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SYNTHESIS OF 3-(3-METHOXY-2-NITRO-3-PHENYLPROPYL)-9H-CARBAZOLE FROM FRIEDEL-CRAFTS REACTION

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ABSTRACT

A new method for the Synthesis of 3-(3-methoxy-2-nitro-3-phenylpropyl)-9H-carbazole *via*Friedel-Crafts reaction through nitroolefins derivatives. This the first type Friedel-Crafts reaction of the nitroolefin derived from Bayliss-Hillman mediated by con. H_2SO_4 thus giving a simple synthesis of substituted olefin derivatives. Although various electron deficient alkenes such as α,β-unsaturated carbonyl compounds, nitriles, sulfones and phosphonates have been employed as substrates in the nitroolefin reaction. This technology also opens new opportunity to make application of compounds.

Keywords: Friedel-Crafts reaction, nitroolefin, carbazole, Methanol, K_2CO_3, nitro methane, methane sulphonic acid, benzaldehyde.

INTRODUCTION

The reaction is a well-known coupling reaction of aldehydes and activated olefins catalyzed by tertiary amines or tertiary phosphines.[1-5] The B-H reaction is a new carbon-carbon bond forming reaction producing a functional class of well-applied molecules and the adducts have been employ for various organic transformations.[6-10] The Baylis-Hillman adducts have been successfully utilized as synthons in numerous named reactions for example Heck reaction, Diels-Alder reaction, Aldol condensation, Claisen rearrangement, Friedel-Crafts reation[11-15] etc. The Friedel-Crafts reaction is one of the most commonly used reactions in organic chemistry whose applications in intellectual as well as industrial fields have been well documented.[16, 17] The Friedel-Crafts reaction on Baylis-Hillman reaction was to begin with reported by Basavaiah et al, following his pioneering work different reports have appeared in association with Friedel-Crafts chemistry on Baylis-Hillman reaction. The nitroaldol or Henry reaction is a standard aldol-type reaction connecting an aldehyde and a nitroolefin.[18-20]

EXPERIMENTAL

3-(3-methoxy-2-nitro-3-phenylpropyl)-9H-carbazole

To a stimulated solution of (*E*)-3-(2-nitro-3-phenylallyl)-9H-carbazole (**1**) (0.52g, 2 mmol) in MeOH (10 mL) and K_2CO_3 (0.28g, 2 mmol) was added at RT. The reaction mixture was motivated at RT for 2 h. After achievement of reaction, the mixture was moved into the water and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The collective organic layer was washed with brine (20 mL), and dried in excess of anhydrous Na_2SO_4 and the combined organic layer was evaporated. The plain product thus obtained was purified by column chromatography (5%, EtOAc/hexanes) to supply the preferred compound 3-(3-methoxy-2-nitro-3-phenylpropyl)-9H-carbazole (**3a**) in excellent yield (67%) as a colorless solid.

3-(3-methoxy-2-nitro-3-phenylpropyl)-9H-carbazole (3a) Yield: 65 %, IR (KBr): 3458, 1635, 1572, 1526. $cm^{-11,}$ HNMR: δ 2.65 (d, 2H), 2.97 (s, 3H),3.27 (dd, 1H), 4.36 (d, 1H), 7.31-7.92 (m, 12H), 10.34

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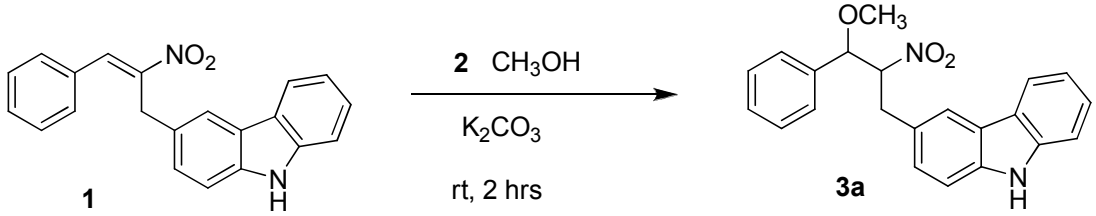
(bs, 1H). ^{13}CNMR ($CDCl_3$, 75 MHz): δ 17.24, 19.31, 30.77, 57.16, 125.85, 126.92, 130.23, 120.31, 130.84, 131.42, 131.96, 132.25, 133.15, 134.62, 135.23, 135.55.Mass (m/z): 360 (M^+) Anal. Calcd for $C_{22}H_{20}N_2O_3$C, 73.32; H, 5.59; N, 7.77Found C, 73.35; H, 5.60; N, 7.75.

