Int. J. Chem. Sci.: 6(4), 2008, 1800-1803

MONTMORILLONITE K 10 CLAY CATALYZED MICROWAVE SYNTHESIS OF MIKANECIC ACID DIESTERS FROM BAYLIS-HILLMAN ADDUCTS

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ABSTRACT

Montmorillonite K 10 clay catalyzed synthesis of mikanecic acid diesters from Baylis-Hillman adducts is reported under microwave irradiation.

Key words: Montmorillonite K 10 clay, Mikanecic acid diesters, Baylis-Hillman adducts.

INTRODUCTION

Microwave–induced Organic Reaction Enhancement (MORE) chemistry reactions are extremely fast, cleaner than conventional reactions and lead to higher atom economy (less chemical waste)[1-3]. Because of short time requirement, ease of workability and eco-friendliness, microwaves provide an alternative green approach. It can be termed as 'e-chemistry' because it is easy, effective, economical and eco-friendly and is believed to be a step towards Green Chemistry[4-8]. Recently, use of inorganic solid supports[9] as catalysts has been developed for solvent-free reactions resulting in milder conditions and easy experimental procedures. Clay catalyzed organic reactions[10] are gaining importance owing to their inexpensive nature and special catalytic attributes in heterogeneous reactions.

Construction of quaternary carbon center has been one of the challenging and attractive areas in synthetic organic chemistry, because a number of biologically active natural products contain such structural sub-units[11-14].

4-Vinyl-1-cyclohexene-1,4-dicarboxylic acid (Mikanecic acid) is a terpenoid dicarboxylic acid, and it has attracted our attention owing to its special feature of having

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vinylic quaternary carbon center in a functionalized six membered cyclic system. Mikanecic acid was isolated in 1936 by Manske[15] from the products of alkaline hydrolysis of the alkaloid Mikanoidine obtained from *Senecio mikakioides otto*. Many works have appeared regarding the history[16], characterization and synthesis of racemic Mikanecic acid[17]. The reaction of acetaldehyde with suitable acrylates in the presence of DABCO afforded Baylis-Hillman adducts[18-24] **(1a-1c)** which on treatment with Montmorillonite K 10 clay led directly to the formation of mikanecic acid diesters **(2a-2c)**, through Diels-Alder type self-dimerization of 1,3-butadiene-2-carboxylate (Table 1).

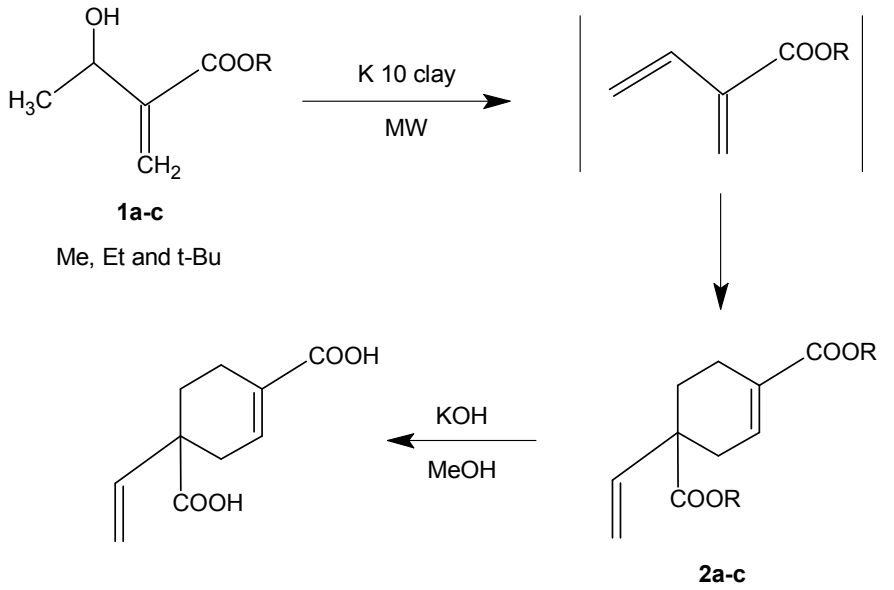

Table 1 : Synthesis of mikanecic acid diesters[a,b]

Substrate	Reaction time (minutes)	product	Yield[c] (%)
1a	3	2a	52
1b	5	2b	58
1c	4	2c	49

[a]All reactions were carried out in 0.01 mole scale of Baylis-Hillman adduct mixed with montmorillonite K 10 clay (1 g) and the reaction mixture was subjected to microwave irradiation at 600 W for specified time. After completion of the reaction (monitered by TLC), the reaction mixture was cooled to room temperature. Methanol (30

mL) was added to the reaction mixture, the clay is filtered off, and the filtrate was digested with cold water. The solid separated was filtered and recrystallized from methanol to give products, which were characterized.

[b]Satisfactory IR, NMR spectral data were obtained.

[c]Isolated yield after column chromatography (2% ethylacetate in hexane).

This method represents an indirect way of performing Diels-Alder reaction involving the same molecule as diene and dienophile generated *in situ;* thus, demonstrating the synthetic potentiality of the Baylis-Hillman reaction[25-31] leading to the synthesis of racemic mikanecic acid.

ACKNOWLEDGEMENTS

One of the authors (SR) thanks the Chairman, Vice-Charman, Principal and Dean, RMK College of Engineering and Technology, Chennai for their constant support and encouragement. Two authors (KS and RA) are grateful to the Principal and Managing Board of Islamiah College, Vaniyambadi, Vellore for their encouragement. The authors also thank the RSIC, CDRI, Lucknow and RSIC, IIT, Chennai for the use of their instrumentation facilities.

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Accepted : 01.11.2008