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# Novel C-C Bond Cleavage from Arylacetonitriles in Alcohols to Aryl Carboxylic Esters using Potassium Iodide and Catalytic Amount of Samarium

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**Abstract:** A novel way to cleave the carbon–carbon bond from arylacetonitriles in alcohols to their corresponding aryl carboxylic esters using potassium iodide and a catalytic amount of samarium under mild and neutral conditions is described. Useful yields of the reaction can be obtained with electron-deficient subsistent groups in aromatic rings, and the yields are higher when the subsistent group is an electron-withdrawing group (EWG) rather than an electron-donating group (EDG). Products were characterized by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and MS.

Keywords: Arylacetonitrile, aryl carboxylic ester, C-C bond cleavage, potassium iodide, samarium

Since samarium diiodide was introduced into organic synthesis by Kagan,<sup>[1]</sup> it caused a great public interest in organic synthesis using the samarium reagent.<sup>[2–5]</sup> Now, many new reactions have been found to be relevant to several samarium reagents such as samarium metal,<sup>[6,7]</sup> samarium/auxiliary systems,<sup>[5]</sup> samarium diiodide<sup>[8–10]</sup> and triiodide.<sup>[11]</sup> In samarium/auxiliary systems, there are many reactions promoted by Sm/cat.I<sub>2</sub>, Sm/Cp<sub>2</sub>TiCl<sub>2</sub>, Sm/TiCl<sub>4</sub>, Sm/TMSCl, Sm/DMF, and so on. Our group has also reported research on samarium/auxiliary systems.<sup>[4,5]</sup>

Esters are among the most widespread of naturally occurring compounds. The ester linkage is also present in animal fats and other

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biologically important molecules. Many approaches to synthesizing esters have been reported, including direct and indirect methods.<sup>[12]</sup> More recently, many new methods to prepare aryl carboxylic esters were described, for example, (a) direct conversion of aldehydes in alcoholic solvents to their corresponding ester products utilizing oxone or peroxovanadium as the oxidant;<sup>[13,14]</sup> (b) conversion of electron-deficient aryl alkyl ketones to aryl esters in methanol;<sup>[15]</sup> (c) condensation reaction of carboxylic acids with alcohols to provide esters promoted by dimethylmalonyl-trialkylphos phoranes.<sup>[16]</sup>

Herein we report a novel C-C bond cleavage from arylacetonitriles in alcohols to their corresponding aryl carboxylic esters using potassium iodide and a catalytic amount of samarium. Reaction steps are outlined in Scheme 1. Yields of products are obtained using potassium iodide and a catalytic amount of samarium (Table 1). Products were characterized by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and MS.

To the best of our knowledge, this is the first time aryl carboxylic esters have been prepared in one pot directly from arylacetonitriles and methanol using potassium iodide and a catalytic amount of samarium. The Sm/KI system is easy to obtain and insensitive to air. The success of this methodology was further demonstrated by carbon–carbon cleavage from 4nitrophenylacetonitrile with other alcohols such as 1-propanol, which gives 89% yield of the corresponding esters. Esters of more branched alcohols such as 2-propanol and tert-butyl alcohol could be obtained with long reaction times and in poor yields as reported in Table 1. The reaction rate and yield of the major product have been affected by catalytic amounts of samarium. Yield of the side product (4,4'-azoxybisbenzoic acid dimethyl ester) largely decreases, and the corresponding aryl carboxylic esters were obtained in good to excellent yields. Unfortunately, 3-nitrophenylacetonitrile and 4-methoxyphenylacetonitrile consistently give poor conversion and poor yields of the corresponding esters.

In conclusion, we have demonstrated a simple and effective one-pot protocol to transform arylacetonitriles to aryl carboxylic esters by novel C-C bond cleavage in alcohols. The Sm/KI system is easy to obtain and insensitive to air. It uses easily available reagents and creates fewer side products in the reaction. The Sm/KI system would make a suitable practical method.



*Scheme 1.*  $R^1 = H, p-C1, p-NO_2, m-NO_2, p-OCH_3; R = Methyl, Ethyl, Pr, i-Pr, t-Bu, benzyl, cyclohexyl.$ 

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Entry	$R^1$	R	Temp (°C)	Time (h)	Yields $(\%)^a$
2a	$p-NO_2$	CH <sub>3</sub>	rt	24	92
2b	$p-NO_2$	CH <sub>3</sub>	rt	72	$63^{b}$
2c	$p-NO_2$	CH <sub>3</sub> CH <sub>2</sub>	rt	24	90
2d	p-NO <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	rt	24	89
2e	p-NO <sub>2</sub>	i-Pr	50	72	76
2f	p-NO <sub>2</sub>	t-Bu	50	72	$5^c$
2g	p-NO <sub>2</sub>	PhCH <sub>2</sub>	rt	48	80
2h	p-NO <sub>2</sub>	Cyclohexyl	rt	72	62
2i	Н	CH <sub>3</sub>	50	72	$14^c$
2j	<i>p</i> -Cl	CH <sub>3</sub>	rt	48	74
2k	p-Cl	CH <sub>3</sub> CH <sub>2</sub>	rt	48	60
21	<i>p</i> -OCH <sub>3</sub>	CH <sub>3</sub>	rt	72	2
2m	m-NO <sub>2</sub>	CH <sub>3</sub>	rt	72	38

Table 1. Reaction conditions and yields of aryl carboxylic esters

<sup>a</sup>Isolated yields based on arylacetonitrilles.

