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Short Communication

Metal free synthesis of homoallylic alcohols promoted by ultrasound

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ABSTRACT

The use of ultrasound irradiation to promote the allylation of aldehydes containing different functionalities with potassium allyltrifluoroborates is described. The method features the use of a minimum amount of acetone as solvent, without any other catalyst or promoter. The products were obtained in high yields, short reaction times, at room temperature and without the need of further purification.

1. Introduction

The addition of an allylic organometallic reagent to a carbonyl compound is an important synthetic method, not only to afford the formation of a new carbon–carbon bond and the introduction of two new functionalities, an alcohol and a double bond, but also because these can be used for further transformations [1].

Thus, the development and application of allylic organometallic reagents have attracted attention with several approaches already described based on the use of allylic organometallics [2] or organometalloid [3] reagents, as well as electrochemical based methods [4].

Some allylic organometallics present drawbacks such as the difficulty to handle due to its Lewis base character, which requires the use of strictly anhydrous conditions and because of competing Wurtz coupling reactions [5].

Thereby, the search for more efficient synthetic methods based on the use of less expensive and easy to handle reagents have attracted considerable interest from chemists. Moreover, the development of methods focusing on environmentally benign reactions has become particularly prominent [6]. In this context, the use of ultrasound in organic synthesis has attracted considerable attention, not only because it can easily promote organic transformations which normally requires drastic conditions, but also because it can enhance the reaction rate and increase the yield [7].

Herein, we wish to describe an environmentally benign reaction for the synthesis of homoallylic alcohols based on the reaction of potassium allyltrifluoroborate and aldehydes containing different functional groups promoted by ultrasound without the use of any metal or additive.

2. Materials and methods

2.1. Materials

All solvents used were previously purified and dried in agreement with the literature [8]. Compounds **1a–o** and *E*-crotylboronic acid pinacol ester were purchased from Aldrich Chemical Co. and used as received. All other commercially available reagents and solvents were used as received. Reactions were monitored by thin-layer chromatography on 0.25 mm E. Merck silica gel 60 plates (F254) using UV light, vanillin and *p*-anisaldehyde as visualizing agents. All compounds were sufficiently pure for use in further experiments, unless indicated otherwise.

2.2. Instrumentation

^{1}H (300 MHz) NMR and ^{13}C (75 MHz) NMR data were recorded in $CDCl_3$ or DMSO-d_6. The chemical shifts are reported as delta (δ) units in parts per million (ppm) relative to the solvent residual peak as the internal reference. ^{11}B (128 MHz) and ^{19}F (376 MHz) NMR spectra were recorded in DMSO-d_6. Spectra were calibrated using $BF_3{\bullet}Et_2O$ (0.0 ppm) as external reference in the case of ^{11}B NMR and chemical shifts were referenced to external CF_3CO_2H

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(0.0 ppm) in the case of ^{19}F NMR. Coupling constants (*J*) for all spectra are reported in Hertz (Hz). The sonication was performed in an 8890E-DTH ultrasonic cleaner (with a frequency of 47 kHz and a nominal power 35 W; Cole Parmer Co.). The reaction flask was located at the maximum energy area in the cleaner, the surface of reactants was slightly lower than the level of the water. The reaction temperature was controlled by water bath.

2.3. Typical procedures

*2.3.1. Synthesis of potassium allyltrifluoroborate, **2***

To a solution of $B(OMe)_3$ (8.15 mL, 7.59 g, 73.2 mmol) in THF (40 mL) was added dropwise allylmagnesium chloride (30 mL, 60 mmol, 2.0 M in THF) at −78 °C. The mixture was stirred for 30 min. The ice bath was removed. The yellow solution with a white precipitate was allowed to reach the room temperature over a 1 h period. Then, it was cooled to 0 °C and KHF_2 (23.4 g, 300 mmol) was added in one portion. This was followed by the dropwise addition of H_2O (30 mL). The ice bath was removed. The mixture was stirred for 30 min and then concentrated under high vacuum. The white solid was extracted with hot acetone (4 × 100 mL). The extracts were filtered through a Celite pad and the filtrate was concentrated *in vacuo* to afford a white solid. The solid was purified by dissolving in the minimum amount of hot acetone, followed by cooling to room temperature and precipitation with Et_2O. The solution was allowed to stand for 20 min to complete precipitation. The precipitate was collected and dried under high vacuum to yield 3.37 g (38%) of the title compound as a white solid powder, which can be stored at room temperature without degradation. ^{1}H NMR (300 MHz, DMSO-d_6) δ 5.85–5.74 (m, 1H, $CH_2{=}CH$), 4.56 (d, *J* = 17.2 Hz, 1H, $CH_2{=}CH$), 4.49 (d, *J* = 9.6 Hz, 1H, $CH_2{=}CH$), 0.92 (br s, 2H, CH_2BF_3K); ^{13}C NMR (75 MHz, DMSO-d_6) δ 142.9, 108.9; ^{11}B NMR (128 MHz, DMSO-d_6) δ 4.21 (q, $J_{11B,19F}$ = 61.3 Hz, BF_3K); ^{19}F NMR (376 MHz, DMSO-d_6) δ −136.4 ($J_{19F,11B}$ = 61.3 Hz, BF_3K). The NMR data are in agreement with previously reported literature values [3a].

