

# The use of boron carbide powder as an efficient green catalyst for Friedel-Crafts chemistry

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**Abstract:** Boron carbide (B<sub>4</sub>C) as finely powdered solid functions has been found to function as an efficient, green, non-toxic, and easily recoverable heterogeneous catalyst system for the Friedel-Crafts alkylation and acylation reaction.

**Keywords:** Friedel-Crafts alkylation; Friedel-Crafts acylation; boron carbide catalyst; green chemistry. ©2021 ACG Publication. All right reserved.

## 1. Introduction

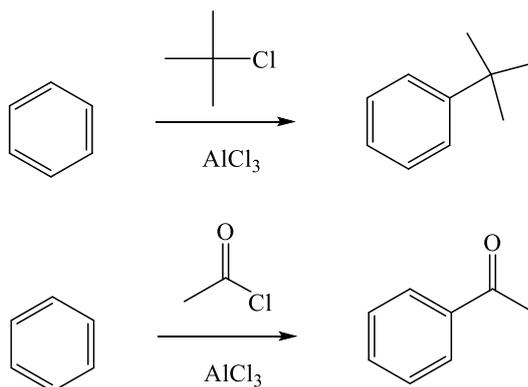
The Friedel-Crafts reaction is among the cornerstone methods in organic chemistry by which a carbon-carbon bond can be formed between an appropriately electron rich aromatic ring sp<sup>2</sup> carbon with a Lewis acid-activated alkyl halide or acyl halide to afford a C(sp<sup>2</sup>)-C(sp<sup>3</sup>) bond or a C(sp<sup>2</sup>)-C(sp<sup>2</sup>) bond, respectively (Scheme 1)<sup>1</sup>. Many of the Lewis acids used for this reaction, such as aluminum chloride, are utilized stoichiometrically, are corrosive, not particularly atom economic, and after use generate hazardous waste by-products which require remediation<sup>2</sup>. More recently in order to address such issues with the Friedel-Crafts acylation reaction, heterogenous catalytic methods for the condensation of carboxylic acids with arenes utilizing Al<sub>2</sub>O<sub>3</sub>/P<sub>2</sub>O<sub>5</sub> as a noncorrosive and environmentally benign catalyst to prepare aryl ketones have been reported<sup>3</sup>. While other Lewis acid systems such as zeolites are less corrosive and are catalytic, they have been reported to have somewhat limited use based upon their pore size, which precludes their use with sterically demanding systems<sup>4</sup>.

## 2. Background

Boron carbide (B<sub>4</sub>C) is one of the hardest known ceramic materials (nicknamed “black diamond”)<sup>5</sup> with semi-conductor properties<sup>6</sup> and industrial applications such as an abrasive<sup>7</sup> and a potent neutron absorber<sup>8</sup>. While there are many other uses for this ceramic, we reasoned that such a compound rich in boron might function as a Lewis acid catalyst. To this end, we carried out a brief study<sup>9</sup> in order to ascertain the effectiveness of B<sub>4</sub>C as catalyst for both the Friedel-Crafts alkylation and acylation reactions.

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**Scheme 1.** Examples of traditional Friedel-Crafts alkylation and acylation reactions

### 3. Experimental

#### 3.1. Chemicals and Analysis

All reagents and methyl *t*-butyl ether were purchased commercially from Sigma-Aldrich and were used without any purification. Boron carbide powder (99+%; 325 mesh) was purchased from Alfa-Aesar and was used without purification. The identity of the products was determined based upon comparison of melting point/boiling point descriptions in the literature and <sup>1</sup>H NMR spectra (400 MHz) with authentic samples and recorded on a Bruker Biospin Ascend 400 MHz Nuclear Magnetic Resonance Spectrometer using CDCl<sub>3</sub> as solvent and TMS as an internal standard.

