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MICROWAVE ASSISTED SYNTHESIS OF 3-PHENYLCOUMARINS UNDER SOLVENT FREE CONDITIONS USING TRITON-B ADSORBED ON FLYASH AS SOLID SUPPORT

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Abstract

An eco-friendly efficient procedure for the synthesis of 3-phenylcoumarins is described by the reaction of 2-hydroxybenzaldehydes with benzylcyanides in presence of Triton-B adsorbed on flyash as solid support using microwave radiations under solvent free conditions.

Keywords: 2-Hydroxybenzaldehydes, benzylcyanides, triton-B, 3-phenylcoumarins, microwave irradiation, solvent free reaction.

Introduction

Coumarins constitute an important class of compounds because of their vast range of applications such as anticoagulants[i], anti-HIV agents[ii,iii], anthelmintics, hypnotics, insecticides[iv-vi] etc. These compounds have also been used as additives in food, perfumes, cosmetics and laser dyes[vii]. 3-Phenylcoumarins, a sub class of naturally occurring coumarins, have been synthesized by Perkin condensation[viii] of salicylaldehydes and phenylacetic anhydrides in presence of potassium salt of phenylacetic acid. Due to harsh reaction conditions, required compounds are obtained in low yields. The reaction has also been modified in various ways including use of $PhPOCl_2/Et_3N$ as condensing agent[ix] and condensation[x] of acetothiomorpholide with 2-hydroxybenzaldehyde in presence of $POCl_3$ to get the required compounds in 30-50% yield. 3-Phenylcoumarins have also been obtained by condensation of 2-hydoxybenzaldehydes with phenylacetic anhydride in benzene-aqueous potassium carbonate biphase medium using phase transfer catalysis[xi]. In a recent report[xii], 3-phenylcoumarins have been prepared by a two step process involving initial esterification of 2-hydroxybenzaldehydess in presence of $POCl_3$-pyridine followed by cyclization of 2-arylacetoxysalicylaldehyde with KOH in pyridine. The methods listed above suffer from the disadvantage like use of hazardous solvents and poor yields.

Results and Discussion

Herein we wish to report a new highly efficient synthesis of 3-phenylcoumarins making use of benzylcyanide rather than phenylacetic acid or its derivatives. Salicylaldehydes on condensation

with benzylcyanide in presence of triton-B adsorbed on flyash as solid support using microwave radiations have yielded the required 3-phenylcoumains in 80-90% yield.

Validity of the above procedure was shown by preparing differently substituted 3-phenylcoumarins and identity of the compounds was confirmed from their IR and ^{1}H NMR spectra.

Table 1. Synthesis of 3-phenylcoumarins

Compounds	R_1	R_2	R_3	R_4	R_5	Time (sec)	Yield (%)	M.P. (^oC)	Lit. M.P. (^oC)
I	H	H	H	H	H	20	89	138-39	142[xiii]
II	H	H	CH_3	H	H	30	85	143-44	146-47[xiii]
III	H	H	Cl	H	H	25	84	165-66	193-94[xiv]
IV	H	H	Br	H	H	25	86	98-99	187-88[xv]
V	H	OCH_3	H	H	H	30	87	122-23	126[xvi]
VI	H	OCH_3	H	OCH_3	H	35	88	178	180[xvii]
VII	H	H	H	H	OCH_3	30	84	140	142-44[xviii]
VIII	H	H	CH_3	H	OCH_3	30	79	143-44	140-41[xix]
IX	H	H	Cl	H	OCH_3	35	85	187-88	190[xix]
X	H	H	Br	H	OCH_3	30	84	199-200	201-02[xix]
XI	H	OCH_3	H	H	OCH_3	25	92	185-86	186[xx]
XII	H	OCH_3	H	OCH_3	OCH_3	30	90	160-61	163-65[xxi]

