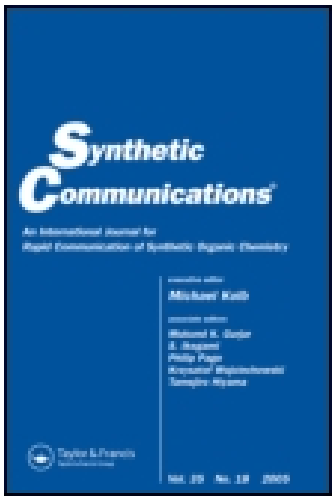

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A FACILE ONE-POT SYNTHESIS OF METHYL(2E)-2-METHYLALK-2-ENOATES FROM BAYLIS-HILLMAN ADDUCTS UNDER MICROWAVE IRRADIATION

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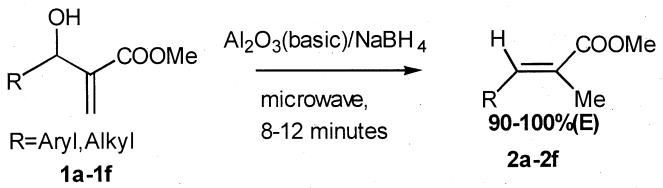
ABSTRACT

A facile procedure for the synthesis of the title compound is described.

In connection with our research on the Baylis-Hillman reaction,[1–3] I herein report a simple and efficient methodology for the stereoselective synthesis of methyl(**2E**)-2-methylalk-2-enoates from Baylis-Hillman adducts using basic Al_2O_3 and $NaBH_4$ under microwave irradiation.[4–6] The synthetic scheme employed is outlined below. The experimental result is given in the table 1.

The [**E**]-selectivity in these reactions can be possibly explained on the basis of a mechanism proposed by our research group.[7] Although I did not



Scheme 1.

Table 1. Synthesis of Methyl(2E)-2-methylalk-2-enoates[a,b]

Substrate	R	Power (%)	Time[d] (minutes)	T[f]/°C	Product	Yield (%)[c]	*E*:*Z*[e]
1a	C_6H_5	10	10	165	**2a**[9]	90	95:05
1b	4-MeC_6H_4	10	10	129	**2b**	80	95:05
1c	4-ClC_6H_4	10	10	131	**2c**	83	100:0
1d	2-ClC_6H_4	10	10	100	**2d**	81	95:05
1e	2,4-ClC_6H_4	10	08	170	**2e**	81	94:06
1f	n-propyl	10	12	173	**2f**	72	90:10

[a]All reactions were carried out on a 5 mM scale of the alcohol (**1a–1f**) with basic Al_2O_3 (5 mM) and $NaBH_4$ (5 mM) under microwave irradiation.
[b]Satisfactory spectral data were obtained for all compounds.
[c]Isolated yields of the product after column chromatography (1% EtOAc in hexane).
[d]The reaction completed within the time specified in the table.
[e]Stereochemical assignments and isomeric purities were based on difference in chemical shifts and integration ratios of olefinic protons in ^1H NMR analysis.
[f]Final temperature reached by the reaction mixture.

encounter any accident during these studies, I recommend extreme caution for reactions on larger scale.

In summary I have developed a facile and practical method for the stereoselective synthesis of methyl(***2E***)-2-methylalk-2-enoates using a solventless system, basic Al_2O_3 and $NaBH_4$ with 3-hydroxy-2-methylenealkanoates under microwave irradiation.

EXPERIMENTAL

General

All the required Baylis-Hillman products were obtained by the reaction of the corresponding aldehydes with methyl acrylate in the presence of a catalytic amount of DABCO according to the literature procedure.[8]

General Procedure

$NaBH_4$ (0.189 g, 5 mM) and basic Al_2O_3 (0.509 g, 5 mM) is thoroughly mixed with alcohol **1a–1f** (5 mM) in a test tube and placed in microwave oven and irradiated for the time specified in the **Table 1**. At the end of exposure to microwaves, the reaction mixture was cooled to room

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temperature, monitored on TLC (hexane: EtOAc, 8:2, v/v), the product is extracted into methylene chloride (20 mL). Removal of solvent under reduced pressure and purification on silica gel using 1% EtOAc in hexane afforded the required products **2a–2f** in good yields with high (**E**)-stereoselectivity (**Table 1**).

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9. **Spectral data obtained for 2a**: ^{1}H NMR ($CDCl_3$): δ 2.13 (s, 3H), 3.63 & 3.83 (2s, 3H), 6.71 & 7.69 (2s, 1H), 7.19–7.42 (m, 5H). The peak at δ 7.69 was assigned to the olefinic proton of the [**E**]-isomer and a very minor peak at δ 6.71 was assigned to the olefinic proton of the [**Z**]-isomer in very small amounts (6%); ^{13}C NMR ($CDCl_3$): δ 13.72, 127.68, 128.47, 128.73, 129.89, 135.64, 141.21, 174.56; IR (KBr): 1712, 1620 cm^{-1}.

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