Supporting Information. Hydroboration with Pyridine Borane at Room Temperature

Julia M. Clay, Edwin Vedejs*

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Experimental

Alkenes **12a**, **18a-e**, β -methylstyrene, and alkynes **9a**, **9d**, **9e**, and **9f** were used without further purification as obtained from either Acros or Aldrich. $\text{Py}\cdot\text{BH}_3$ (from Aldrich) was purified by filtration through a plug of silica gel (1:1/ Et_2O : hexanes) to remove excess pyridine. Activation was accomplished using resublimed iodine (as purchased) from Acros. Known alkenes **12b**¹³, **12c**¹⁴, **12d**¹⁵, **12f**¹⁶, **12g**¹⁷ and alkyne **9b**¹⁸, **9c**¹⁸, and **9g**¹⁹ were prepared according to literature procedures.

Synthesis of *N,N*-dibenzyl-5-hexenamine (12e): 5-Hexen-1-ol (0.72 mL, 6 mmol) was combined with triethylamine (1.6 mL, 12 mmol) in 20 mL of CH_2Cl_2 and cooled to 0 °C. Toluenesulfonyl chloride (1.3 g, 7.2 mmol) was added. After 1 h the reaction was warmed to room temperature and allowed to stir for an additional 3 h. The reaction was then poured into 20 mL of water and the aqueous layer was extracted with 2 x 20 mL of CH_2Cl_2 . The combined organic layers were dried with Na_2SO_4 and the solvent was removed (rotatory evaporator) to provide a light yellow oil. The material was purified by silica gel chromatography (5:1 Et_2O /Hexanes) to provide 1.45 g (95% yield) of tosylated product. This material (635 mg, 2.5 mmol) was combined with di-benzyl amine (0.58 mL, 3 mmol) in EtOH (15 mL) and stirred at 70 °C for 12 h. Upon completion, the reaction mixture was cooled to room temperature and partitioned between 10 mL of 1M KOH and 30 mL of CH_2Cl_2 . The organic layer was collected and the aqueous layer was extracted 2 x 15 mL with CH_2Cl_2 . The combined layers were dried over Na_2SO_4 and the solvent was removed (rotatory evaporator) to afford a light yellow oil. The crude mixture was purified by silica gel chromatography (3:1 hexanes/ Et_2O) to afford 396 mg of **12e** (84%).

12e: analytical tlc on K6F silica get 60A, 3:1 hex/Et₂O, R_f= 0.5. ESMS for C₂₀H₂₅N; M+1, m/z= 280.2; IR (neat, cm⁻¹) 3062, 2929, 2793, 1640, 1601; 400 MHz NMR (CDCl₃, ppm) δ 7.35-7.15 (10H, m), 5.72 (1H, ddt, J= 17.2, 10.0, 6.8 Hz), 4.95-4.85 (2H, m), 3.5 (4H, s), 2.37 (2H, t, J= 7.2 Hz), 1.93 (2H, m), 1.54 (2H, m), 1.39 (2H, m); ¹³C NMR (125.7 MHz, CDCl₃, ppm) δ 140.0, 139.0, 128.7, 128.1, 126.7, 114.3, 58.3, 53.1, 33.5, 26.5, 26.4.

Representative Procedure for the Hydroboration/Oxidation of Alkenes Using Activated Amine Boranes.

Purified Py•BH₃ (1 mL, 10 mmol) was added to a flask containing 50 mL of CH₂Cl₂ (nitrogen atmosphere). Solid I₂ (1.2 g, 5 mmol) was then added in several portions at 0 °C. After vigorous gas evolution had ceased the solution was warmed to room temperature and β-methylstyrene (1.3 mL, 10 mmol) was added. After 2 h the solution was cooled to 0 °C and MeOH (10 mL), 20% (aq) NaOH (5 mL) and 30% (aq) H₂O₂ (5 mL) were added. This mixture was allowed to stir at room temperature for an additional 2 h. The solution was then poured into a separatory funnel and diluted with 20 mL Et₂O and 15 mL H₂O and acidified with dilute HCl (aq). The water layer was washed 2 x 20 mL with Et₂O and dried with MgSO₄. Solvent was removed (rotatory evaporator) to afford a 15:1 mixture of alcohols **7** and **8**, 1.14 g (92%).

The hydroboration and oxidation of alkenes **12a-g**, to afford alcohols **13a**, **13b**²⁰, **13c**²¹, **13d**²², **13e**, **13f**²³ and **13g**²⁴ was performed at 20% scale (0.2 mmol of alkene) following the above procedure except in the following cases. For the hydroboration of **12d-g**, py•BH₃ and I₂ were used with the alkene in a 2:1:1/py•BH₃:I₂:alkene molar ratio. The oxidative work-up that followed the hydroboration of **12d** and **12g** employed THF (2 mL), H₂O (2 mL) and NaBO₃•H₂O (600 mg, 60 mmol) instead of the traditional MeOH/NaOH/H₂O₂ oxidation method.

Aminoalcohols **13a-d** and **13f-g** were identified by comparison with published data, and **13e** was characterized as follows.