#### 3.2. General Procedure

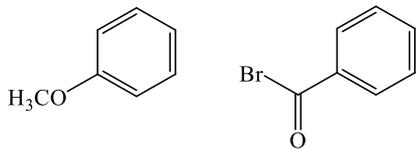
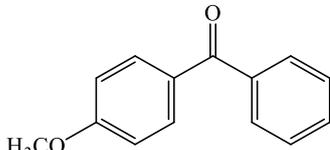
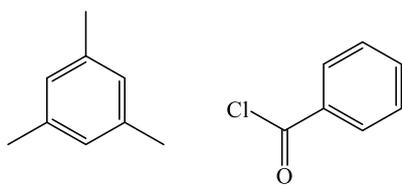
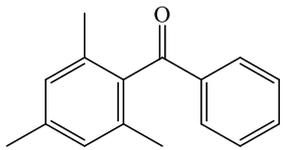
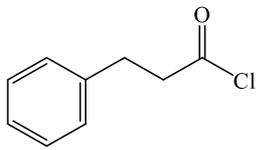
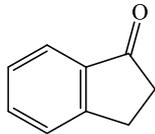
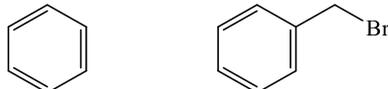
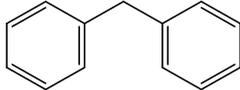
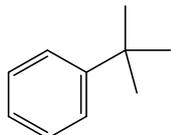
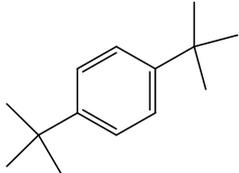
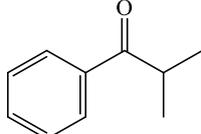
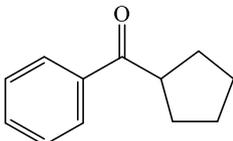
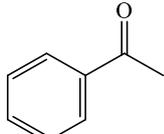
A 2-necked round bottom flask (100 – 250 mL) was charged with a mixture of the aromatic system (1 eq), the acyl halide or alkyl halide (1 eq), and B<sub>4</sub>C (1.0 – 18 mol%). The mixture was then heated neat or to reflux in methyl *t*-butyl ether or benzene for the time indicated in the procedure. Workup is as described for each compound prepared.

### 4. Present Study

Reactions of the alkyl or acyl halides with appropriately electron rich aryl substrates proved successful using simple equipment setups without rigorous pre-drying employing B<sub>4</sub>C as the catalyst. Yields typically were observed to be moderate to good. The reaction can be run either neat or with a solvent such as *t*-butyl methyl ether or benzene with product yields ranging from moderate to good. The catalyst can be isolated by simple filtration.

*p*-Methoxybenzophenone (**3a**): A 250 mL round bottom flask equipped with a magnetic stir bar and reflux condenser was charged with anisole (5.40 g; 50 mmol), benzoyl bromide (9.30 g; 50 mmol), methyl *t*-butyl ether (50 mL), and boron carbide (0.5 g; 9.0 mmol) and the resulting mixture was heated at reflux for 12h. The resulting mixture was allowed to cool to room temperature and was filtered to remove the catalyst. A small amount of NaHCO<sub>3</sub> was added to remove excess benzoyl bromide. Removal of the benzene *in vacuo* and recrystallization of the residue from MeOH afforded pure *p*-methoxybenzophenone (**3a**) (5.63 g; 53% yield); mp = 60-61 °C (lit.<sup>10</sup> mp = 60-62 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.88 (s, 3H, OCH<sub>3</sub>), 6.95-6.98 (m, 2H), 7.47 (dd, *J* = 7.5, 7.8 Hz, 2H), 7.54-7.58 (m, 1H), 7.75 (dd, *J* = 1.4, 8.4 Hz, 2H), 7.82-7.84 (m, 2H). Using benzoyl chloride in place of benzoyl bromide in the procedure gave comparable results.

