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International Journal of Current Research Vol. 6, Issue, 05, pp.6580-6581, May, 2014 INTERNATIONAL JOURNAL OF CURRENT RESEARCH

RESEARCH ARTICLE

$\label{eq:K2CO_3} CATALYZED USING SYNTHESIS OF MIKANECIC ACID DIESTERS FROM BAYLIS HILLMAN ADDUCTS FORMED USING TICL_4$

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ARTICLE INFO

ABSTRACT

Article History: Received 09th February, 2014 Received in revised form 16th March, 2014 Accepted 18th April, 2014 Published online 20th May, 2014

Key words:

Mikanecic acid, TiCl₄, K₂Co₃, Baylis-Hillman adducts Diels-Alder type reaction. A novel method for the synthesis of a terpenoid, Mikanecic acid diesters from Baylis-Hillman adducts, (alkyl-3-hydroxy-2-methylenepropanoates by treatment with aldehyde react with various acrylates catalyzed by $TiCl_4$) 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-1cyclohexene-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. Mikanecicacid 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 Mikanecicacid (Sydnes et al., 1975), K₂Co₃, catalyzed (Swati Ojha et al., 2007; Singh and Batra

2008) organic reactions aregaining 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, K_2Co_3 , catalyzed synthesis of Mikanecic acid diesters in fairly good, K_2Co_3 yields.

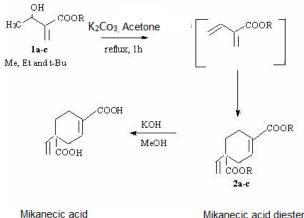
Numerous chemical and physical methods have been developed to accelerate the Baylis-Hillman reaction, overcoming traditional slow reaction rates (weeks or months). Among Lewis acids, TiCl₄ has been successfully utilized to promote the Baylis-Hillman reaction in the presence of Lewis base catalysts. The 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-Aldertype 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 CHNanalyzer. Spectra were recorded on a Perkin Elmer IRspectrophotometer. 1H- NMR spectra was run in (CDCl3) solvent at 200 MHz on a NMRspectrophotometer (chemical

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shifts in δ ppm). 13CNMR Spectra were run in (CDCl3) solvent at 50 MHz on a NMR spectrophotometer (chemical shifts in δ ppm).

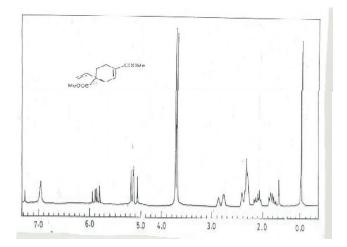


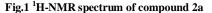
Mikanecic acid diester

Scheme 1: Synthesis of Mikanecic acid diesters

Table 1. Synthesis of Mikanecic acid diesters a,b	Table 1.	. Synthesis	of Mikanecic	acid diesters a,b
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Substrate	Reaction time	Product	Yield (%)
1a	1h	2a	55
1b	1h	2b	56
1c	1h	2c	59





General Procedure for the Synthesis of Mikanecic Acid

The experimental procedure is very simple and straight forward. As shown in Scheme 1, the reaction Can be carried out with 0.01 mole scale of Baylis-Hillman adduct in Methanol in the presence of, K_2Co_3 (0.2 equiv.) were refluxed for 1 hr. After completion of their action (monitored by TLC), usual workup and column chromatographic purification (hexane/ether, 5:1) gave products, which were characterized by IR, NMR spectral data. The results obtained are very much consistent with literature report. The spectral and analytical data of the compound 2a:

IR (neat): 1712, 1640 cm-1; 1H-NMR (200 MHz, CDCl3): δ 1.71-1.90 (1H, m), 2.08-2.16 (1H, m), 2.28-2.44 (3H, m), 2.72-2.92 (1H, m), 3.69 (3H, s), 3.73 (3H,s), 5.12-5.20 (2H, m), 5.78-5.98 (1H, m), 6.97 (1H, m); Anal. Calcd for C12H16O4: C, 64.28; H, 7.14 %.Found: C, 63.34; H, 6.92%.

Spectral data for Mikanecic acid: IR (KBr): 1690, 1640 cm-1; 1H-NMR (200 MHz, CDCl3): & 1.67-2.82(6H, m), 5.02-5.29 (1H, m), 5.75-6.04 (1H, m), 6.85(1H, m), 12.42 (2H, s, br); 13C-NMR (50 MHz,CDCl3): 8 21.58, 29.09, 31.70, 46.53, 114.55, 129.31, 136.78, 140.29, 167.66, 175.21; EI-MS: m/z 196 (M·); Anal. Calcd for C10H12O4: C, 61.22; H, 6.12 %. Found: C, 57.48; H, 6.50 %.

Conclusion

As a conclusion, this paper described a facile synthesis of Mikanecic acid diesters from Baylis-Hillman adducts, (alkyl-3hydroxy-2-methylenepropanoates) which on treatment with K₂Co₃ led Directly to the formation of Mikanecic acid diesters, through Diels-Alder type self-dimerization of 1, 3-Butadiene-2carboxylate. The method represented here is an indirect way of performing the Diels-Alder type reaction involving the same molecule can act as diene and dienophile thus utilizing the synthetic potentiality of Baylis-Hillman adducts.

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