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Potassium Iodide Catalyzed Synthesis of Mikanecic Acid Diesters from Baylis Hillman Adducts.

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ABSTRACT

Mikanecic acid diesters from Baylis-Hillman adducts, which on treatment with potassium Iodide 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.
Key Words: Mikanecic acid, KI, Baylis-Hillman adducts Diels-Alder type reaction.

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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 [1-4], 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 [5-8].

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 [9] from the products of alkaline hydrolysis of the alkaloidMikanoidine obtained from *Senecio mikakioides otto*.Many works have appeared regarding the history [10], characterization and synthesis of racemic Mikanecicacid [11].

KI catalyzed [12,13] 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, KI catalyzed synthesis of Mikanecic acid diesters in fairly good yields.
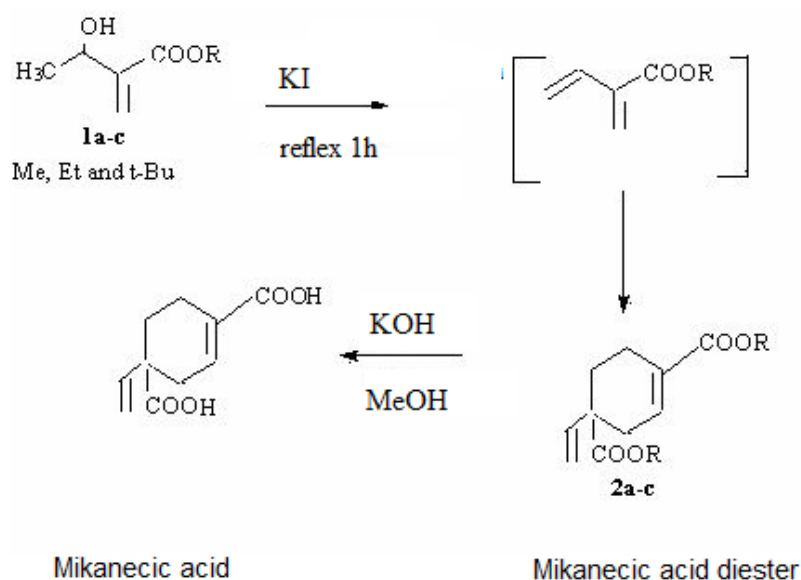

Scheme 1: Synthesis of Mikanecic acid diesters

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, TiCl$_4$ 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 , TiCl$_4$ afforded Baylis-Hillman adducts [13-17] (**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.

