcd\ for\ C_{12}H_{15}\mbox{ON}\ +\ H:\ 190.1226,\ found\ 190.1221;\ m.p.\ 94\mbox{-}95\ C.$ 

N-(1-Phenylethyl) benzamide (6b)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) &: 1.61 (d, J = 7.0 Hz, 3H), 5.34 (qd, J = 7.0 and 7.2 Hz, 1H), 6.35 (bs, 1H), 7.26-7.52 (m, 8H), 7.76-7.78 (m, 2H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) &: 21.7, 49.2, 126.2, 126.9, 127.4, 127.4, 128.5, 128.7, 131.4, 134.6, 143.1, 166.5; IR (KBr): 3354, 2974, 1631 cm<sup>-1</sup>; HRMS (FAB-MS) m/z calcd for C<sub>15</sub>H<sub>15</sub>ON + H: 226.1226, found 226.1222; m.p. 113-115°C.

1,1,3-Trimethyl-3-phenyl-2,3-dihydro-1H-indene(7)

Colorless oil; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) $\delta$ : 1.01 (s, 3H), 1.33 (s, 3H), 1.68 (s, 3H), 2.18 (d, J = 13.0 Hz, 1H), 2.41 (d, J = 13.0 Hz, 1H), 7.01-7.32 (m, 9H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) $\delta$ : 30.3, 30.6, 30.9, 42.8, 50.7, 59.2, 122.5, 125.0, 125.4, 126.6, 126.7, 127.2, 127.9, 148.7, 151.0, 152.2; IR (neat): 2957, 1444, 757 cm<sup>-1</sup>; EI-MS m/z (rel intensity): 236 (M<sup>+</sup>, 18).

## **3 RESULTS AND DISCUSSION**

The reaction was performed as follows. Benzonitrile(1), 1-phenylethyl acetate(2), iodine, and a small amount of water were placed in a reaction tube and stirred with heating. After the reaction, an aqueous solution of sodium thiosulfate was added in order to remove the iodine, and the product was isolated. After purification, the spectro-

scopic data confirmed the structure of the isolated amide compound, N-(1-phenylethyl)benzamide(3), indicating that the "Ritter reaction" had occurred to form an amide linkage from the ester and the nitrile. A possible reaction mechanism is shown in **Scheme 1**.

Water in the reaction system reacts with iodine to produce hydrogen iodide, which acts as an acidic catalyst. 1-Phenylethyl acetate then reacts with hydrogen iodide to form a cationic intermediate. Acetic acid is eliminated from the cationic intermediate to produce another cationic intermediate. The lone electron pair of the nitrile group attacks this cation to form cationic intermediate (I). The lone electron pair of water attacks cationic intermediate (I) to form intermediate(II). Proton elimination then occurs to produce intermediate(II), which tautomerizes to form the amide linkage.

The optimum conditions for the formation of (3) were investigated. The results are tabulated in **Table 1**. First, the amount of water was studied, since it was essential for the generation of hydrogen iodide as the acidic catalyst. Amide (3) was still obtained in 39% yield even when no water was added (entry 1). Moisture in the air may have reacted with the iodine in the reaction system. When the molar ratio of iodine: water was 0.2: 1 (entry 2), amide (3) was obtained in 82% yield. However, when the amount of water was further increased to 0.2: 2, the yield decreased slightly



Scheme 1

(entry 3). Thus, the optimized molar ratio of iodine: water was determined to be 0.2: 1. Next, the iodine loading was studied (entries 2, 4, and 5). When the molar ratio of benzonitrile: iodine was 1: 0.2, the highest yield (82%) was obtained (entry 2). The reaction temperature was also investigated (entries 6-10) for a reaction time of 6 h. When the temperature was  $80^{\circ}$ C, the highest yield (72%) was obtained. However, when the temperature was raised to  $90^{\circ}$ C, the yield decreased slightly (entry 10). Next, the reaction duration was investigated (entries 2, 11-14). When the reaction time was 18 h, the highest yield was obtained (82%). When the reaction time was increased to 24 h, the yield decreased to 77% (entry 14). Finally, the molar ratio of (1): (2) was studied (entries 2, 15-17). When the molar ratio of (1): (2) was changed from 1: 2 to 1: 5, the yield remained almost the same. From these results, the most suitable conditions were determined: molar ratio of nitrile: iodine: water = 1: 0.2: 1.0, molar ratio of nitrile: ester = 1: 3, temperature =  $80^{\circ}$ C and reaction time = 18 h.

Using these conditions, the reactions of 1-phenylethyl acetate (2) with other aromatic nitriles were carried out. The results are summarized in **Table 2**. When benzonitriles containing an electron-withdrawing chloro group, such as

4-chlorobenzonitrile (entry 1) and 2-chlorobenzonitrile (entry 3), were used, the amide yields decreased. 4-Methoxybenzonitrile, having an electron-releasing methoxy group, was used in place of benzonitrile (entry 2), but the yields were similar in both cases. When 2-cyanonaphthalene (entry 4) or 2-cyanofuran (entry 5) was used, the yield was low(below 30%). In the case of 4-cyanopyridine, no amide compound was obtained (entry 6).

The reactions of aliphatic nitriles with 1-phenylethyl acetate (2) were performed. The results are indicated in **Table 3**. The yield in the case of 2,2-dimethylpropanenitrile (entry 3) was higher than those in the cases of ethyl cyanide (entry 1) and isobutyronitrile (entry 2). This was due to the higher electron density on the nitrogen atom as a result of the three electron-donating methyl groups. The yield in the case of the saturated nitrile (entries 4 and 5). We previously reported that the reaction of 1-phenylethanol with ethyl cyanide gave the corresponding amide compound in 71% yield<sup>4)</sup>. However, using 1-phenylethyl acetate instead of the alcohol improved the yield of the amide compound to 76% (entry 1).

