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$LiBF_4$-Catalyzed three-component coupling of an aldehyde, acetic anhydride and allyltrimethylsilane/TMSCN

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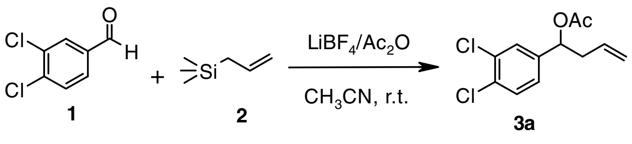
Abstract—Lithium tetrafluoroborate is found to be an efficient catalyst for allylation and cyanation of aldehydes with allyltrimethylsilane and trimethylsilyl cyanide in the presence of acetic anhydride at room temperature to produce homoallylic acetates and α-cyano acetates in excellent yields. A solution of 10 mol % of $LiBF_4$ in acetonitrile provides a convenient reaction medium to carry out allylation and cyanation reactions under very mild and neutral conditions.

The stereoselective addition of allylmetal reagents to aldehydes, imines, and epoxides is an important carbon–carbon bond forming reaction in organic synthesis.[1] Lewis acid catalyzed carbon–carbon bond forming reactions are of great significance in organic synthesis because of their high reactivity, selectivity, and mild reaction conditions.[2] Despite a number of methods for the allylation of aldehydes and acetals with allyltrimethylsilane,[3,4] only a few methods have been reported for the allylation of diacetates.[5] Moreover, many of these methods produce a mixture of products and thus the desired products are obtained in low to moderate yields especially with methoxy-substituted benzaldehydes.[5] Although transition metal salts typically catalyze the allylation or cyanation reactions,[3–5] new catalytic systems are being explored continuously in search of improved efficiencies and cost effectiveness. Furthermore, the development of a simple and neutral alternative would extend the scope of this transformation.

The catalytic properties of lithium perchlorate in diethyl ether (LPDE) as a mild Lewis acid are well documented and involve specific solute–Li interactions with complexation to diethyl ether and the less nucleophilic bulky counterion ClO_4^-.[6] However, the inherently hazardous nature of perchlorate limits its use to specific cases and only on a small scale. Acetonitrile solutions of $LiBF_4$ are safe and efficient catalytic media for various organic transformations[7] and the catalytic applications of lithium tetrafluoroborate have recently been reviewed.[8] However, there have been no reports on the use of lithium tetrafluoroborate for the preparation of homoallylic acetates and α-cyano acetates from aldehydes and allyltrimethylsilane/TMSCN.

Herein, we report the use of lithium tetrafluoroborate as a novel Lewis acid catalyst for the allylation and cyanation of aldehydes with allyltrimethylsilane and trimethylsilyl cyanide to produce allylic acetates and α-cyano acetates in excellent yields under very mild conditions. Accordingly, treatment of 3,4-dichlorobenzaldehyde **1** with allyltrimethylsilane 2 and acetic anhydride in the presence of 10 mol % lithium tetrafluoroborate in acetonitrile gave 1-(3,4-dichlorophenyl)-3-butenyl acetate **3a** in 85% yield (Scheme 1).

The catalytic activity of lithium tetrafluoroborate provided the incentive for further study of reactions with various aldehydes, and several substituted benzaldehydes reacted smoothly with allyltrimethylsilane in the presence of 10 mol % $LiBF_4$ at ambient temperature to give the corresponding homoallylic acetates (Table 1,



Scheme 1.

Keywords: Aldehydes; Lithium tetrafluoroborate; Allylic acetates; α-Cyano acetates.

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Table 1. $LiBF_4$-catalyzed allylation and cyanation of aldehydes

