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Eco-Friendly and Recyclable Silica Gel : An Efficient Catalyst for the Synthesis of 14-Aryl-14H-Dibenzo[a,j] Xanthenes

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Abstract*: A simple and highly effective approach has been established for synthesizing 14-aryl-14H-dibenzo[a,j]xanthene derivatives through the condensation of substituted benzaldehyde and β-naphthol. The reaction was catalyzed by Silica gel(Silica gel and carried out using both microwave irradiation and conventional methods. The key benefits of this method include a shorter reaction time, high product yield, and environmentally friendly features, such as the use of a non-toxic, cost-effective, and recyclable heterogeneous catalyst, eliminating the need for hazardous solvents and toxic catalysts.*

Keywords: Dibenzo[a,j]xanthene, Titanium dioxide, Aldehyde, β-Naphthol, Green synthesis.

I. INTRODUCTION

Heterocyclic compounds remain a crucial area of research in organic chemistry due to their broad spectrum of biological applications (1). Among them, xanthenes, particularly benzoxanthenes, have gained significant interest because of their diverse biological and therapeutic properties, including: Antiviral activity (2) Antibacterial effects (3) Anti-inflammatory properties (4) Use in photodynamic therapy (PDT) (5) Function as antagonists of the paralyzing action of zoxazolamine (6) Xanthenes are also found in natural pigments isolated from various plant species (7). Beyond biological applications, benzoxanthenes are utilized in: Dye industries (8) Laser technology (9) Various synthetic approaches have been explored to obtain xanthenes and benzoxanthenes, including: Cyclodehydration reactions (10) Trapping of benzynes with phenols (11) Alkylation of heteroatoms (12)Specifically, 14H-dibenzo[a,j]xanthenes and their analogs have been synthesized using: β-Naphthol with formamide (13) β-Naphthol with carbon monoxide (14)

II. CHALLENGES IN CLASSICAL METHODS

Conventional synthesis of benzoxanthene derivatives often requires:

Prolonged reaction times ,Harsh reaction conditions,Large quantities of organic solvents Unsatisfactory yields (15-18) These limitations necessitate the development of improved synthetic methods that are more efficient and environmentally friendly.

Role of Silica gel(Silica gel as a Catalyst

Silica gel(Silica gel has proven effective in various organic transformations, including: Biginelli reaction (19a) Beckmann rearrangement (19b) Synthesis of dihydropyrazines (19c) Quinoxalines synthesis (19d) Piperazines formation (19e) Recent synthesis of 2,4,5-triarylimidazoles (19f) the advantages of TiO_2 in organic synthesis include: Ease of handling ,Eco-friendlines, Mild reaction conditions,Cost-effectiveness, Recyclability ,High catalytic activity as a heterogeneous Lewis acid

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Given these benefits, TiO_2 was selected as the catalyst for synthesizing 14-aryl-14H-dibenzo[a,j]xanthenes via the condensation of substituted benzaldehydes and β-naphthol.

Green Chemistry and Microwave-Assisted SynthesisGreen chemistry aims to develop environmentally sustainable chemical processes.

Microwave irradiation has been recognized as an efficient heating method in organic synthesis (20a). Key benefits of microwave-assisted organic synthesis (MAOS) include: Drastic reduction in reaction time Lower energy consumption High product yields Simple and convenient experimental procedures (20b)

Therefore, microwave irradiation was employed as a greener alternative for the synthesis of 14H-dibenzo[a,j]xanthene derivatives.

III. EXPERIMENTAL SECTION

General Information

The synthesized compounds were previously known, and their physical and spectral data matched those of authentic samples. All reagents and substituted benzaldehydes were procured from commercial suppliers and used without further purification. Melting points were measured using an open capillary apparatus and are uncorrected. Spectral Analysis:IR spectra: Recorded using a Perkin-Elmer FT spectrophotometer (KBr disc method). NMR spectra: Recorded on a Varian 500 MHz spectrometer using $CDCl_3$ as a solvent and TMS as an internal standard. Reaction progress was monitored via thin-layer chromatography (TLC).

General Procedure for the Synthesis of 14-Aryl-14H-Dibenzo[a,j]Xanthenes

Microwave-Assisted Method

Reaction Setup: A Borosil beaker (50 mL) was used. Substituted benzaldehyde (1 mmol), β-naphthol (2 mmol), and TiO_2 (1 mol%) were mixed. Reaction Execution: The reaction mixture was stirred using a glass rod. Irradiation was performed in a microwave oven at 720 W for the time specified in Workup Process: After completion, the mixture was diluted with 15 mL ethyl acetate and stirred. The solid catalyst (Silica gel was separated by filtration and washed with ethyl acetate.The catalyst was further purified by washing with 10 mL hot acetone, dried, and reused.The organic layer was dried over anhydrous Na_2SO_4.The solvent was evaporated under reduced pressure to obtain pure products (3a–l) in high yields.