**Table 1.** Products and yield of reactions by boron carbide powder catalyst

Reactants	Products	Compound	% Yield
		<b>3a</b>	53
		<b>3b</b>	56
		<b>3c</b>	33
		<b>3d</b>	70
		<b>3e</b>	80
		<b>3f</b>	75
		<b>3g</b>	66
		<b>3h</b>	62
		<b>3i</b>	68

**2,4,6-Trimethylbenzophenone (3b):** A 125 mL round bottom flask equipped with a magnetic stir bar and reflux condenser was charged with mesitylene (4.80 g; 40 mmol), benzoyl chloride (5.60 g; 40

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mmol), *t*-butyl methyl ether (50 mL), and boron carbide (0.5 g; 9.0 mmol) and the resulting mixture was heated at reflux for 24h. The resulting mixture was allowed to cool to room temperature and was concentrated *in vacuo*. The residue was taken up in 100 mL of a 1:1 acetone/EtOH solution. Slow evaporation provided pure 2,4,6-trimethylbenzophenone **3b** (5.02 g; 56%); mp = 33.5-35 °C (lit<sup>11</sup> mp = 35 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.08 (s, 6H, CH<sub>3</sub>), 2.33 (s, 3H, CH<sub>3</sub>), 6.91(s, 2H), 7.43 (2H, t, *J* = 7.8 Hz), 7.56 (1H, t, *J* = 7.8 Hz), 7.80 (2H, d, *J* = 8.57 Hz).

*1-Indanone (3c)*: A 125 mL round bottom flask was charged with benzenepropanoyl chloride (3.00 g; 20 mmol), 50 mL of *t*-butyl methyl ether, and boron carbide (0.2 g; 3.6 mmol). The mixture was stirred at reflux for 24 h. The resulting mixture was allowed to cool to room temperature and was concentrated *in vacuo*. The residue was taken up in 100 mL of a 1:1 acetone/EtOH solution. Slow evaporation provided pure 1-indanone **3c** (0.87 g; 33% yield); mp 41-42 °C (lit<sup>12</sup> mp = 42 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.68 (t, 2H, *J* = 5.7 Hz, CH<sub>2</sub>C=O), 3.15 (t, 2H, *J* = 5.7 Hz ArCH<sub>2</sub>), 7.36 (t, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.59 (t, *J* = 7.1 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H).

*Diphenylmethane (3d)*: A 250 mL round bottom flask was charged with benzyl bromide (7.40 g; 40 mmol), 50 mL of benzene, and boron carbide (0.2 g; 3.6 mmol). The mixture was stirred at reflux for 24 h. The resulting mixture was allowed to cool to room temperature and was filtered to remove the catalyst. The residue was then concentrated *in vacuo* to afford 5.40 g of the crude product. Distillation afforded pure diphenylmethane **3d** (4.69g; 70 %), bp = 117-119 °C/8 mm Hg (lit<sup>13</sup> bp = 117 °C/8-9 mm Hg); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.96 (s, 2H, CH<sub>2</sub>), 7.36 – 7.75 (m, 10H).

*t-Butylbenzene (3e)*: A 125 mL round bottom flask equipped with a magnetic stir bar and reflux condenser was charged with benzene (50 mL), *t*-butyl chloride g; 4.63g, 50 mmol), and boron carbide (0.5 g; 9.0 mmol) and the resulting mixture was heated at reflux for 24h. The resulting mixture was allowed to cool to room temperature and was concentrated *in vacuo*. The residue was distilled to provide pure *t*-butylbenzene **3e** (5.34 g, 80 %), bp = 167-170 °C (lit<sup>14</sup> bp = 167-169 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.32 (s, 9H, CH<sub>3</sub>), 7.01 – 7.44 (m, 5H, ArH).