RESULTS AND DISCUSSION

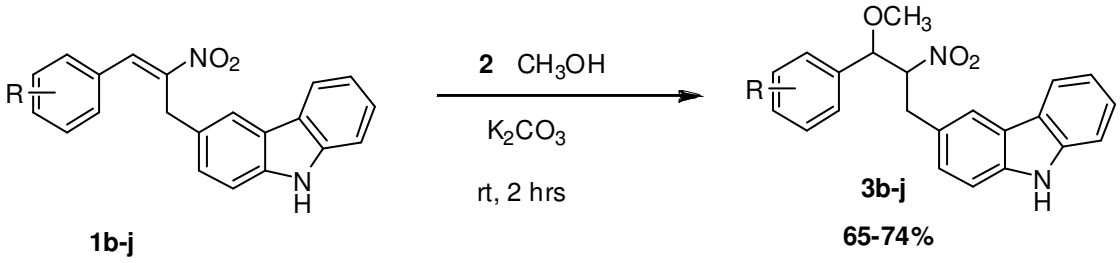
To implement our idea, first we have selected the Baylis-Hillman adduct (*E*)-2-nitro-3-phenylprop-2-en-1-ol (**1**) consequent from benzaldehyde and nitro methane as starting material for the Friedel-Crafts reaction. The greatest results were obtained when the addition of a catalytic amount of methane sulphonic acid to the solution of a B.H adduct in 9H-carbazole at room temperature, productively led to the preferred product (*E*)-3-(2-nitro-3-phenylallyl)-9H-carbazole The fresh carbazole product was treated with methanol and K_2CO_3at room temperature led to the beloved anticipated 3-(3-methoxy-2-nitro-3-phenylpropyl)-9H-carbazole**3a** in excellent yield (Scheme-1).



Scheme-1

The synthesized carbazole creation **3a** was characterized by ^{1}H &^{13}C NMR spectral analyses. The ^{1}H NMR spectrum of compound **3a** showed one doublet for the aryl methyl protons at δ 2.65 and CH-NO_2 appear as a double doublet at δ 3.27. The methoxy proton was experimental as a singlet at δ 2.97 and $CHOCH_3$ acetylene protons came out as a doublet at δ 4.36. The aromatic protons appeared as multiplets in the section of δ 7.31-7.92 and the NH proton appeared as a broad singlet at δ 10.34.

Expectant by this results we organized a variety of carbazole and successfully transformed them into their consequent methoxy derivatives **3b-j,** according to Scheme-2.



R = 2-Me 4-Me 2-MeO, 4-MeO, 3,4-$(MeO)_2$
3,4-(OCH_2O), 2-Cl-,3-Cl, 4-Cl, 3,4-$(Cl)_2$

Scheme-2

CONCLUSION

In conclusion, this technology represents the Friedel-Crafts reaction of the Baylis-Hillman reaction derived from nitroolefins. A simple synthesis of 3-(3-methoxy-2-nitro-3-phenylpropyl)-9H-carbazole derivatives. Variety of carbazole was used for the first time in Nucleophilic replacement reaction on Baylis-Hillman adducts derived from nitro olefins. This technology also opens new opportunity to make a library of compounds.

Table-1: Synthesis of 3-(3-methoxy-2-nitro-3-phenylpropyl)-9H-carbazole from friedel-crafts reaction

S.No.	Carbazole	Methyloxy	Yield
1a	C_6H_5	3a	67
1b	2-Me	3b	69
1c	4-Me	3c	70
1d	2-MeO	3d	60
1e	4-MeO	3e	68
1f	3,4-$(MeO)_2$	3f	71
1g	3,4-(OCH_2O)	3g	70
1h	2-Cl	3h	68
1i	3-Cl	3i	67
1j	4-Cl	3j	68

[a]All reactions were accepted with 2 mmol scale of carbazole (1a-j),[b]All products gave acceptable IR, ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz), mass spectral data and elemental analyses. [c]Yields of the clean products (3a-j) obtained following column chromatography (silica gel, (3a-j) 5% EtOAc in hexanes

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