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Synthesis of Novel class of (*E*)-*N*-(2-nitro-3-phenylallyl)aniline using H_2SO_4 Derived from Baylis–Hillman Adduct

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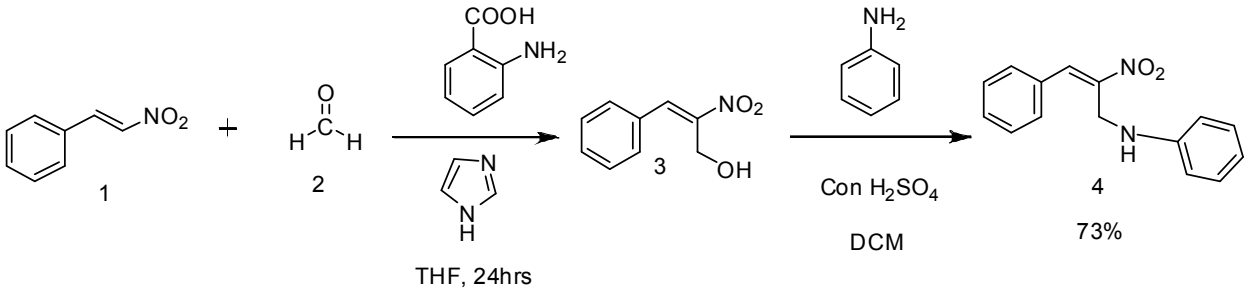
Abstract : In conclusion, we have successfully developed for the synthesis of bromo and it is deriveties of Baylis–Hillman adducts derived from nitroolefins. This novel class of bromo and amine derivatives can be utilized as building blocks for wide variety of organic compounds. We also developed a facile method for the transformation of these bromides into an interesting and novel class of trisubstituted triallylamines which are core unit of dendrimers, thus demonstrating the synthetic utility of the bromo derivatives of the Baylis–Hillman adducts. Hence this novel protocol opens new opportunities for the preparation of libraries of wide variety of new molecules.
Keywords : Baylis-Hillman adducts, paraformaldehyde imidazole and anthranilic. (*E*)-*N*-(2-nitro-3-phenylallyl)aniline.

Introduction

The importance and growth of the Baylis-Hillman reaction, to a large extent, can also be attributed to the enormous applications of the Baylis-Hillman adducts in synthetic chemistry[1-3]. The Baylis-Hillman adducts containing a minimum of three functional groups in close proximity are valuable substrates for various organic reactions and transformations[4-7]. Thus the Baylis-Hillman adducts have been successfully employed as substrates in a number of named and unnamed reactions, such as, Friedel-Crafts reaction, Johnson-Claisen rearrangement, hydrogenation reaction, nucleophilic reactions, hydroxylation, Heck reaction etc[8,9]. The Baylis-Hillman adducts have also been systematically used as valuable synthons or starting materials for synthesis of representative natural products, unnatural products, and bioactive molecules. Also efforts have been successfully made for the transformation of the Baylis-Hillman adducts and their derivatives into various trisubstituted alkenes with defined stereochemistry and heterocyclic and carbocyclic molecules of biological importance. The Baylis-Hillman reaction, which involves the coupling of activated vinyl compounds with electrophiles under the catalytic influence of a tertiary amine, gives rise to adducts, so called Baylis-Hillman adducts, with a new stereocenter and has proven to be a very useful carbon-carbon bond-forming method in the synthesis of highly functionalized molecules.1 As the activated vinyl compounds, various compounds have been used in the Baylis-Hillman reaction including acrylates, acrylonitrile, vinyl ketones, vinyl sulfones and acrylamides[10-15]. However, among the activated vinyl compounds acrylamide has not been used much for the synthesis of the corresponding Baylis-Hillman adducts due to its sluggish reactivity.[11-22] .We planned to

