Eggshell or Ti-Al/Al₂O₃ Nano-Composite: An Efficient, Rapid and Green Synthesis of 4-H-Benzo[b]Pyrans as Important Pharmaceutical Compounds in Water at Ambient Temperature

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4-H-Benzo[b]pyrans and their derivatives are of considerable interest due to their pharmacological activities, such as spasmolytic, diuretic, anti coagulant, anti-cancer, anti-ancaphylactia activity. In addition, they have shown to act as cognitive enhancers, for the treatment of neurodegenerative disease, including Huntington's disease, Alzheimer's disease, amyotrophic lateral Sclerosis, AIDS associated dementia and Down's syndrome as well as for the treatment of Schizophrenia and myoclonus. Thus a synthetic interest has that included methodological improvements of the original reaction conditions.

A variety of reagents were employed to catalyze these reactions. Many of these methods involve expensive reagents, acidic conditions, long reaction times, low yields, use of excess of reagents/catalyst and use of toxic organic solvents and complicated work-up methods. According to the principle of safe chemistry, synthetic method should be designed to use substances that exhibit little or no toxicity to human health and environment. In this regard, we wish to report herein, a new, simple, mild and ecofriendly method for the synthesis of 4-H-Benzo[b]pyrans via a one-pot three-component tandem Knoevonagel-cyclo condensation reaction using eggshell as a natural catalyst or Ti-Al/Al₂O₃ nano-composite as a new heterogeneous catalyst with high catalytic activity and reusability in very short reaction time in water base media.

A mixture of aromatic aldehyde, malononitrile and dimedone in H₂O at the ambient temperature, were stirred thoroughly in the presence of a catalytic amount of Ti-Al/Al₂O₃ nano-composite (0.01g) or powder eggshell (0.1 g) to afford the 4-H-Benzo[b]pyrans in excellent yields. After completion of the reaction, the reaction mixture was washed with warm ethanol (3 x 30 mL). After cooling, the crude products were precipitated. Pure 4-H-Benzo[b]pyran was obtained in high yields without any use of more purification.

It was interested the Ti-Al/Al₂O₃ nano-composite or eggshell be reused in three cycles. So, the presented procedure is very simple and clean, safe, environmentally friendly due to use water as green solvent, use of cheap, available and high effective catalysts, more efficient and easier work-up than reported methods. To the best of our knowledge, this procedure provides the first example of catalytic application of eggshell in organic reactions.

![Chemical structure](image)

Catalyst: Ti-Al/Al₂O₃ nano-composite or eggshell

REFERENCES