Conventional Heating Method

Reaction Setup: A 50 mL round-bottom flask was used. A mixture of substituted benzaldehyde (1 mmol), β-naphthol (2 mmol), and TiO_2 (1 mol%) was prepared.

Reaction Execution:The mixture was heated in an oil bath at 100°C for the time specified in Workup Process: The product was isolated and purified following the same procedure as described in the microwave method .

IV. RESULTS AND DISCUSSION

Continuing our research efforts toward developing simple, efficient, and high-yielding synthetic methods for benzoxanthenes (21) and various heterocyclic compounds (22), we report an improved and convenient approach for the condensation of substituted benzaldehydes with β-naphthol using Silica gel(Silica gel as a catalyst (Figure 1). Optimization of the Reaction Conditions

Initial Reaction Trials The reaction between benzaldehyde and β-naphthol was conducted using Silica gel(1 mol%) as a catalyst under two different conditions: Microwave irradiation (720W power) Conventional oil bath heating at 100°C Under microwave conditions, the reaction was completed in just 50 seconds with an excellent conversion rate of 90%.Using the conventional heating method, the reaction required 20 minutes and yielded 88% conversion.

Effect of Catalyst Amount Increasing the catalyst concentration beyond 1 mol% did not result in any significant improvement in reaction time or yield.This indicates that 1 mol% of TiO_2 is sufficient to efficiently catalyze the condensation reaction under both microwave and conventional heating conditions.

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Influence of Substituents on the Reactivity

The reaction was performed using benzaldehydes with both electron-withdrawing and electron-donating groups. It was observed that: Electron-donating groups enhanced the reactivity, leading to faster reactions and higher yields. Electron-withdrawing groups resulted in relatively longer reaction times and slightly lower yields. This trend suggests that the electronic nature of substituents significantly affects the efficiency of benzoxanthene formation. Characterization of the Products

The obtained products were characterized using: Physical constants (melting point) Comparison with authentic samples Spectroscopic techniques (IR and NMR analysis) Catalyst Reusability and Industrial Relevance

Importance of Catalyst Reusability

Reusability is a crucial factor for scaling up the reaction for industrial applications, as it reduces costs and aligns with green chemistry principles.

Evaluation of Catalyst Recycling The recyclability of TiO_2 was tested in a model reaction.The catalyst was recovered, washed, and reused for up to four cycles without any noticeable reduction in its catalytic activity.The results (Table 2) confirm that TiO_2 remains highly efficient even after multiple reuses.

Synthesis of 14-aryl-14H-dibenzo [a,j] Xanthenes catalyzed Titanium dioxide[a]

S.No	Entry	R	MW	Conventional	M.P.(^{0}C)			
			Time (sec)	Yield (%)	Time (min)	Yield (%)	Found	
1	3a	H	90	85	30	85	181	181
2	3b	4-Cl	90	85	20	83	280	280
3	3c	3-F	90	85	20	84	267	267
4	3d	2-Cl	90	85	15	85	216	216
5	3e	4-NO_2	90	85	10	82	314	314
6	3f	2-NO_2	90	85	10	83	293	293
7	3g	3-NO_2	90	85	15	82	212	212
8	3h	4-OMe	90	85	15	83	203	203
9	3i	4-Me	90	85	25	87	226	226
10	3j	4-OH	90	85	20	82	141	141
11	3k	2-OMe, 4-OH	90	85	25	82	169	169
12	3l	2-OMe, 5-OMe	90	85	15	84	168	168
					30	82		
S.No	Entry	1	2	3	4	5		
1	Cycle[b]	Fresh	First reuse	Second reuse	Third reuse	Fourth reuse		
2	Yield (%)[c]	90	90	89	88	88		

Recycling of Silica gelfor the 14-aryl-14H-dibenzo [a,j] xanthenes[a]

V. CONCLUSION

A facile and high-yielding method for synthesizing 14-aryl-14H-dibenzo[a,j]xanthenes was successfully developed.The microwave-assisted method proved to be more efficient than conventional heating, offering shorter reaction times and higher yields.Silica gel(Silica gel proved to be an effective, reusable, and eco-friendly catalyst for this transformation.The methodology is simple, cost-effective, and scalable, making it suitable for industrial applications.

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