*1,4-Di-t-Butylbenzene (3f)*: A 125 mL round bottom flask equipped with a magnetic stir bar and reflux condenser was charged with *t*-butylbenzene (2.68 g; 20 mmol), *t*-butyl chloride (3.70 g; 40 mmol), and boron carbide (0.5 g; 9.0 mmol) and the resulting mixture was heated at 60 °C for 18h. The resulting mixture was allowed to cool to room temperature and was diluted with *t*-butyl methyl ether (50 mL). The mixture was filtered to remove the catalyst and was washed with 10% NaHCO<sub>3</sub> (aq) (2 x 25 mL). The organics were dried (MgSO<sub>4</sub>), filtered, and concentrated *in vacuo* to provide a clear semi-crystalline solid. This crude material was recrystallized from MeOH to provide 1,4-di-*t*-butylbenzene **3f** (2.86g, 75%), mp = 75-77 °C (lit<sup>15</sup> mp = 76.5-77.5 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.32 (s, 18H, CH<sub>3</sub>), 7.33 (s, 4H, ArH).

*Isobutyrophenone (3g)*: A 125 mL round bottom flask equipped with a magnetic stir bar and reflux condenser was charged with benzene (50 mL), isobutyroyl chloride (5.33g, 50 mmol), and boron carbide (0.5 g; 9.0 mmol) and the resulting mixture was heated at reflux for 24h. The resulting mixture was allowed to cool to room temperature and was concentrated *in vacuo*. The residue was distilled to provide pure isobutyrophenone **3g** (4.88g, 66%), bp = 99-102 °C/8 mm Hg (lit<sup>16</sup> bp = 98-100 °C /8 mm Hg); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.22 (d, *J* = 6.9 Hz, 6 H), 3.57 (9m, 1 H), 7.47 (dd, *J* = 7.5, 7.8 Hz, 2 H), 7.54-7.55 (m, 1 H), 7.95 (dd, *J* = 1.4, 7.8 Hz, 2 H).

*Cyclopentylphenone (3h)*: A 125 mL round bottom flask equipped with a magnetic stir bar and reflux condenser was charged with benzene (50 mL), cyclopentenoyl chloride (6.73g, 50 mmol), and boron carbide (0.5 g; 9.0 mmol) and the resulting mixture was heated at reflux for 24h. The resulting mixture was allowed to cool to room temperature and was concentrated *in vacuo*. The residue was distilled to provide pure cyclopentylphenone **3h** (5.44g, 62%), bp = 124-127 °C/8 mm Hg (lit<sup>17</sup> bp = 126 °C/8 mm

Hg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.62-1.74 (m, 4H), 1.90-1.94 (m, 4H), 7.46 (dd,  $J = 7.2, 7.8$  Hz, 2 H), 7.53-7.56 (m, 1 H), 7.98 (dd,  $J = 1.4, 8.8$  Hz, 2 H).

*Acetophenone (3i)*: A 125 mL round bottom flask equipped with a magnetic stir bar and reflux condenser was charged with benzene (50 mL), acetyl chloride (3.92g, 50 mmol), and boron carbide (0.5 g; 9.0 mmol) and the resulting mixture was heated at reflux for 24h. The resulting mixture was allowed to cool to room temperature and was concentrated *in vacuo*. The residue was distilled to provide pure acetophenone **3i** (4.08g, 68%), bp = 72-74 °C/4 mm Hg (lit<sup>18</sup> bp = 70-71 °C /3 mm Hg);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.57 (s, 3H,  $\text{CH}_3$ ); 7.32 – 7.70 (m, 3H, ArH); 7.94 (d, 2H,  $J = 7.1$  Hz; ArH).

In conclusion, boron carbide has been proven to be an efficient green catalyst in both Friedel-Crafts acylation and alkylation chemistry void of significant processing issues compared to traditionally used catalyst systems such as  $\text{AlCl}_3$ .