6-(N,N-Dibenzylamino)hexanol (13e): analytical tlc on K6F silica get 60A, 1:1 Et₂O/Hexanes R_f= 0.29; ESMS for C₂₀H₂₇NO; M+1, m/z= 298.2; IR (neat, cm⁻¹) 3300 (br), 2935, 2852, 2797, 1493; 500 MHz NMR (CDCl₃, ppm) δ 7.36 (4H, m), 7.30 (4H, m), 7.22 (2H, m), 3.59 (2H, t, 6.5 Hz), 3.54 (4H, s), 2.40 (2H, t, 7.0 Hz), 1.52 (4H, m), 1.27 (4H, m); ¹³C NMR (125.7 MHz, CDCl₃, ppm) δ 140.0, 128.8, 128.1, 126.7, 63.0, 58.3, 53.2, 32.7, 32.1, 26.9, 25.5.

Representative Procedure for the Hydroboration/Oxidation of Alkynes Using Activated Amine Boranes.

Py•BH₃ (60 μL, 0.6 mmol) was added to a flask containing 3 mL of CH₂Cl₂. I₂ (76 mg, 0.3 mmol) was then added in one portion. After gas evolution had ceased **9a** (175 μL, 1.2 mmol) was added. After 2 h, MeOH (3 mL), 20% (aq) NaOH (1 mL) and 30% (aq) H₂O₂ (1 mL) were added. This mixture was allowed to stir for an additional 2 h. The reaction mixture was then poured into a separatory funnel and diluted with 15 mL CH₂Cl₂ and 15 mL H₂O. The water layer was washed 2 x 10 mL with CH₂Cl₂ and dried with Na₂SO₄ and solvent was removed (rotatory evaporator). The crude mixture was purified by silica gel chromatography (2:1 hexanes/Et₂O) to afford **10a**, 102 mg (64%). Alkynes **9b-g** were hydroborated in a similar manner to produce the known ketones **10a-g** and **11a**, **11b**²⁵, and **11c-g**. Isomer ratios were established by ¹H NMR assay.

Representative Procedure for the Synthesis of Monoalkyl Potassium Trifluoroborate Salts (19).

Py•BH₃ (0.2 mL, 2 mmol) was added to a flask containing 5 mL of CH₂Cl₂ and the reaction was cooled to 0 °C. Next, I₂ (253 mg, 1 mmol) was added in portions. After gas evolution had ceased, styrene (**18a**) (0.23 mL, 2mmol) was added and the reaction was allowed to stir at room temperature for 4 h. The CH₂Cl₂ was removed and MeOH (3 mL) and KHF₂ (4.5M) (5 mL) was added to give a heterogeneous mixture that was stirred for 30 min. The solution was diluted with CH₃CN (5 mL), solvent was removed (rotatory evaporator), and the crude product was placed under vacuum (30 minutes). CH₃CN (10 mL) was then added to the crude mixture, the resulting suspension was filtered, and the filtrate was concentrated (rotatory evaporator). The residue was then dissolved in acetone (5 mL) and ether (1 mL) was slowly added until precipitation occurred. The resulting precipitate was isolated via filtration and dried to provide the desired product **19a**, 356 mg (84%), identical according to NMR comparisons with commercial **19a**.

Potassium alkyltrifluoroborate salts **19b-e** were prepared in a similar manner. The known **19b**, **19c**, and **19e** were identified by comparison with published data,²³ and **19d** was characterized as follows:

Potassium 2-Phenylethyltrifluoroborate (19d): ESMS for C₉H₁₁BF₃; M⁻, *m/z*= 187.1; IR (neat, cm⁻¹) 2952, 2892, 2460, 1623; 500 MHz NMR (CD₃CN, ppm) δ 7.25 (5H, m), 2.81 (1H, m), 1.21 (3H, d J= 4.5 Hz), 0.48 (2H, m); ¹³C NMR (125.7 MHz, CD₃CN, ppm) δ 148.7, 128.2, 126.3, 125.7, 40.6, 24.6, 13.7; ¹⁹F NMR (CD₃CN, ppm) δ -138.3.

An attempt to use **19a** as prepared above for palladium-catalyzed coupling with 2-bromotoluene according to ref. 12b gave no product, so a variation of the KHF₂ step and workup method was evaluated. The solid residue after initial removal of CH₂Cl₂ was stirred with KHF₂ (1 g), CH₃CN

(15 mL) and water (2 mL) for 30 min. After solvent removal (aspirator; vacuum pump, 30 min), the residue was extracted with CH₃CN (10 mL), filtered, and the filtrate was evaporated. The residue was washed with CH₂Cl₂ to remove traces of pyridine. The solid residue (69%) was then warmed to 50 °C with 5 mL CH₃CN, the suspension was filtered, and the filtrate was allowed to cool. The resulting precipitate was collected to afford **19a** (32%) having the same NMR spectrum as before. This material did undergo palladium catalyzed coupling with 2-bromotoluene according to the procedure of ref. 12b to afford (2-CH₃C₆H₄)CH₂CH₂Ph, 66% yield. However, the solid obtained in 69 % yield, did not undergo coupling, suggesting the presence of an unknown contaminant that interferes with the palladium coupling procedure.

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