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OPPI BRIEF

A Convenient Synthesis of 3-Butenylamine

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In connection with a project in our laboratory we required an efficient, safe, and scalable synthesis of 3-butenylamine (4-amino-1-butene) (**1**). Although such homoallylic amines are well known,[1] syntheses of the parent 3-butenylamine are sparse. Galand[2] reported the hydrogenation of allyl cyanide with zinc-copper couple to give **1** in unspecified yield. Roberts[3] described a three-step sequence to give **1** *via* benzenesulfonation of 3-butenyl alcohol (allylcarbinol), displacement of benzenesulfonate with azide ion, and reduction of the azide with lithium aluminum hydride to give **1** in 61.5% from the benzenesulfonate. Both Roberts[3] and later Brown[4] noted that lithium aluminum hydride reduction of 3-butenonitrile (allyl cyanide) was unsatisfactory, perhaps due to the acidity of the α-hydrogens of the nitrile. Brown[5] nicely circumvented this obstacle by employing the less basic aluminum hydride, and was able to reduce 3-butenonitrile to **1** in 55% yield. However, we were only able to obtain **1** in 8–12% yield using aluminum hydride. Courtois[6] reported the synthesis of **1** in 40% yield *via* the reaction of allyl aluminum bromide with (methoxymethyl)-*N*,*N*-bis(trimethylsilyl) amine.

Contrary to these reduction protocols for accessing **1**, we envisaged a direct amination strategy making use of the venerable Gabriel amine synthesis[7] in combination with a Mitsunobu reaction.[8] Our successful synthesis of **1** using this methodology is shown in *Scheme 1*. Thus, reaction of commercially available 3-butenyl alcohol (**2**) with phthalimide (**3**), triphenylphosphine, and diethyl azodicarboxylate (DEAD) gave the expected phthalimide **4** in 85% yield. Cleavage of **4** with hydrazine yielded 3-butenylamine (**1**) in 54% yield following distillation.

In conclusion, we report a simple, convenient, and potentially scalable preparation of 3-butenylamine in two steps that avoids the use of air-sensitive hydride and aluminum reagents and possibly explosive azide intermediates.

Experimental Section

General

Melting points were determined in open capillaries with either a Mel-Temp Laboratory Devices apparatus or a Buchi 510 apparatus and are uncorrected. The elemental analysis

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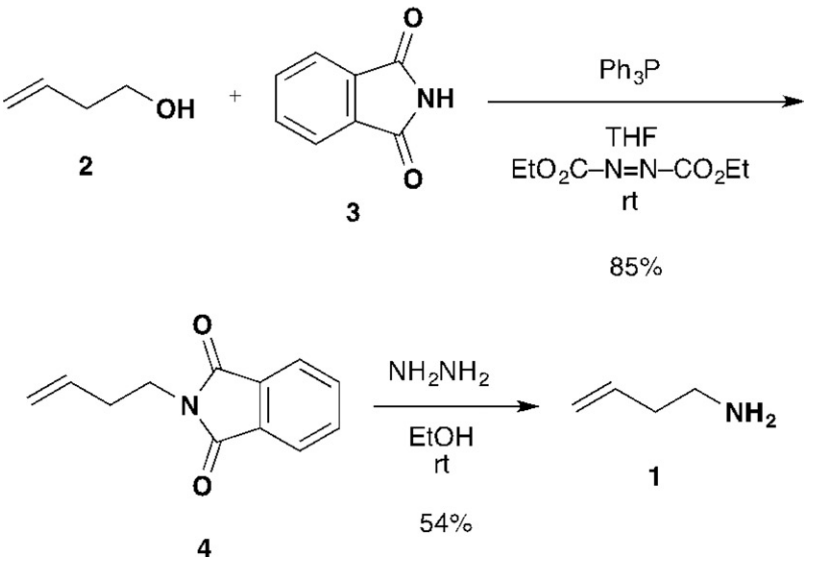
Scheme 1



Scheme 1

was performed by Atlantic Microlabs, Atlanta, GA. Infrared spectra were recorded on a Perkin-Elmer 599 instrument. ^{13}C NMR and 300 MHz ^{1}H NMR spectra were recorded on a Varian XL-300 multinuclear Fourier transform NMR. Mass spectra were obtained on a Finnigan 4023 GC/MS system. Flash chromatography was carried out using Silicycle ultra pure silica gel 60A (230-400 mesh). Tetrahydrofuran (THF) was distilled from Na/benzophenone.

N-(3-Butenyl)phthalimide (4)

To a solution of 3-buten-1-ol (**2**) (2.00 g, 0.0277 mol; Fluka), phthalimide (**3**) (4.08 g, 0.0277 mol), and triphenylphosphine (7.27 g, 0.0277 mol) in THF (65 mL) was added dropwise over 15 min a solution of diethyl azodicarboxylate (4.82 g, 0.0277 mol) in THF (10 mL) with ice bath cooling to maintain the reaction temperature at 20–25 °C. The resulting solution was stirred at room temperature for 40 h and then concentrated *in vacuo*. Flash chromatography with ether-hexane (1:4) furnished 4.75 g (85%) of **4** as analytically pure, colorless needles: mp 53–54.5 °C; IR (KBr) 3950 (m), 2940 (m), 1775 (s), 1695 (vs), 1620 (s), 1435 (s), 1400 (s), 1365 (s), 1340 (s), 1300 (m), 1260 (m), 1180 (m), 1060 (s), 970 (m), 940 (s), 870 (m), 805 (m), 720 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.00–7.50 (m, 4H), 6.20–5.30 (m, 1H), 5.26–4.83 (m, 2H), 3.78 (t, $J = 7$ Hz, 2H), 2.46 (q, $J_1 = J_2 = 7$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 168.0, 134.3, 133.6, 131.8, 122.9, 117.2, 37.0, 32.6; MS *m/e* (relative intensity) 201 (M^+, 6), 161 (10), 160 (100), 133 (8), 105 (10), 104 (14), 85 (6), 83 (6), 77 (32), 76 (26), 75 (8), 71 (11), 69 (11), 57 (35), 56 (14), 55 (20), 51 (15), 50 (21).

Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.62; H, 5.51; N, 6.96. Found: C, 71.59; H, 5.53; N, 6.92.

3-Butenylamine (1)

A solution of **4** (2.00 g, 9.94 mmol) in 95% EtOH (10 mL) was treated with 85% hydrazine hydrate (0.78 g, 0.016 mol) and stirred overnight at room temperature. The resulting suspension was treated with 10% aqueous HCl (10 mL) and the precipitated material was filtered off and washed with H_2O (2 x 5 mL). The combined filtrate and washings were concentrated to a small volume, filtered again, and then diluted with H_2O (15 mL) and extracted with ether (2 x 25 mL). The aqueous acid layer was basified with 50% aqueous NaOH and extracted with ether (3 x 25 mL). The combined ethereal extracts were dried (K_2CO_3) and distilled at atmospheric pressure through a Vigreux column (10 cm) to give 0.58 g (54%) of amine **1** (bp 75–77 °C), (lit.[5] bp 76–77 °C); IR (neat) 3370 (s), 3300 (s), 3085 (m), 2980 (s), 2935 (s), 2880 (s), 1640 (m), 1435 (m), 1060 (m), 990 (m), 910 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.15–5.40 (m, 1H), 5.23–4.80 (m, 2H), 2.85–2.60 (m, 2H), 2.40–2.00 (m, 2H), 1.36 (s, 2H).

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