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Synthesis of (*E*)-4-nitro-5-phenylpent-4-en-2-one derived from Baylis–Hillman Adduct

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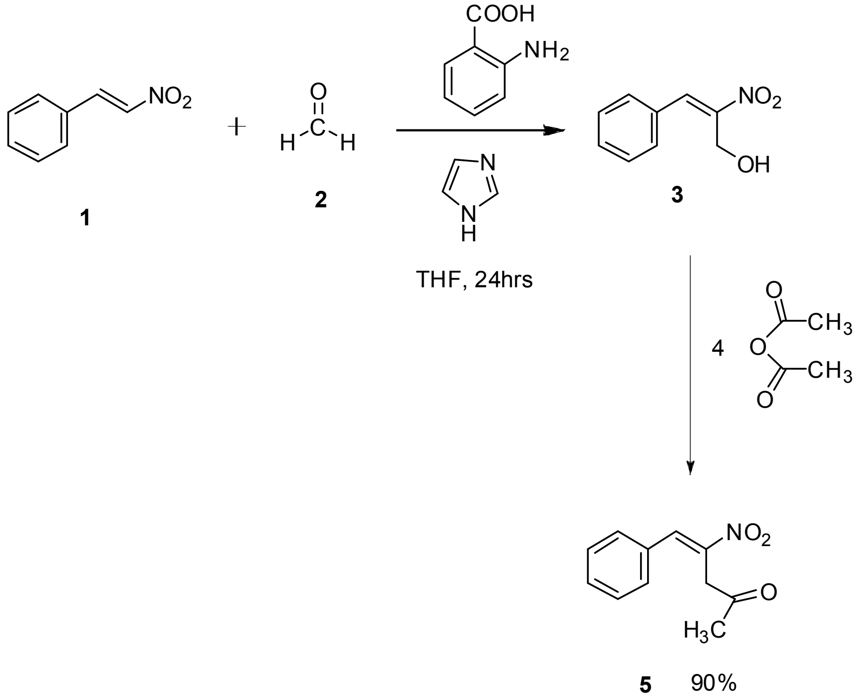
Abstract : Development of a new protocol for the preparation of (*E)*-4-nitro-5-phenylpent-4-en-2-one *via* Friedel-Crafts reaction using Baylis-Hillman adducts. The Friedel-Crafts reaction of the Baylis-Hillman adducts derived from nitroolefins mediated by concentrated acetic anhydride thus providing a simple synthesis (*E)*-4-nitro-5-phenylpent-4-en-2-one derivatives. This methodology also opens new opportunity to make library of compounds.

Keywords : Baylis-Hillman adducts, paraformaldehyde imidazole and anthranilic. (*E*)-4-nitro-5-phenylpent-4-en-2-one.

Introduction

The Baylis-Hillman reaction is a well known coupling reaction of aldehydes and activated alkenes catalyzed by tertiary amines or tertiary phosphines.[1-5] The Baylis-Hillman reaction is an emerging carbon-carbon bond forming reaction producing an useful class of highly functionalized molecules and the adducts have been utilized for various organic transformations [6-10].The Baylis-Hillman adducts have been effectively utilized as synthons in several named reactions such as Heck reaction, Diels-Alder reaction, Aldol condensation, Claisen rearrangement, Friedel-Crafts reation[11-15] etc. The Friedel-Crafts reaction is one of the most widely used reactions in organic chemistry whose applications in academic as well as industrial fields have been well documented[16,17].The Friedel-Crafts reaction on Baylis-Hillman adducts was initially reported by Basavaiah et al, following his pionioring work various reports have appeared in connection with Friedel-Crafts chemistry on Baylis-Hillman adducts Reaction of nitroalkenes with bromomethyl acrylate in the presence of DBU affords nitro dienes Conjugate addition of DBU to a nitroalkene gives a nitronate anion that in the presence of acrylate reacts as previously described, leading to ammonium salt that upon elimination of DBU affords nitro diene. (Hetero)aryl-R-nitro-enals (densely combine a (hetero)aromatic ring, a CdC double bond, a nitro group and a formyl group to form an extended π system, where three functionalities of demonstrated utility in synthesis, namely, a (hetero)arylvinyl unit, an unsaturated nitroalkene, and intimately coexist sharing a common double bond. Attractive as this combination of structural and functional features could be, (hetero)aryl-R-nitro-enals have nevertheless been essentially overlooked and their properties and synthetic potential unexplored[18-20].We decided to prepare the nitro alcohol compound derived from nitroolefins, which will open new avenues for synthetic transformations. In continuation of our research interest in the field of Baylis–Hillman chemistry, we planned to synthesize (*E)*-4-nitro-5-phenylpent-4-en-2-one. 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 bromide 3 was treated with anhydride in THF for 1 h at room temperature to provided successfully the desired (*E*)-4-nitro-5-phenylpent-4-en-2-one 5 in 95% yield after work up followed by column chromatography.

