



K₂CO₃ CATALYZED USING SYNTHESIS OF MIKANECIC ACID DIESTERS FROM BAYLIS HILLMAN ADDUCTS FORMED USING TiCl₄

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ABSTRACT

A novel method for the synthesis of a terpenoid, Mikanecic acid diesters from Baylis-Hillman adducts, (alkyl-3-hydroxy-2-methylenepranoates by treatment with aldehyde react with various acrylates catalyzed by TiCl₄) which on treatment with potassium carbonate led directly to the formation of Mikanecic acid diesters, through Diels-Alder type self-dimerization of 1,3-butadiene-2-carboxylate is reported using with potassium carbonate. The product is obtained in good yield.

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INTRODUCTION

Synthetic organic chemistry is one of the most developing, expanding and successful branches of Science. During the last fifteen years, synthetic organic chemistry has seen enormous growth (Reshetova and Ustynyuk 2004; Zhao *et al.*, 2004; Zoupy *et al.*, 1998; Gangadasu *et al.*, 2006), not only in terms of development of new methodologies for construction of carbon-carbon and carbon-hetero atom Bonds but also in terms of development of new reagents, catalysts, strategies, transformations and Technologies often involving the concepts of atomeconomy. Construction of quaternary carbon center have been one of the challenging and attractive areas in synthetic areas in synthetic organic chemistry, because a number of biologically active natural products contain such structural sub-units (Martin 1980; Romo and Mayer 1991; Angelo *et al.*, 1992; Das *et al.*, 2004). 4-vinyl-1-cyclohexene-1,4-dicarboxylic acid (Mikanecic acid) is a terpenoid dicarboxylic acid, has attracted our attention owing to its special feature of having vinylic quaternary carbon center in functionalized six membered cyclic system. Mikanecic acid was isolated in 1936 by Manske (Manske 1936) from the products of alkaline hydrolysis of the alkaloid Mikanoidine obtained from *Senecio mikakioides otto*. Many works have appeared regarding the history (Fuji 1993), characterization and synthesis of racemic Mikanecic acid (Sydnes *et al.*, 1975), K₂CO₃, catalyzed (Swati Ojha *et al.*, 2007; Singh and Batra

2008) organic reactions regaining importance owing to their inexpensive nature and special catalytic attributes in heterogeneous reactions. In view of this and in continuation of our ongoing program to develop environmentally benign protocols, we, herein, report, K₂CO₃, catalyzed synthesis of Mikanecic acid diesters in fairly good, K₂CO₃, yields.

Numerous chemical and physical methods have been developed to accelerate the Baylis-Hillman reaction, overcoming traditional slow reaction rates (weeks or months). Among Lewis acids, TiCl₄ has been successfully utilized to promote the Baylis-Hillman reaction in the presence of Lewis base catalysts. The reaction of acetaldehyde with suitable acrylates in the presence of, TiCl₄ afforded Baylis-Hillman adducts (Singh and Batra 2008; Tadashi Kataoka *et al.*, 2000; Jingsong *et al.*, 2003; Alan R. Katritzky *et al.*, 2008; Firouzabadi and Jafarpour 2008) (1a-1c) which on treatment with (0.2 equiv.) led directly to the formation of Mikanecic acid diesters (2a-2c), through Diels-Alder type self-dimerization of 1,3-butadiene-2-carboxylate (Scheme 1, Table 1, Fig. 1) which on hydrolysis gave Mikanecic acid.

Experimental

Melting points were determined in an open capillary tube with a Buchi melting point apparatus and are uncorrected. Elemental analyses were carried out using Perkin-Elmer 240C CHN-analyzer. Spectra were recorded on a Perkin Elmer IR spectrophotometer. ¹H-NMR spectra was run in (CDCl₃) solvent at 200 MHz on a NMR spectrophotometer (chemical

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