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## References

- [1] Olah, G.A. *Friedel-Crafts Chemistry*, **1973**, Hoboken, NJ: Wiley.
- [2] Helmboldt, O.; Hudson, L. Keith; Misra, C.; Wefers, K.; Heck, W.; Stark, H.; Danner, M.; Rösch, N. "Aluminum Compounds, Inorganic". *Ullmann's Encyclopedia of Industrial Chemistry*. **2007**, Weinheim: Wiley VCH.
- [3] Hajipour, A.R.; Zarei, A.; Khazdooz, L.; Ruoocho, A.E. Simple and efficient procedure for the Friedel-Crafts acylation of aromatic compounds with carboxylic acids in the presence of  $\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$  under heterogeneous conditions. *Synth. Commun.* **2009**, *39*, 2702-2722.
- [4] Sartori, G.; Maggi, R. Use of solid catalysts in Friedel–Crafts acylation reactions. *Chem. Rev.* **2006**, *106*, 1077–1104.
- [5] Sokhansanj, A.; Hadian, A.M. Purification of attrition milled nano-size boron carbide powder". *2nd International Conference on Ultrafine Grained & Nanostructured Materials (UFGNSM). Int. J. Modern Physics: Conference Ser.* **2012**, *5*, 94–101.
- [6] Domnich, V.; Reynaud, S.; Haber, R.A.; Chhowalla, M. Boron carbide: structure, properties, and stability under stress. *J. Am. Ceram. Soc.* **2011**, *94* (11), 3605–3628.
- [7] Menard, J.C.; Thibault, N.W. "Abrasives." *Ullmann's Encyclopedia of Industrial Chemistry*. **2007**, Weinheim: Wiley VCH.
- [8] Weimer, A.W. Carbide, nitride, and boride materials. *Synthesis and Processing* Chapman & Hall, **1997**, London, New York, p. 330.
- [9] Dumas, P.E. Boron carbide as an effective Friedel-Crafts type catalyst. US Patent **2008**, US 7,393,970 B2 (2 pages)
- [10] Jafarpour, F.; Rashidi-Ranjbar, P.; Kashani, A. Easy-to-execute carbonylative arylation of aryl halides using molybdenum hexacarbonyl. Efficient synthesis of unsymmetrical diaryl ketones. *Eur. J. Org. Chem.* **2011**, 2128-2132.
- [11] Montagne, P.J. Action of alcoholic potassium hydroxide solutions on ketones. I. *Recl. Trav. Chim. Pays Bas.* **1909**, *27*, 327-359.
- [12] Baddeley, G.; Rasburn, J. W.; Rose, R. Decarboxylation of *p*- and *o*-formylcinnamic acids to *p*-formylstyrene and 1-indanone. *J. Am. Chem. Soc.* **1949**, *71*, 2429-2431.
- [13] Ju, T. Y.; Wood, C. E.; Garner, F. H. Cetane numbers and physical properties of normal alkylbenzenes and other hydrocarbons. III. Evaluation of alkylbenzenes and certain related hydrocarbons as Diesel fuels. *J. Institute Petroleum* **1942**, *28*, 159-171.
- [14] Huston, R.C.; Barrett, W.T. Fragmentation of alcohols in the presence of aluminum chloride. II. 2,3,3-trimethyl-2-butanol. *J. Org. Chem.* **1946**, *11*, 657-663.
- [15] Johnson, C.E.; Adams, C. E. *m*-Di-*tert*-butylbenzene. U.S. Patent **1947**, US 2,429,691 (2 pages).

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- [16] Moureu, C.; Mignonac, G. Ketisoketimines. *Compt. Rend.* **1914**, *159*, 149-152.
- [17] Elphimoff-Felkin, I.; Tchoubar, B. The stability of carbonium ions as a function of structure IV. Nitrous deamination of 1-(1-aminoalkyl)cyclopentanes. *Compt. Rend.* **1953**, *237*, 726-728.
- [18] Leonard, N.J.; Boyd, S.N.; Jr. Cinnolines. I. Synthesis of aminoacetophenones and aminopropiophenones. *J. Org. Chem.* **1946**, *11* 405-418.

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