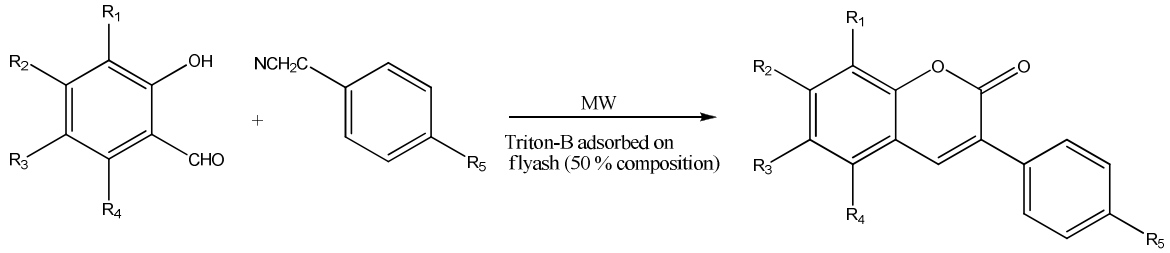
Experimental

Melting points were determined in open capillary tubes and are uncorrected. IR spectra were recorded on Perkin-Elmer spectrum BX-series FTIR and ^{1}H NMR spectra on Bruker Avance II 400 MHz NMR spectrometer using tetramethylsilane as internal standard. The reaction was carried out in domestic microwave oven (Samsung, Model No. CE118KF, output energy 900W, frequency 2450 MHz) using 30% power for all experiments.

General Experimental Procedure

A mixture of *o*-hydroxybenzaldehyde (5 mmol), benzylcyanide/*p*-methoxybenzylcyanide (5 mmol) and the base i.e. triton-B adsorbed on flyash (50% composition) was prepared by adding few drops of acetone, air dried and was subjected to microwave radiations. Completion of the reaction was checked on TLC and reaction mixture was dissolved in chloroform. Organic layer was filtered to remove flyash and solvent was distilled off from filterate. The residue was washed with water, dried and recrystallized from ethanol to get the desired product.

Scheme 1. Synthesis of 3-phenylcoumarins



Spectral data of compounds (I-XII)

I. IR (KBr): 1715 cm^{-1} (C=O)
^1H NMR ($CDCl_3$): δ 7.05-7.60 (m, 9H, Ar-H), 7.65 (s, 1H, H-4).
II. IR (KBr): 1720 cm^{-1} (C=O)
^1H NMR ($CDCl_3$): δ 2.28 (s, 3H, CH_3), 7.20-7.60 (m, 8H, Ar-H), 7.65 (s, 1H, H-4).
III. IR (KBr): 1720 cm^{-1} (C=O)
^1H NMR ($CDCl_3$): δ 7.30-7.65 (m, 8H, Ar-H), 7.90 (s, 1H, H-4).
IV. IR (KBr): 1720 cm^{-1} (C=O)
^1H NMR ($CDCl_3$): δ 7.25-7.60 (m, 8H, Ar-H), 7.80 (s, 1H, H-4).
V. IR (KBr): 1720 cm^{-1} (C=O)
^1H NMR ($CDCl_3$): δ 3.80 (s, 3H, OCH_3), 6.70-7.65 (m, 8H, Ar-H), 7.70 (s, 1H, H-4).
VI. IR (KBr): 1713 cm^{-1} (C=O)
^1H NMR ($CDCl_3$): δ 3.90, 3.95 (2s, 3H each, 2×OCH_3), 6.40-7.70 (m, 7H, Ar-H), 8.30 (s, 1H, H-4).
VII. IR (KBr): 1720 cm^{-1} (C=O)
^1H NMR ($CDCl_3$): δ 3.80 (s, 3H, OCH_3), 6.85-7.70 (m, 8H, Ar-H), 7.75 (s, 1H, H-4).
VIII. IR (KBr): 1718 cm^{-1} (C=O)
^1H NMR ($CDCl_3$): δ 3.90 (s, 3H, OCH_3), 6.90-7.70 (m, 7H, Ar-H), 7.80 (s, 1H, H-4).
IX. IR (KBr): 1720 cm^{-1} (C=O)
^1H NMR ($CDCl_3$): δ 3.95 (s, 3H, OCH_3), 6.95-7.75 (m, 7H, Ar-H), 7.85 (s, 1H, H-4).
X. IR (KBr): 1713 cm^{-1} (C=O)
^1H NMR ($CDCl_3$): δ 3.90 (s, 3H, OCH_3), 6.90-7.70 (m, 7H, Ar-H), 7.80 (s, 1H, H-4).
XI. IR (KBr): 1715 cm^{-1} (C=O)
^1H NMR ($CDCl_3$): δ 3.85, 3.90 (2s, 3H each, 2×OCH_3), 6.85-7.65 (m, 7H, Ar-H), 7.75 (s, 1H, H-4).
XII. IR (KBr): 1718 cm^{-1} (C=O)
^1H NMR ($CDCl_3$): δ 3.90 (s, 6H, 2×OCH_3), 3.95 (s, 3H, OCH_3), 6.74-7.60 (m, 6H, Ar-H), 8.20 (s, 1H, H-4).

Conclusion

Present method is rapid, efficient one step process for the synthesis of 3-phenylcoumarins. Moreover, it avoids the use of toxic solvents at any stage of the reaction.

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