

Short communication

## $I_2$ - $SiO_2$ : An efficient heterogeneous catalyst for the Johnson–Claisen rearrangement of Baylis–Hillman adducts<sup>☆</sup>

Biswanath Das<sup>\*</sup>, Anjoy Majhi, K. Ravinder Reddy, Katta Venkateswarlu

*Organic Chemistry Division-I, Indian Institute of Chemical Technology, Hyderabad 500007, India*

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### Abstract

Baylis–Hillman adducts can efficiently undergo the Johnson–Claisen rearrangement by treatment with triethyl orthoacetate in the presence of  $I_2$ - $SiO_2$  as a heterogeneous catalyst for stereoselective conversions into ethyl alk-4-enoates in high yields.

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**Keywords:** Baylis–Hillman adduct; Johnson–Claisen rearrangement;  $I_2$ - $SiO_2$ ; Ethyl alk-4-enoates; Heterogeneous catalyst

The Baylis–Hillman reaction [1] provides multifunctional allyl alcohols, known as adducts which have been employed as intermediates in organic synthesis [2]. They can undergo the acid-catalyzed Johnson–Claisen rearrangement [3] on treatment with triethyl orthoacetate to form trisubstituted alkenes [4]. A trisubstituted alkene moiety has frequently been observed in natural bioactive compounds including pheromones and antibiotics [5]. The Johnson–Claisen rearrangement of Baylis–Hillman adducts is a simple access to this moiety.

In continuation of our work [6] on heterogeneous catalysts in relation to their applications in organic synthesis we have recently observed that iodine adsorbed on silica ( $I_2$ - $SiO_2$ ) can efficiently catalyze the Johnson–Claisen rearrangement of Baylis–Hillman adducts **1** (Scheme 1).

The products, ethyl alk-4-enoates **2** were formed in high yields (70–91%) (Table 1). The reaction was complete within 30 min. The yield was found not to be changed even if the reaction was continued for 1.5 h. The adducts containing both ester and nitrile moieties underwent the rearrangement smoothly. The alkenes **2** were produced in stereoselective manner. When they contained an ester group at C-4, they were obtained with high (*E*)-selectivity, if R is an aryl group and with high (*Z*)-selectivity, if R is an alkyl group. However, alkenes **2** having a nitrile group

were formed with (*Z*)-selectivity. The stereochemistry of the prepared alkenoates could easily be derived from <sup>1</sup>H NMR spectra by comparison of the positions of their vinyl protons with those of the known and structurally related trisubstituted alkenes [4,7]. Similar stereochemistry was also observed [4] earlier for the acid-catalyzed Johnson–Claisen rearrangement products of the Baylis–Hillman adducts.

The catalyst,  $I_2$ - $SiO_2$ , can easily be prepared from its readily available ingredients, iodine and silica gel (100–200 mesh). It works under heterogeneous conditions and can conveniently be handled and removed from the reaction mixture by simple filtration. Thus the experimental procedure using this catalyst is very simple. In recent years, heterogeneous catalysts have gained much importance due to their interesting efficiency as well as economic and environmental benefits. In the present conversion  $I_2$ - $SiO_2$  has successfully been utilized for the preparation of trisubstituted alkenes from the Baylis–Hillman adducts. With only silica no product was formed and with only iodine mixture of products were obtained under the present experimental conditions. In absence of the used catalyst ( $I_2$ - $SiO_2$ ) only a minor conversion (~20–25%) was observed even after heating the adducts with triethyl orthoacetate overnight under reflux.

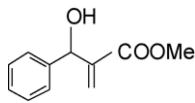
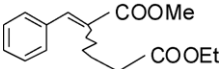
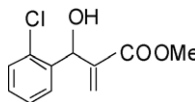
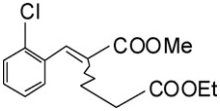
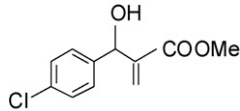
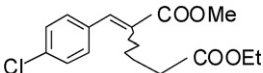
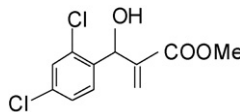
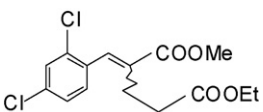
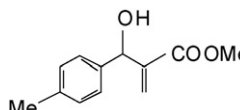
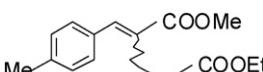
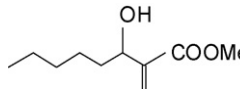
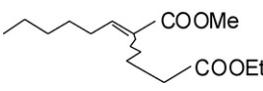
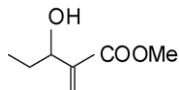
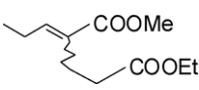
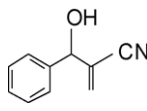
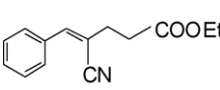
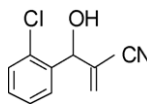
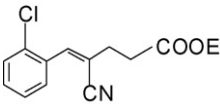
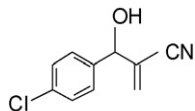
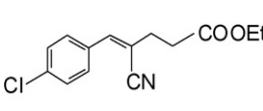
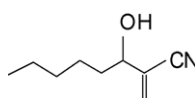
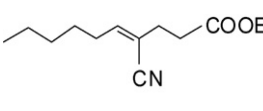
In conclusion, we have carried out the Johnson–Claisen rearrangement of the Baylis–Hillman adducts efficiently using a simple heterogeneous catalyst,  $I_2$ - $SiO_2$  for stereoselective preparation of trisubstituted alkenes (alk-4-enoates) in high yields.

