SYNTHESIS OF TRIS (4-((E)-2-NITRO-3-(PHENYLAMINO) PROP-1-ENYL) PHENYL) AMINE DERIVED FROM BAYLIS–HILLMAN ADDUCT

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ABSTRACT

In conclusion, we have successfully developed for the synthesis of bromo and it is derivatives 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.


INTRODUCTION

The Morita-Baylis-Hillman reaction (MBH) is a base catalyzed carbon–carbon bond formation process which involves electron-deficient alkenes and aldehydes. Nucleophilic bases such as amines and phosphines2, 3 are necessary since the commonly accepted mechanism4 involves an initial conjugate addition of the catalyst to the activated alkene leading to a zwitterionic enolate, whose reaction with the aldehyde is followed by a reversible elimination of the base to generate the product. Different types of activated alkenes such as cyclic and acyclic, unsaturated ketones, aldehydes, esters, amides, nitriles, and alkenes substituted by nitro groups, sulfoxides, sulfones, sulfonic acids, or phosphonate and amine derivatives have been used in the MBH reaction. Nitroalkenes are widely known as reactive electrophilic substrates suitable for conjugate additions as well as cycloadditions reactions, but when involved in Baylis–Hillman processes, these compounds can act as allyl-type nucleophiles.

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.1–5 (Hetero)aryl-R-nitro-R-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 R,-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-R-enals have nevertheless been essentially overlooked and their properties and synthetic potential unexplored.6–9

This idea, we decided to prepare the bromo compound derived from nitroolefins, which will open new avenues for synthetic transformations.16–20 In continuation of our research interest in the field of Baylis–Hillman chemistry,15–20 we planned to synthesize tris(4-[(E)-2-nitro-3-(phenylamino)prop-1-enyl]phenyl)amine.

To demonstrate our approach, we first selected tris (4-[(E)-3-bromo-2-nitroprop-1-enyl]phenyl)amine a bromo 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 aniline in the presence of K₂CO₃ in THF for 1 h at room temperature to provided successfully the desired tris(4-[(E)-3-bromo-2-nitroprop-1-enyl]phenyl)amine 4 in 95% yield after work up followed by column chromatography.

Scheme 1

The 1H NMR spectrum of the compound 4 showed the CH₂ protons as a singlet at δ = 4.52 ppm, The amine proton appears as broad singlet at δ = 2.52 ppm, the olefinic proton as a singlet at δ = 7.97 ppm, and the aromatic protons as multiplets in the region of δ = 7.53–7.62 ppm.
CONCLUSION

In conclusion, we have successfully developed for the synthesis of bromo and its derivatives 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.

ACKNOWLEDGMENTS

We thank AMET University for the financial support. We also thank University of Madras for the NMR facility. Indian institute of Technology, Chennai for IR, and Mass Spectra.

tris(4-((E)-2-nitro-3-(phenylamino)prop-1 enyl)phenyl)amine: (4)Typical Procedure

To a stirred solution of tris(4-((E)-3-bromo-2-nitroprop-1-enyl)phenyl)amine 3, (2.94g, 4 mmol) in THF (15 mL), aniline (2.03 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 H₂O 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 (7.34g, 95%) yield.

IR (KBr): 3429, 1657, 1525, 1324, cm⁻¹

¹H NMR (300 MHz, CDCl₃): δ = 2.52 (bs, 1H) 4.52 (s, 2 H), 7.53–7.62 (m, 27 H), 8.23 (s, 1 H).

¹³C NMR (75 MHz, CDCl₃): δ = 57.61, 110.14, 128.15, 130.24, 131.23, 131.46, 138.89, 144.51, 145.37, 147.62.

MS: m/z = 773 (M+). Elemental Analysis for C₄₅H₃₉N₇O₆: Calculated: C, 69.84; H, 5.08; N, 12.67; Found: C, 69.83; H, 5.07; N, 12.68.

REFERENCES


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