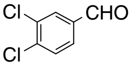
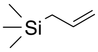
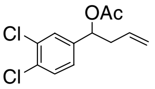
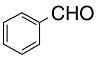
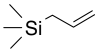
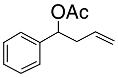
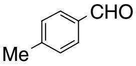
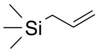
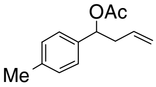
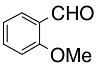
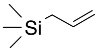
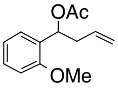
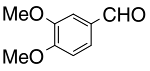
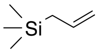
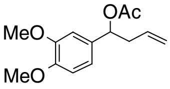
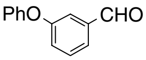
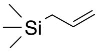
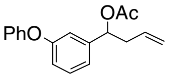
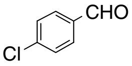
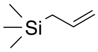
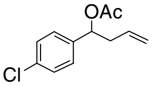
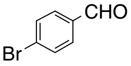
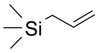
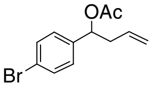
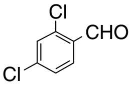
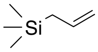
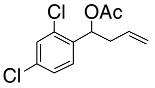
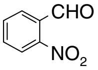
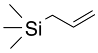
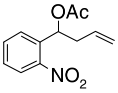
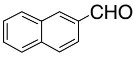
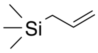
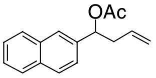
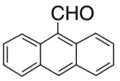
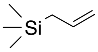
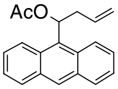
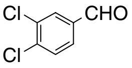
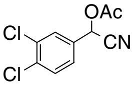
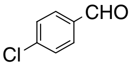
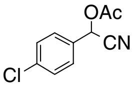
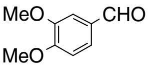
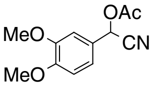
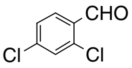
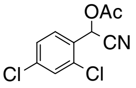
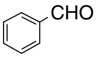
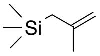
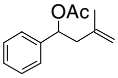
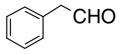
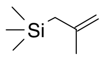
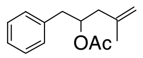
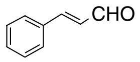
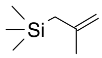
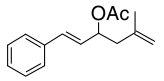
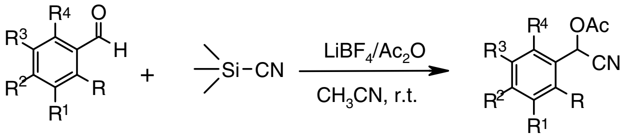
Entry	Aldehyde **1**	TMS-X	Product **3**[a]	Time (h)	Yield[b] (%)
a				1.5	85
b				2.0	75
c				2.5	70
d				2.5	80
e				2.5	80
f				2.0	70
g				1.5	80
h				2.0	70
i				1.5	85
j				2.5	70
k				2.5	75
l				2.5	75
m		TMSCN		2.0	80
n		TMSCN		2.0	80
o		TMSCN		2.5	75
p		TMSCN		2.0	80
q				1.5	79

Table 1 (*continued*)

Entry	Aldehyde **1**	TMS-X	Product **3**[a]	Time (h)	Yield[b] (%)
r				2.0	85
s				2.5	75

[a] All products were characterized by ^{1}H NMR, IR and mass spectroscopy.

[b] Yield refers to pure products after chromatography.



Scheme 2.

entries a–l). Both electron-rich and electron-deficient aromatic aldehydes gave homoallylic acetates in good yields. However, no bis-allylated products were obtained from methoxy-substituted benzaldehydes, as is normally observed under acidic conditions.[4c,5a,c] Furthermore, treatment of aryl aldehydes with TMSCN in the presence of acetic anhydride gave the corresponding α-cyano acetates in high yields (Table 1, entries m–p; Scheme 2).

This reaction also proceeded well with substituted allyltrimethylsilane and aldehydes to give the corresponding homoallylic acetates (Table 1, entries q–s). In all cases, the reactions proceeded efficiently at ambient temperature and the products were obtained in high yields with high selectivity.[9] To determine the efficiency of this procedure, we also performed the reactions with various other lithium salts such as lithium perchlorate and lithium triflate. Lithium tetrafluoroborate was found to be the most effective and gave the best results. Furthermore, the reactions were also carried out using 10 mol % $LiClO_4$ in acetonitrile to compare the efficiency of lithium perchlorate and lithium tetrafluoroborate. In this reaction media, high temperature (refluxing acetonitrile) and longer reaction times (6–12 h) were typically required to achieve comparable yields as to those obtained with $LiBF_4$. As solvent, acetonitrile appeared to give the best results. The limited solubility of $LiBF_4$ in common organic solvents restricted an extensive solvent study. Among various tetrafluoroborates, $NaBF_4$, NH_4BF_4, $CuBF_4$, and $AgBF_4$, $LiBF_4$ was found to be more effective in terms of conversion. In the absence of catalyst, the reactions did not proceed even under reflux conditions for a long reaction time (8–12 h). The use of $LiBF_4$ makes this procedure very mild, simple, and convenient. The scope of this method is illustrated with respect to various aldehydes and allyltrimethylsilane/TMSCN and the results are presented in Table 1.

In summary, a solution of 10 mol % of lithium tetrafluoroborate in acetonitrile was shown to be a highly efficient and convenient catalytic medium for the preparation of homoallylic acetates and α-cyano acetates in a one-pot operation from aldehydes, acetic anhydride, and allyltrimethylsilane/trimethylsilyl cyanide. In addition to its simplicity, and mild reaction conditions, this method is clean and provides high yields of products making it a useful and attractive strategy for the preparation of homoallylic acetates and α-cyano acetates under neutral conditions.

Acknowledgement

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References and notes

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9. *General procedure*: (a) *Conversion of aldehyde into homoallylic acetate*: A mixture of aldehyde (5 mmol), allyltrimethylsilane (6 mmol) and lithium tetrafluoroborate (10% of w/w aldehyde) in dichloromethane was stirred at 23 °C for 30 min and then acetic anhydride (5 mmol) was added and the stirring was continued for 2–3 h. After completion

of the reaction as indicated by TLC, the reaction mixture was diluted with water (20 mL) and extracted with dichloromethane (2 × 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo, and purified by column chromatography on silica gel (Merck, 100–200 mesh; ethyl acetate–hexane, 1:9) to afford pure homoallylic acetate.