<sup>b</sup>Not added samarium.

<sup>c</sup>Yields by GC-MS.

## **EXPERIMENTAL**

Chemicals were purchased from Aldrich. Thin-layer chromatography (TLC) on commercial plates of silica gel  $GF_{254}$  was used to monitor the progress of the reactions. Yields refer to isolated products after purification. Melting points were determined on a Yanaco melting-point apparatus and are uncorrected. Infrared (IR) spectra were taken on a Nicolet 230 FT-IR spectrophotometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker Avance 500 DMX and 400 DMX spectrometer using TMS as internal standard. Elemental analysis was measured on a Eager 200. GC-MS spectrum was obtained from HP 6890, 5973.

#### Typical Procedure for Synthesis of Aryl Carboxylic Esters

Potassium iodide (0.19 g, 1.1 mmol) and alcohol (10 mL) were placed in a three-necked, round-bottom flask with magnetic stirring bar. Then samarium powder (0.015 g, 0.1 mmol) and arylacetonitrile (1 mmol) were added. The reaction mixture was stirred for an appropriate time at room temperature or with heat. After filtration and removal of solvents, the crude product was obtained and purified by column chromatography on silica gel using acetic ether/hexane as eluents.

## Data

**4-Nitro-benzoic acid methyl ester (2a):** Yield 92%; pale yellow solid; mp:  $93-95^{\circ}$ C (lit.<sup>[17]</sup> 93-94°C); <sup>1</sup>H NMR (500, CDCl<sub>3</sub>)  $\delta_{\text{H}}$ : 8.30 (d, J = 9.0 Hz, 2 H), 8.22 (d, J = 9.0 Hz, 2 H), 3.99 (s, 3 H); <sup>13</sup>C NMR (500, CDCl<sub>3</sub>)  $\delta_{\text{C}}$ : 165.44 (C), 150.82 (C), 135.75 (C), 130.97 (CH), 123.81 (CH), 53.09 (CH<sub>3</sub>); IR $v_{\text{max}}$  (KBr)/cm<sup>-1</sup>: 3079, 2958, 1719, 1609, 1525, 1348, 1276, 1103, 822.

**4-Nitro-benzoic acid ethyl ester** (**2c**): Yield 90%; pale yellow solid; mp: 54– 56°C (lit.<sup>[18]</sup> 55–57°c); <sup>1</sup>H NMR (500, CDCl<sub>3</sub>)  $\delta_{\text{H}}$ : 8.29 (d, J = 9.0 Hz, 2 H), 8.22 (d, J = 9.0 Hz, 2 H), 4.44 (q, J = 7.0 Hz, 2 H), 1.43 (t, J = 7.0 Hz, 3 H); IR $v_{\text{max}}$  (KBr)/cm<sup>-1</sup>: 3119, 2990, 1717, 1607, 1526, 1351, 1281, 1104, 841.

**4-Nitro-benzoic acid propyl ester** (**2d**): Yield 89%; pale yellow solid; mp:  $32-33^{\circ}$ C (lit.<sup>[19]</sup>  $34^{\circ}$ C); <sup>1</sup>H NMR (500, CDCl<sub>3</sub>)  $\delta_{\text{H}}$ : 8.28 (d, J = 9.0 Hz, 2 H), 8.22 (d, J = 9.0 Hz, 2 H), 4.34 (t, J = 7.0 Hz, 2 H), 1.81–1.85 (m, 2 H), 1.05 (t, J = 7.5 Hz, 3 H);  $\text{IR}v_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ : 3109, 2968, 1719, 1606, 1524, 1341, 1271, 1103, 874, 721.

**4-Nitro-benzoic acid isopropyl ester (2e):** Yield 76%; pale yellow solid; mp:  $104-105^{\circ}$ C (lit.<sup>[20]</sup> 104-106°C); <sup>1</sup>H NMR (500, CDCl<sub>3</sub>)  $\delta_{\rm H}$ : 8.28 (d, J = 9.0 Hz, 2 H), 8.20 (d, J = 9.0 Hz, 2 H), 5.28-5.30 (m, 1 H), 1.40 (d, J = 6.0 Hz, 6 H);  $\rm IRv_{max}(\rm KBr)/\rm cm^{-1}$ : 3116, 2923, 1713, 1607, 1523, 1347, 1282, 1100, 841.