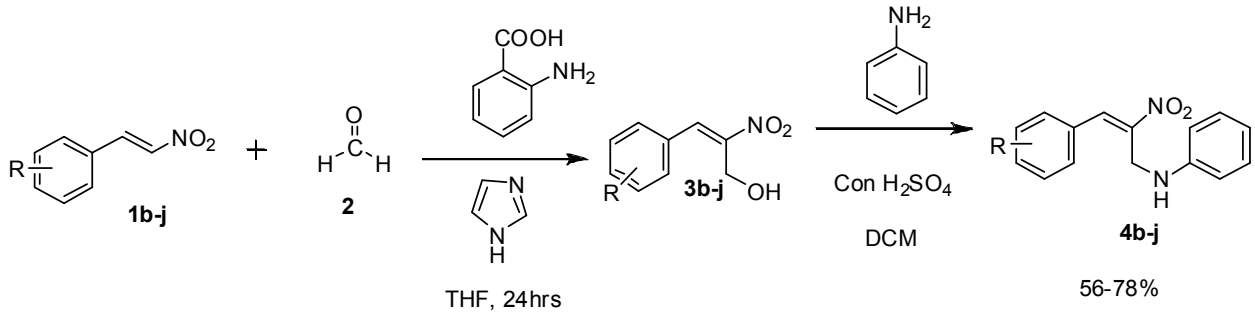
synthesize (*E*)-*N*-(2-nitro-3-phenylallyl)aniline. To demonstrate our approach, we first selected nitro alcohol a derivative of the Baylis–Hillman (BH) adduct obtained via the reaction of benzaldehyde and nitromethan, as the starting material for the generation of the required precursor (3) with a view to obtain the desired compound. The best results were obtained when BH alcohol 3 was treated with amine in the presence of Con H_2SO_4 in DCM for 1 h at room temperature to provided successfully the desired (*E*)-*N*-(2-nitro-3-phenylallyl)aniline 4 in 73% yield after work up followed by column chromatography.

Scheme-1



The ^{1}H NMR spectrum of the compound 4 showed the CH_2 protons as a singlet at δ = 4.51 ppm, The amine proton appears as broad singlet at δ = 2.57 ppm, the olefinic proton as a singlet at δ = 8.25 ppm, and the aromatic protons as multiplets in the regionn of δ = 7.43–7.56 ppm.

Scheme-2



R = 2-Me, 4-Me, 4-Et, 4-*i*-Pr, 4-OMe, 3,4-di-OMe, 3,4-OCH_2O-, 4-F, 2-Cl, 4-Cl

Encouraged by this result, we utilized a variety of (*E)*-2-nitro-3-phenylprop-2-en-1-ol (3b-j) as starting materials for the synthesis of (*E*)-*N*-(2-nitro-3-phenylallyl)aniline. Treatment of the compounds 3b-j with aniline under Con H_2SO_4 successfully led to the desired (4b-j) in 56-78% yields.

Conclusion

In conclusion, we have successfully developed for the synthesis of (*E)*-2-nitro-3-phenylprop-2-en-1-ol and it is deriveties of Baylis–Hillman adducts derived from nitroolefins. This novel class of (*E)*-2-nitro-3-phenylprop-2-en-1-ol and amine derivatives can be utilized as building blocks for wide variety of organic compounds. Hence this novel protocol opens new opportunities for the preparation of libraries of wide variety of new molecules

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(*E*)-*N*-(2-nitro-3-phenylallyl) aniline: (4) Typical Procedure

To a stirred solution of *(E)*-2-nitro-3-phenylprop-2-en-1-ol **3**, (2.94g, 4 mmol) in DCM and con H_2SO_4 (.5 mL), aniline (2.03 mL) was added at r.t... The mixture was stirred well at r.t. for about 1 h. On completion of the reaction (TLC analysis), the mixture was poured into H_2O and the aqueous layer was extracted with EtOAc (3 × 10mL). The combined organic layers were washed with brine (10 mL) and concentrated. The crude product thus obtained was purified by column chromatography (EtOAc–hexanes) to provide 4 (6.34g, 73%) yield.

IR (KBr): 3429, 1657, 1525, 1324, cm^{-1}

^1H NMR (300 MHz, CDCl3): δ = 2.57 (bs, 1H) 4.51 (s, 2 H), 7.43–7.56 (m, 10 H), 8.25 (s, 1 H). ^{13}C NMR (75 MHz, CDCl3): δ = 57.64, 110.13, 128.17, 130.24, 131.23, 131.46, 138.89, 144.51, 145.37, 147.61, 148.71

MS: *m/z* = 254 (M+). Elemental Analysis for $C_{15}H_{14}N_2O_2$ Calculated: C, 70.85; H, 5.55; N, 11.02; Found: C, 70.83; H, 5.57; N, 11.03;

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