

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

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Abstract: Boron carbide (B₄C) 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

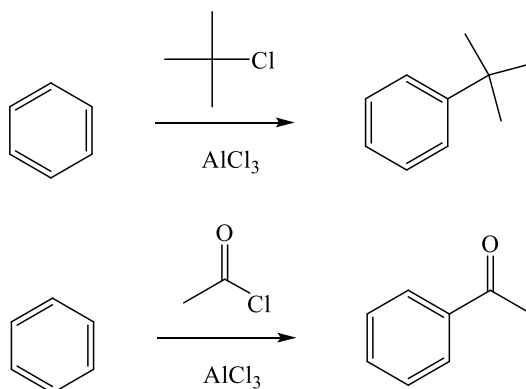
The Friedel-Crafts reaction is among the cornerstone methods in organic chemistry by which a carbon-carbon bond can be formed between an appropriately electron rich aromatic ring sp² carbon with a Lewis acid-activated alkyl halide or acyl halide to afford a C(sp²)–C(sp³) bond or a C(sp²)–C(sp²) bond, respectively (Scheme 1)¹. 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 remediation². 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 Al₂O₃/P₂O₅ as a noncorrosive and environmentally benign catalyst to prepare aryl ketones have been reported³. 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 systems⁴.

2. Background

Boron carbide (B₄C) is one of the hardest known ceramic materials (nicknamed “black diamond”)⁵ with semi-conductor properties⁶ and industrial applications such as an abrasive⁷ and a potent neutron absorber⁸. 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 study⁹ in order to ascertain the effectiveness of B₄C 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 ¹H NMR spectra (400 MHz) with authentic samples and recorded on a Bruker Biospin Ascend 400 MHz Nuclear Magnetic Resonance Spectrometer using CDCl₃ as solvent and TMS as an internal standard.

3.2. General Procedure

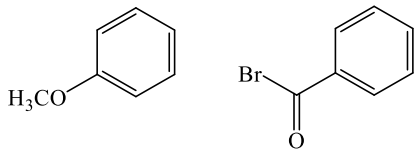
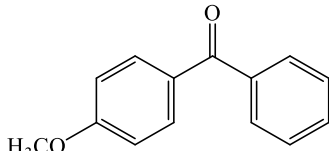
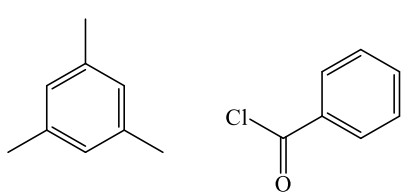
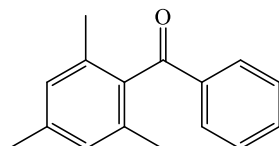
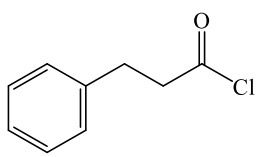
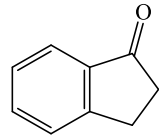
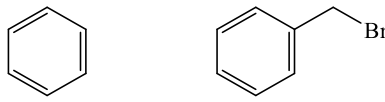
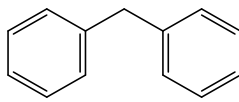

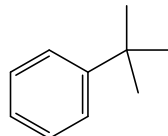

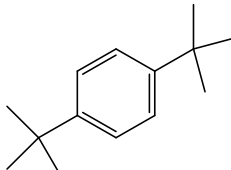

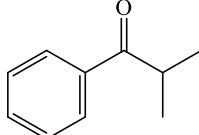
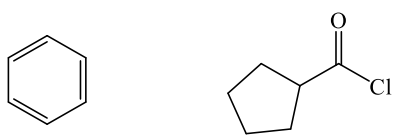
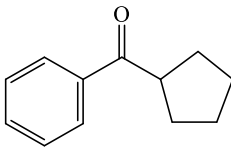

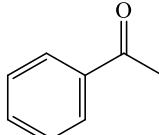
A 2-necked round bottom flask (100 – 250 mL) was charged with a mixture of the aromatic system (1 eq), the acyl halide or alkyl halide (1 eq), and B₄C (1.0 – 18 mol%). The mixture was then heated neat or to reflux in methyl *t*-butyl ether or benzene for the time indicated in the procedure. Workup is 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 B₄C 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 NaHCO₃ 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.¹⁰ mp = 60-62 °C); ¹H NMR (CDCl₃): δ 3.88 (s, 3H, OCH₃), 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
		3a	53
		3b	56
		3c	33
		3d	70
		3e	80
		3f	75
		3g	66
		3h	62
		3i	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 (lit¹¹ mp = 35 °C); ¹H NMR (CDCl₃): δ 2.08 (s, 6H, CH₃), 2.33 (s, 3H, CH₃), 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 (lit¹² mp = 42 °C); ¹H NMR (CDCl₃): δ 2.68 (t, 2H, *J* = 5.7 Hz, CH₂C=O), 3.15 (t, 2H, *J* = 5.7 Hz ArCH₂), 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 (lit¹³ bp = 117 °C/8-9 mm Hg); ¹H NMR (CDCl₃): δ 3.96 (s, 2H, CH₂), 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 (lit¹⁴ bp = 167-169 °C); ¹H NMR (CDCl₃): δ 1.32 (s, 9H, CH₃), 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% NaHCO₃ (aq) (2 x 25 mL). The organics were dried (MgSO₄), 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 (lit¹⁵ mp = 76.5-77.5 °C); ¹H NMR (CDCl₃): δ 1.32 (s, 18H, CH₃), 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), isobutyryl 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 (lit¹⁶ bp = 98-100 °C /8 mm Hg); ¹H NMR (CDCl₃): 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 (lit¹⁷ bp = 126 °C/8 mm

Hg); ^1H NMR (CDCl_3): δ 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 (lit¹⁸ bp = 70-71 °C /3 mm Hg); ^1H NMR (CDCl_3): δ 2.57 (s, 3H, 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 AlCl_3 .

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