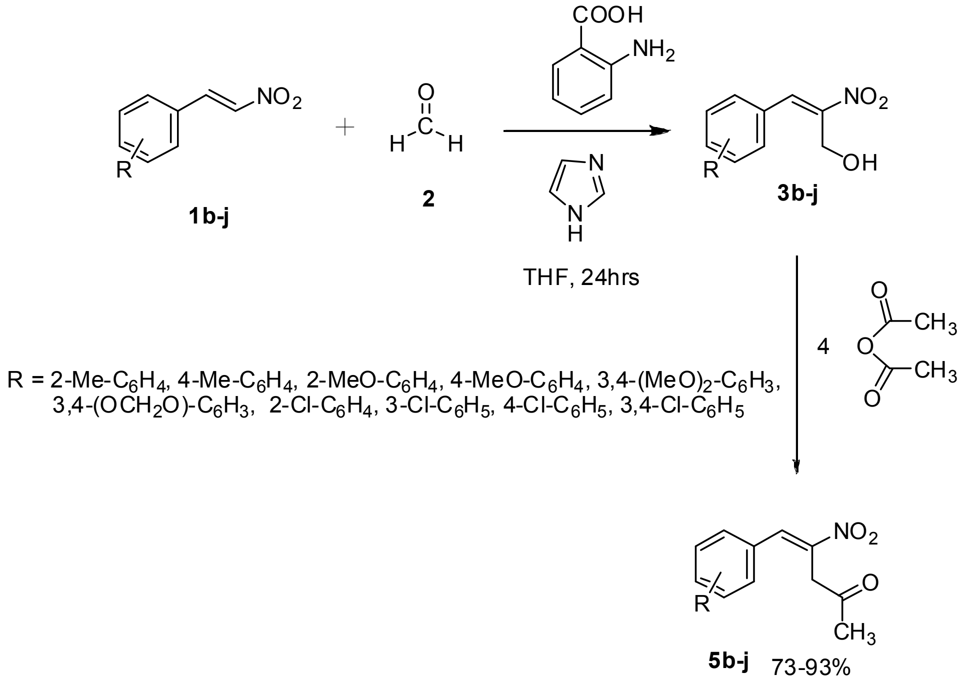
Scheme 1



The ^1H NMR spectrum of the compound **5** showed the CH_2 protons as a singlet at $\delta = 4.32$ ppm, The OAc proton appears as singlet at $\delta = 3.72$ ppm, the olefinic proton as a singlet at $\delta = 7.93$ ppm, and the aromatic protons as multiplets in the regionn of $\delta = 7.51–7.65$ppm.

Encouraged by this results we prepared variety of Baylis-Hillman adducts and successfully transformed them into their corresponding (*E*)-4-nitro-5-phenylpent-4-en-2-one derivatives **5b-j,** according to scheme 2.

Scheme 2



Conclusion

In conclusion, we have successfully developed for the synthesis of nitroalcohol and it is deriveties of Baylis–Hillman adducts derived from nitroolefins. This novel class of (*E*)-4-nitro-5-phenylpent-4-en-2-one can be utilized as building blocks for wide variety of organic compounds. We also developed a facile method for the transformation of these nitro alcohol an interesting and novel class of (*E*)-4-nitro-5-phenylpent-4-en-2-one which are core unit of dendrimers, thus demonstrating the synthetic utility of the acetate derivatives of the Baylis–Hillman adducts. Hence this novel protocol opens new opportunities for the preparation of libraries of wide variety of new molecules.

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(*E)*-4-nitro-5-phenylpent-4-en-2-one (5)Typical Procedure

To a stirred solution of nitro alcohol , (.36g, 2 mmol) in THF (15 mL), acetic anhydride (1.03 mL) was added at r.t... The mixture was stirred well at r.t. for about 2 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 (1.34g, 90%) yield.

IR (KBr): 3423, 1652, 1527, 1321, cm^{-1}

^{1}H NMR (300 MHz, CDCl3): δ = 3.72 (s, 3H) 4.32 (s, 2 H), 7.51–7.65 (m, 5 H), 8.27 (s, 1 H). ^{13}C NMR (75 MHz, CDCl3): δ = 57.61, 110.14, 128.15, 131.23,144.51, 147.62, 176.89.

MS: *m*/*z* = 205 (M+). Elemental Analysis for $C_{11}H_{11}NO_3$Calculated: C, 64.38; H, 5.40; N, 6.83; Found: C, 64.36; H, 5.42; N, 6.84;

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