*2.3.2. Synthesis of potassium E-crotyltrifloroborate, **4***

To a solution of *E*-crotylboronic acid pinacol ester (0.5 g, 2.75 mmol) in MeOH (12 mL) was added dropwise a 4.5 M solution of KHF_2 (2.0 mL) over a 30 min at 0 °C. The mixture was stirred for additional 30 min at room temperature and concentrated under high vacuum. The residual solids were extracted with 20% MeOH in acetone (3 × 10 mL). The combined extracts were concentrated close to the saturation point and Et_2O was added until no more precipitation was observed. The solid was collected, washed with Et_2O (2 × 10 mL), and dried under high vacuum to give 300 mg (60%) of the title compound as a white powdered solid. ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.43–5.36 (m, 1H, CH_3–C*H*), 4.96–4.91 (m, 1H, CH═C*H*–CH_2), 1.51 (d, *J* = 5.9 Hz, 3H, C*H*$_3$–CH), 0.92 (br s, 2H, C*H*$_2$$BF_3K$); RMN ^{13}C (75 MHz, DMSO-d_6) δ 135.0, 117.9, 18.2; RMN ^{11}B (128 MHz, DMSO-d_6) δ 6.21 (q, $J_{11B,19F}$ = 61.4 Hz, BF_3K); RMN ^{19}F (376 MHz, DMSO-d_6) δ −136.4 ($J_{19F,11B}$ = 61.4 Hz, BF_3K). The NMR data are in agreement with previously reported literature values [3i].

*2.3.3. General procedure for the allylation of aldehydes (**1a–o**) with potassium allyltrifluoroborate (**2**) promoted by ultrasound*

To a solution of the appropriate aldehyde **1a**–**o** (1.0 mmol) in acetone (0.5 mL) was added potassium allyltrifluoroborate **2** (177 mg, 1.20 mmol). The mixture was placed in an ultrasound bath for the time indicated on Table 2 and then diluted with EtOAc (5 mL) and washed with water (2 × 15 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure to yield **3a**–**q** without the need of further purification. The data for all synthesized compounds match with the literature [3a].

*2.3.3.1. (**3a**) (E)-1-Phenylhexa-1,5-dien-3-ol.* ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.21 (m, 5H, H_{Aryl}), 6.61 (dd, *J* = 15.9, 1.2 Hz, 1H, PhC*H* = CH), 6.24 (dd, *J* = 15.9, 6.3 Hz, 1H, PhCH = C*H*), 5.86 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H, C*H* = CH_2), 5.22–5.14 (m, 2H, CH = C*H*$_2$), 4.40–4.33 (m, 1H, C*H*OH), 2.50–2.33 (m, 2H, CHC*H*$_2$), 1.78 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.5, 134.0, 131.5, 130.2, 128.5, 127.6, 126.4, 118.3, 71.6, 41.9.

*2.3.3.2. (**3b**) 1-(Furan-2-yl)but-3-en-1-ol.* ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 1.8, 0.9 Hz, 1H, H_{Het}), 6.34 (dd, *J* = 2.1, 1.8 Hz, 1H, H_{Het}), 6.26 (dd, *J* = 2.1, 0.9 Hz, 1H, H_{Het}), 5.81 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H, C*H* = CH_2), 5.23–5.13 (m, 2H, CH = C*H*$_2$), 4.76 (dd, *J* = 6.6, 6.3 Hz, 1H, C*H*OH), 2.66–2.60 (m, 2H, CHC*H*$_2$), 2.05 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9; 141.9; 133.6, 118.6, 110.1, 106.1, 66.9, 40.1.

