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A Facile Synthesis of 1,3,5-Triaryl Benzenes from Acetophenone Diethyl Ketals in the Presence of Acetyl Chloride and SmCl<sub>3</sub>

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## A FACILE SYNTHESIS OF 1,3,5-TRIARYL BENZENES FROM ACETOPHENONE DIETHYL KETALS IN THE PRESENCE OF ACETYL CHLORIDE AND SmCl<sub>3</sub>

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Abstract: Samarium trichloride,  $SmCl_3$ , has been found to be an efficient catalyst for the synthesis of 1,3,5-triaryl benzenes from acetophenone diethyl ketals in the presence of acetyl chloride under solvent of pentane and mild conditions.

Samarium trichloride has been extensively utilized for a number of organic synthetic reactions as Lewis acid catalyst in the last decade.<sup>1-2</sup> Recently, we have reported a simple and convenient transformation of acetals and ketals to the corresponding aldehydes and ketones with excellent conversions by acetyl chloride-samarium trichloride system.<sup>3</sup>

In the extensive study of this reaction, we found that, in stead of acetophenone, 1,3,5-triphenyl benzene was obtained in high yield from acetophenone diethyl ketal by acetyl chloride in the catalytic amount of samarium trichloride. Triaryl benzenes are a class of important compounds in the electrode and electroluminescent devices.<sup>4</sup> In the present communication, we wish to report this facile method for the synthesis of triaryl benzenes from acetophenone

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scheme



**Table** Synthesis of triaryl benzenes from acetophenone diethyl ketals by acetyl chloride in the presence of catalytic amount samarium trichloride<sup>1</sup>

entry	time (h)	yield $(\%)^2$
a	2	85
b	2	83
с	2	83
d	2	88
e	8	67
f	10	60
g	24	40

1. 5% SmCl<sub>3</sub> to substrate, 2.5 e.q of acetyl chloride to ketal; room temperature.

2. yield of isolated product.

diethyl ketals by acetyl chloride in the presence of samarium trichloride under solvent of pentane and mild conditions. The results are summerized in table.

As shown in table, catalyzed by SmCl<sub>3</sub>, acetophenone diethyl ketals can be conveniently converted to the corresponding triaryl benzenes with moderate to good yields in the presence of acetyl chloride. Alkyl and electron-donating groups increased the reactivity of the ketals (entries a,b,c,d). Electronwithdrawing groups attenuated the reactivity of substrates (entries e,f,g). These results showed this reaction had the strong electronic effect.

The present methodology has the advantage of rapid reaction, sole product, mild conditions and manipulate. The study of using other lanthanide trichlorides is in research.

#### General procedure

To a solution of  $SmCl_3$  (0.5 mmol), acetophenone diethyl ketal (10 mmol) and pentane (15 mL), acetyl chloride (12 mmol) was dropped under nitrogen atmosphere. After stirring for proper time at room temperature, the reaction was quenched by a mixture of benzene (20 mL) and H<sub>2</sub>O (10 mL). The organic layer was separated and washed with the saturated aqueous solution of Na<sub>2</sub>CO<sub>3</sub> and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Concentrated and recrystalized, a needle crystal was obtained.

## 1,3,5-triphenyl benzene (a)<sup>5</sup>

Recrystallized from *n*-hexane. m p 171.0-172.0 °C; IR (KBr): 1590, 1570 (m, Ar), 750 (s, Ar) cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.9-7.3 (m, 18H, ArH) ppm.

### 1,3,5-tris(4-methyl phenyl) benzene (b)

Recrystallized from *n*-hexane. m p 177.0-178.5 °C; IR (KBr): 2900 (s, CH<sub>3</sub>), 1590, 1560 (m, Ar), 800 (s, Ar) cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  7.8-7.2 (m,15H, ArH), 2.4 (s, 9H, CH<sub>3</sub>) ppm; MS *m/z* (%): 348 (M<sup>+</sup>, 100).

Anal. calc. for C27H24: C, 93.06; H, 6.94. Found: C, 92.77; H, 6.67.

#### 1,3,5-tris(4-iso-propyl phenyl) benzene (c)

Recrystallized from n-hexane. m p 174.5-176.0 °C; IR (KBr): 2900 (s, CH3),1590, 1560 (m, Ar), 800 (s, Ar) cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  7.8-7.2 (m, 15H, ArH), 3.0 (m, 3H, CH), 1.3 (d, 18H, CH<sub>3</sub>) ppm; MS m/z (%): 432 (M<sup>+</sup>, 100). Anal. calc. for C<sub>33</sub>H<sub>36</sub>: C, 91.61; H, 8.39. Found: C, 91.42; H, 8.31.

#### 1,3,5-tris(4-methoxyl phenyl) benzene (d)

Recrystallized from  $\alpha$ -hexane/dichloromethane. m p 142.5-144.0 °C; IR (KBr): 2900 (s, CH<sub>3</sub>), 1590, 1510 (m, Ar), 1260 (s, Ar-O), 820 (s, Ar) cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  7.8-6.9 (m, 15H, ArH), 3.9 (s, 9H, OCH<sub>3</sub>) ppm; MS m/z (%): 396 (M<sup>+</sup>, 100). Anal. calc. for C<sub>27</sub>H<sub>24</sub>O<sub>3</sub>: C, 81.79; H, 6.40. Found: C, 81.54; H, 6.10.

### 1,3,5-tris(4-chlorophenyl) benzene (e)

Recrystallized from *n*-hexane/dichloromethane. m p 256.5-258.0 °C; IR (KBr): 1590, 1500 (m, Ar), 1020 (s, Ar-Cl), 800 (s, Ar) cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  7.8-7.4 (m, 15H, ArH) ppm; MS *m/z* (%): 410 (M<sup>+</sup>, 100) [M]<sup>+</sup>.

Anal. calc. for C<sub>24</sub>H<sub>15</sub>Cl<sub>3</sub>: C, 70.15; H, 3.69; Cl, 25.88. Found: C, 70.18; H, 3.35; Cl, 26.19.

#### 1,3,5-tris(4-bromophenyl) benzene (f)

Recrystallized from *n*-hexane/dichloromethane. m p 280.5-282.0 °C; IR (KBr): 1580, 1480 (m, Ar), 1000 (s, Ar-Br), 810 (s, Ar) cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  7.8-7.5 (m, 15H, ArH) ppm; MS *m/z* (%): 543 (M<sup>+</sup>, 28), 544 (M<sup>+</sup>+H, 100).

Anal. calc. for C<sub>24</sub>H<sub>15</sub>Br<sub>3</sub>: C, 53.08; H, 2.78; Br, 44.14. Found: C, 52.59; H, 2.55; Br, 43.67.

### 1,3,5-tris(4-nitrophenyl) benzene (g)

Recrystallized from chloroform: m p 325.5-327.0 °C; IR (KBr): 1630 (s, NO<sub>2</sub>), 1580, 1550 (m, Ar), 800 (s, Ar) cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  7.8-7.2 (m,15H, ArH) ppm; MS m/z (%): 441(M<sup>+</sup>, 4.4). Anal. calc. for C<sub>24</sub>H<sub>15</sub>N<sub>3</sub>O<sub>6</sub>: C, 62.31; H, 3.43; N, 9.51. Found: C, 62.74; H, 3.18; N, 9.09.

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