(b) *Conversion of aldehyde into α-cyano acetate*: A mixture of aldehyde (5 mmol), trimethylsilyl cyanide (6 mmol) and lithium tetrafluoroborate (10% of w/w aldehyde) in dichloromethane was stirred at 23 °C for 30 min and then acetic anhydride (5 mmol) was added and stirring was continued for 2–3 h. After completion of the reaction as indicated by TLC, the reaction mixture was diluted with water (20 mL) and extracted twice with dichloromethane (2 × 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo, and purified by column chromatography on silica gel (Merck, 100–200 mesh; ethyl acetate–hexane, 1:9) to afford pure α-cyano acetate.

Spectral data for selected products: Compound **3a**: viscous liquid, IR (neat): ν 1737, 1450, 1245, 1031 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.45–7.35 (m, 2H), 7.20–7.10 (m, 1H), 5.80–5.60 (m, 2H), 5.15–5.05 (m, 2H), 2.70–2.45 (m, 2H), 2.10 (s, 3H). EIMS: *m*/*z*: 258 [M$^+$], 217, 174. Compound **3b**: colourless liquid, IR (neat): ν 1737, 1463, 1222, 1024 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.40–7.20 (m, 5H), 5.80 (t, 1H, $J = 7.5$ Hz, 1H), 5.72–5.65 (m, 1H), 5.15–5.00 (m, 2H), 2.75–2.50 (m, 2H), 2.10 (s, 3H). EIMS: *m*/*z*: 190 [M$^+$], 105, 77, 43. Compound **3c**: liquid, IR (neat): ν 1739, 1643, 1237, 1021, 813 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22–7.06 (m, 4H), 5.72 (t, 1H, $J = 6.4$ Hz), 5.69–5.58 (m, 1H), 5.09–4.97 (m, 2H), 2.68–2.29 (m, 2H), 2.45 (s, 3H), 2.04 (s, 3H). EIMS: *m*/*z*: 204 [M$^+$], 120. Compound **3f**: viscous liquid, IR (neat): ν 1739, 1447, 1242, 1025 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.40–7.22 (m, 4H), 7.10–6.90 (m, 5H), 5.78 (t, 1H, $J = 6.8$ Hz), 5.75–5.60 (m, 1H), 5.15–5.00 (m, 2H), 2.70–2.42 (m, 2H), 2.10 (s, 3H). EIMS: *m*/*z*: 282 [M$^+$], 239, 223, 198. Compound **3k**: viscous liquid, IR (neat): ν 1736 1640 1451 1025 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.85–7.72 (m, 4H), 7.49–7.38 (m, 3H), 5.93 (t, 1H, $J = 7.4$ Hz), 5.81–5.57 (m, 1H), 5.15–4.98 (m, 2H), 2.82–2.53 (m, 2H), 2.08 (s, 3H). EIMS: *m*/*z*: 240 [M$^+$], 197, 156. Compound **3m**: colourless liquid, IR (KBr): ν 2943, 2200, 1761, 1568 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.20 (s, 3H), 6.40 (s, 1H), 7.40–7.50 (m, 3H). EIMS: *m*/*z*: 242 [M$^+$], 185, 175, 151, 88, 76, 44. Compound **3o**: liquid, IR (KBr): ν 2930, 2210, 1759, 1590 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.15 (s, 3H), 3.80–3.90 (m, 6H) 6.30 (s, 1H), 6.35 (d, 1H $J = 6.8$ Hz), 6.95 (s, 1H), 7.05 (d, 1H $J = 7.1$ Hz). EIMS: *m*/*z*: 235 [M$^+$] 192, 176, 86, 59, 43. Compound **3p**: liquid, IR (KBr): ν 2930, 2200, 1759, 1590 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.15 (s, 3H), 6.40 (s, 1H), 7.45 (m, 2H), 7.60–7.70 (m, 1H). EIMS: *m*/*z*: 242 [M$^+$], 209, 166, 150, 124, 114, 88. Compound **3r**: colourless liquid, IR (KBr): ν 1740, 1639, 1231, 1023, 817 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.75 (s, 3H), 1.95 (s, 3H), 2.20–2.35 (m, 2H), 2.85 (d, $J = 6.0$ Hz, 2H), 4.70 (s, 1H), 4.80 (s, 1H), 5.20–5.30 (m, 1H), 7.15–7.30 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.9, 22.3, 40.3, 42.2, 72.4, 113.3, 126.4, 128.2, 129.3, 137.5, 141.5, 170.3. EIMS: *m*/*z*: 241(M+Na), 219 (M+1), 203, 187, 159, 134, 104.