Table 1: Synthesis of Mikanecic acid diesters a, b, c

Substrate	Reaction time	Product	Yield (%)
1a	1h	2a	50
1b	1h	2b	52
1c	1h	2c	54
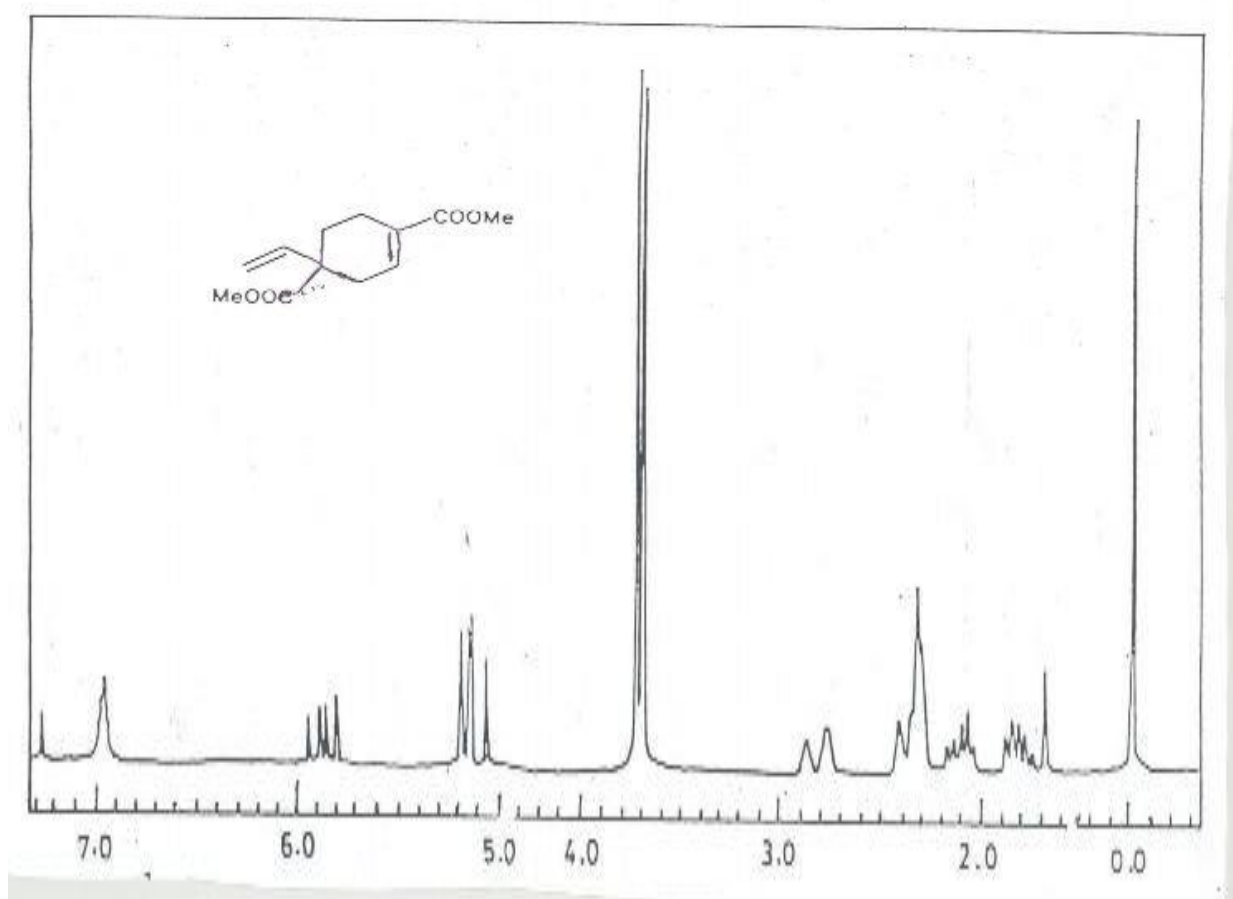
Figure 1: ^{1}H-NMR spectrum of compound 2a

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 IRspectrophotometer. 1H-NMR spectra was run in (CDCl3) solvent at 200 MHz on a NMRspectrophotometer (chemical shifts in δ ppm).

General Procedure for the Synthesis of Mikanecic Acid

As shown in Scheme 1, the reaction Can be carried out with 0.01 mole scale of Baylis-Hillman adduct in acetone in the presence of KI (0.2 equiv.) were refluxed for 1 hr. After completion of their action (monitored by TLC), usual workup and column chromatographic purification (hexane/ether, 5:2) 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): 1715, 1645 cm-1; 1H-NMR (200 MHz, CDCl3): δ 1.76-1.95 (1H, m), 2.09-2.19 (1H, m), 2.27-2.45 (3H, m), 2.76-2.93 (1H, m), 3.68 (3H, s), 3.76 (3H,s), 5.12-5.27 (2H, m), 5.78-5.95 (1H, m), 6.95 (1H, m); Anal. Calcd for $C_{12}H_{16}O_4$: 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): δ 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): δ 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 %.

CONCLUSIONS

As a conclusion, this paper described a facile synthesis of Mikanecic acid diesters from Baylis-Hillman adducts, which on treatment with KI, led Directly to the formation of Mikanecic acid diesters, through Diels-Alder type self-dimerization of 1, 3-Butadiene-2-carboxylate. 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 potentialityof Baylis-Hillman adducts.

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