**4-Nitro-benzoic acid phenyl methyl ester** (**2 g**): Yield 80%; pale yellow solid; mp: 82–84°C (lit.<sup>[21]</sup> 83–84°C); <sup>1</sup>H NMR (500, CDCl<sub>3</sub>)  $\delta_{\rm H}$ : 8.28 (d, J = 9.0 Hz, 2 H), 8.24 (d, J = 9.0 Hz, 2 H), 7.37–7.46 (m, 5 H), 5.41 (s, 2 H);  $\rm IRv_{max}(\rm KBr)/\rm cm^{-1}$ : 3114, 2943, 1713, 1603, 1522, 1341, 1275, 1121, 1101, 845.

**4-Nitro-benzoic acid cyclohexyl ester** (**2 h**): Yield 62%; pale yellow solid; mp: 47–49°C (lit.<sup>[22]</sup> 49–51°C); <sup>1</sup>H NMR (500, CDCl<sub>3</sub>)  $\delta_{\rm H}$ : 8.29 (d, J = 9.0 Hz, 2 H), 8.22 (d, J = 9.0 Hz, 2 H), 5.06–5.08 (m, 1 H), 1.97–1.99 (m, 2 H), 1.80–1.83 (m, 2 H), 1.58–1.63 (m, 4 H), 1.46–1.49 (m, 2 H); IR $v_{\rm max}$ (film)/cm<sup>-1</sup>: 3114, 2856, 1723, 1607, 1530, 1348, 1278, 1115, 842, 720.

**Benzoic acid methyl ester (2i):** Yield 14%; pale yellow oil; bp: 197–199°C (lit.<sup>[23]</sup> 198–200°C.); <sup>1</sup>H NMR (400, CDCl<sub>3</sub>)  $\delta_{\text{H}}$ : 8.04 (d, J = 8.0 Hz, 2 H), 7.55 (t, J = 7.6 Hz, 1 H), 7.41–7.45 (m, 2 H), 3.91 (s, 3 H); IR $\nu_{\text{max}}$ (KBr)/ cm<sup>-1</sup>: 3062, 2955, 1724, 1600, 1451, 1432, 1278, 1111, 823.

**4-Chloro-benzoic acid methyl ester** (**2j**): Yield 74%; pale yellow solid; mp:  $38-39^{\circ}$ C (lit.<sup>[24]</sup>  $39^{\circ}$ C); <sup>1</sup>H NMR (500, CDCl<sub>3</sub>)  $\delta_{\text{H}}$ : 7.98 (d, J = 9.0 Hz, 2 H),

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7.42 (d, J = 9.0 Hz, 2 H), 3.92 (s, 3 H);  $IRv_{max}(KBr)/cm^{-1}$ : 3043, 2960, 1727, 1597, 1495, 1435, 1277, 1092, 823.

**4-Chloro-benzoic acid ethyl ester** (2 k): Yield 60%; pale yellow solid; mp:  $103-105^{\circ}$ C (lit.<sup>[25]</sup>  $103-105^{\circ}$ c); <sup>1</sup>H NMR (500, CDCl<sub>3</sub>)  $\delta_{\text{H}}$ : 7.97 (d, J = 9.0 Hz, 2 H), 7.40 (d, J = 9.0 Hz, 2 H), 4.37 (q, J = 7.0 Hz, 2 H), 1.39 (t, J = 7.0 Hz, 3 H); IR $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup>: 3059, 2985, 1721, 1595, 1490, 1403, 1274, 1092, 827, 760.

**3-Nitro-benzoic acid methyl ester** (**2 m**): Yield 38%; pale yellow solid; mp: 76–78°C (lit.<sup>[26]</sup> 78°C); <sup>1</sup>H NMR (400, CDCl<sub>3</sub>)  $\delta_{\text{H}}$ : 8.88 (s, 1 H), 8.37–8.44 (m, 2 H), 7.66 (t, J = 8.0 Hz, 1 H), 3.99 (s, 3 H); IR $v_{\text{max}}$ (KBr)/cm<sup>-1</sup>: 3093, 2960, 1719, 1615, 1529, 1442, 1351, 1292, 1136.

**4,4'-Azoxybisbenzoic acid dimethyl ester (side product):** Yield 28% (without added samarium); mp 201–203°C (lit.<sup>[27]</sup> 203–205°C),<sup>1</sup>H NMR (500, CDCl<sub>3</sub>)  $\delta_{\rm H}$ : 8.08 (d, J = 9.0 Hz, 2 H), 7.89 (d, J = 8.5 Hz, 2 H), 7.46 (d, J = 9.0 Hz, 2 H), 6.74 (d, J = 8.5 Hz, 2 H), 4.02 (s, 3 H), 3.88 (s, 3 H); <sup>13</sup>C NMR (500, CDCl<sub>3</sub>)  $\delta_{\rm C}$ : 166.82 (C), 157.28 (C), 151.99 (C), 148.51 (C), 136.73 (C), 131.04 (CH), 130.34 (CH), 125.18 (C), 123.36 (CH), 121.25 (CH), 54.75 (CH<sub>3</sub>), 52.10 (CH<sub>3</sub>); IR<sub>max</sub>(KBr)/cm<sup>-1</sup>: 3001, 2946, 1717, 1659, 1524, 1348, 1279, 1104, 861; MS(EI) m/z: 314 (M<sup>+</sup>).

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