The reactions of benzonitrile(1) with three esters were

	CN +	OAc	I <sub>2</sub> / H <sub>2</sub> 0	0		
	1	2	Solvent-free c	onditions	H 3	
Entry	Molar ratio of (1):(2)	I <sub>2</sub> (mmol)	H <sub>2</sub> O (mmol)	Temp. (°C)	Time (h)	Yield (%)
1	1:3	0.20	0	80	18	39
2	1:3	0.20	1.0	80	18	82
3	1:3	0.20	2.0	80	18	75
4	1:3	0.10	1.0	80	18	72
5	1:3	0.15	1.0	80	18	75
6	1:3	0.20	1.0	50	6	10
7	1:3	0.20	1.0	60	6	42
8	1:3	0.20	1.0	70	6	58
9	1:3	0.20	1.0	80	6	72
10	1:3	0.20	1.0	90	6	67
11	1:3	0.20	1.0	80	6	72
12	1:3	0.20	1.0	80	7	74
13	1:3	0.20	1.0	80	8	76
14	1:3	0.20	1.0	80	24	77
15	1:2	0.20	1.0	80	18	77
16	1:4	0.20	1.0	80	18	82
17	1:5	0.20	1.0	80	18	80

#### **Table 1** Reactions of benzonitrile (1) with 1-phenylethyl acetate (2).

All reactions were carried out using 1.0 mmol of (1).

Ar-CN +	OAc <u>I<sub>2</sub> (0.20</u>	mmol) / H <sub>2</sub> O (1.0 mmol)		
AI- ON I	Solv 2	vent-free conditions 30 °C, 18 h	H H	
Entry	Nitrile	Yield (%)		
1	CI	N 66	(4a)	
2	, C	N 82	(4b)	
3	CN	33	(4c)	
4	CN	30	(4d)	
5	CN O	27	(4e)	
6	CN N	0		

**Table 2**Iodine-catalyzed amidation of (2) with aromatic<br/>nitriles.

**Table 4**Iodine-catalyzed amidation of (1) with esters.



<sup>a</sup> The amide compound was not obtained, but (7) was obtained in 90% yield.



R-CN +	OAc 2	/ H <sub>2</sub> O (1.0 mmol) ee conditions 18 h	N H 5
Entry	Nitrile	Yield (%)	
1	CN	76	(5a)
2		69	(5b)
3	CN	81	(5c)
4	<b>∖</b> CN	41	(5d)
5	CN	50	(5e)

investigated. The results are illustrated in **Table 4**. In the reaction of benzyl acetate (entry 1), amidation did not occur at  $80^{\circ}$ C. Upon increasing the reaction temperature to  $120^{\circ}$ C, the corresponding amide *N*-benzylbenzamide (6a) was obtained in 41% yield. This yield was lower than that in the case of 1-phenylethyl acetate (82%, entry 2), which was attributed to the more unstable cationic intermediate from benzyl acetate. In the reaction of 2-phenylpropan-2-yl acetate (entry 3), amidation did not occur at either  $80^{\circ}$ C or  $120^{\circ}$ C. However, at  $120^{\circ}$ C, the cyclic compound 1,1,3-tri-



methyl-3-phenyl-2,3-dihydro-1*H*-indene (7) was obtained in 90% yield. A possible reaction mechanism is shown in **Scheme 2**. The two electron pairs of the carbonyl group in the ester attack the cation of hydrogen iodide, which produces the carbocationic intermediate. Acetic acid is eliminated from the carbocationic intermediate, which forms  $\alpha$ -methylstyrene. A  $\pi$  electron in  $\alpha$ -methylstyrene attacks the cation of hydrogen iodide to produce the tertiary cationic intermediate. A  $\pi$  electron in another  $\alpha$ -methylstyrene attacks the tertiary cationic intermediate, which produces the cyclic compound (7).

The reaction of chiral(-)-bornyl acetate with benzonitrile was studied. First, the reaction was carried out at  $80^{\circ}$ C for 5 h, but the corresponding amide compound was obtained only in 25% yield. Therefore, the reaction was carried out again at 120℃ for 18 h. The racemic amide compound, exo-N-isobornylbenzamide, was obtained in 82% yield. X-ray crystal structural analysis and optical rotation measurements confirmed that the amide compound was a racemate. The proposed reaction mechanism is as follows. Bornyl acetate reacts with hydrogen iodide to eliminate acetic acid. The produced cationic intermediate is known to undergo a 6,2-hydride shift to form two cationic intermediates<sup>13, 14)</sup>. The electron pair on the nitrile group attacks the two cationic intermediates equally. As a result, two amide compounds having different stereostructures are produced, as shown in Scheme 3. We previously reported that the amidation of (-)-borneol with benzonitrile using iodine as the catalyst gave the racemic amide compound<sup>8)</sup>. The same results were obtained when using both the



Scheme 3

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alcohol and the ester.

In conclusion, the reaction of esters with nitriles using iodine as the catalyst under solvent-free conditions produced the corresponding amide compounds. However, the reaction of benzonitrile with 2-phenylpropan-2-yl acetate gave the cyclic compound, 1,1,3-trimethyl-3-phenyl-2,3-di-hydro-1*H*-indene. The amidation depended on the electron density of the nitrogen atom on the nitrile group as well as the stability of the cationic intermediate. The reaction of chiral(-)-bornyl acetate with benzonitrile gave the racemic amide compound, ( $\pm$ )-exo-N-isobornylbenzamide.

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