*2.3.3.3. (**3c**) 1-(2-Nitrophenyl)but-3-en-1-ol.* ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.1, 1.2 Hz, 1H, H_{Aryl}), 7.84 (dd, *J* = 8.1, 1.5 Hz, 1H, H_{Aryl}), 7.65 (td, *J* = 8.1, 1.2 Hz, 1H, H_{Aryl}), 7.43 (td, *J* = 8.1, 1.2 Hz, 1H, H_{Aryl}), 5.97–5.83 (m, 1H, C*H*═CH_2), 5.32 (dd, *J* = 8.4, 3.6 Hz, 1H, C*H*OH), 5.25–5.18 (m, 2H, CH═C*H*$_2$), 2.76–2.67 (m, 1H, CHC*H*$_2$), 2.48–2.37 (m, 2H, CHC*H*$_2$ and O*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7, 139.2, 133.9, 133.4, 128.1, 128.0, 124.3, 119.0, 68.3, 42.8.

*2.3.3.4. (**3d**) 1-(3-Nitrophenyl)but-3-en-1-ol.* ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (t, *J* = 1.5 Hz, 1H, H_{Aryl}), 8.13 (ddd, *J* = 8.1, 2.1, 0,9 Hz, 1H, H_{Aryl}), 7.71 (d, *J* = 8.1 Hz, 1H, H_{Aryl}), 7.53 (t, *J* = 8.1 Hz, 1H, H_{Aryl}), 5.87–5.73 (m, 1H, C*H*═CH_2), 5.22–5.16 (m, 2H, CH═C*H*$_2$), 4.87 (dd, *J* = 8.1, 5.1 Hz, 1H, C*H*OH), 2.63–2.43 (m, 2H, CHC*H*$_2$), 2.19 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.1, 145.9, 133.2, 131.9, 129.3, 122.4, 120.8, 119.6, 72.0, 43.9.

*2.3.3.5. (**3e**) 1-(4-Nitrophenyl)but-3-en-1-ol.* ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.7 Hz, 2H, H_{Aryl}), 7.54 (d, *J* = 8.7 Hz, 2H, H_{Aryl}), 5.86–5.72 (m, 1H, C*H*═CH_2), 5.22–5.16 (m, 2H, CH═C*H*$_2$), 4.87 (dd, *J* = 7.8, 4.5 Hz, 1H, C*H*OH), 2.62–2.40 (m, 2H, CHC*H*$_2$), 2.07 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1, 147.1, 133.1, 126.5, 123.5, 119.5, 72.1, 43.8.

*2.3.3.6. (**3f**) 1-(2-Methoxyphenyl)but-3-en-1-ol.* ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.5, 1.8 Hz, 1H, H_{Aryl}), 7.25 (td, *J* = 7.5, 1.8 Hz, 1H, H_{Aryl}), 6.96 (td, *J* = 8.4, 1.2 Hz, 1H, H_{Aryl}), 6.88 (d, *J* = 8.4 Hz, 1H, H_{Aryl}), 5.85 (ddt, *J* = 17.1, 10.2, 7.5 Hz, 1H, C*H*═CH_2), 5.17–5.09 (m, 2H, CH = C*H*$_2$), 4.96 (dd, *J* = 8.1, 5.1 Hz, 1H, C*H*OH), 3.84 (s, 3H, OMe), 2.64–2.44 (m, 2H, CHC*H*$_2$), 2.41 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 135.1, 131.7, 128.2, 126.7, 120.6, 117.4, 110.3, 69.5, 55.1, 41.8.

*2.3.3.7. (**3g**) 1-(3-Methoxyphenyl)but-3-en-1-ol.* ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 8.1, 7.8 Hz, 1H, H_{Aryl}), 6.86–6.84 (m, 2H, H_{Aryl}), 6.74 (ddd, *J* = 8.1, 2.7, 1.2 Hz, 1H, H_{Aryl}), 5.73 (ddt, *J* = 17.1, 10.2, 7.5 Hz, 1H, C*H*═CH_2), 5.12–5.04 (m, 2H, CH═C*H*$_2$), 4.63 (dd, *J* = 7.5, 5.4 Hz, 1H, C*H*OH), 3.73 (s, 3H, OMe), 2.46–2.39 (m, 2H, CHC*H*$_2$), 1.95 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 145.6, 134.4, 129.3, 118.2, 118.0, 112.8, 111.2, 73.1, 55.1, 43.6.

*2.3.3.8. (**3h**) 1-(4-Methoxyphenyl)but-3-en-1-ol.* ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, *J* = 9.0 Hz, 2H, H_{Aryl}), 6.88 (d, *J* = 9.0 Hz, 2H, H_{Aryl}), 5.79 (ddt, *J* = 16.8, 9.9, 6.6 Hz, 1H, C*H*═CH_2), 5.19–5.10 (m, 2H, CH═C*H*$_2$), 4.68 (t, *J* = 6.6 Hz, C*H*OH), 3.80 (s, 3H, OMe), 2.52–2.47 (m, 2H, CHC*H*$_2$), 2.01 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 136.0, 134.6, 127.0, 118.2, 113.7, 72.9, 55.2, 43.7.