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<sup>\*</sup> Corresponding author. Tel.: +91 40 27160512; fax: +91 40 27160512.

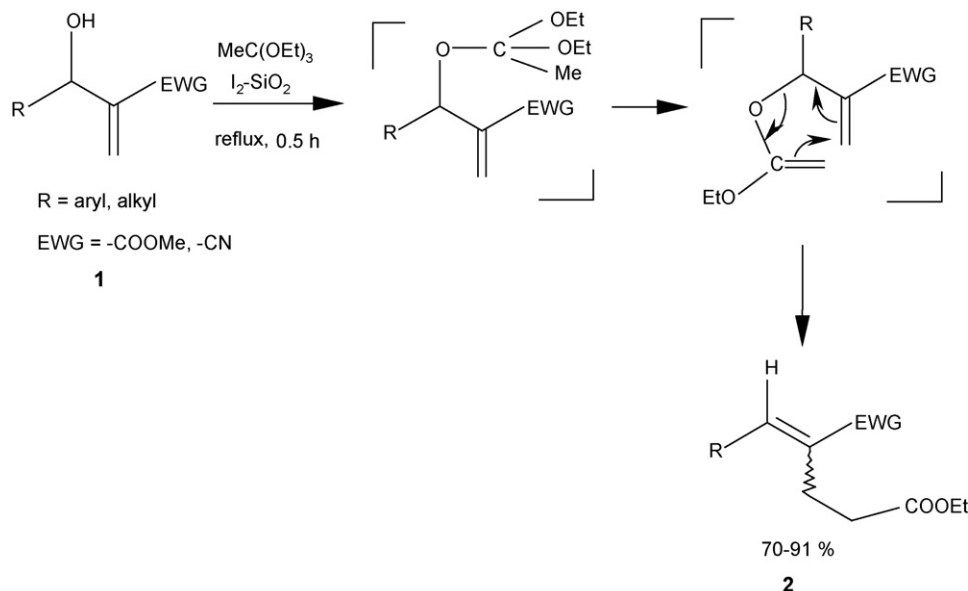
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Table 1  
Synthesis of ethyl alk-4-enoates using  $I_2$ - $SiO_2^a$

Entry	Substrate 1	Product 2	Time (h)	Isolated yield (%)	<i>E:Z</i> <sup>b</sup>
a			0.5	91	81:19
b			0.5	88	85:15
c			0.5	85	79:21
d			0.5	86	77:23
e			0.5	82	80:20
f			0.5	73	22:78
g			0.5	74	25:75
h			0.5	82	0:100
i			0.5	80	0:100
j			0.5	85	0:100
k			0.5	70	0:100

<sup>a</sup> The structures of the alk-4-enoates were determined from their spectral (IR, <sup>1</sup>H NMR and MS) and analytical data.

<sup>b</sup> *E:Z* was determined from <sup>1</sup>H NMR spectral analysis.



Scheme 1.

## 1. Experimental

### 1.1. Preparation of the catalyst

Commercial iodine (2 g) and silica gel (100–200 mesh) (2 g) were taken in a culture tube and mixed thoroughly for 30 min. The prepared catalyst was kept in the closed tube.

### 1.2. General procedure for Johnson–Claisen rearrangement

To a mixture of Baylis–Hillman adduct (1 mmol) and triethyl orthoacetate (5 mmol)  $\text{I}_2\text{-SiO}_2$  (30 mg) was added. The mixture was heated under reflux and the reaction was monitored by TLC. After completion the mixture was filtered and the filtrate was concentrated. The residue was subjected to column chromatography over silica gel using 3% EtOAc in hexane as eluent to furnish pure alk-4-enoate.

The spectral (IR,  $^1\text{H}$  NMR and MS) data of some representative alkenes are given below.

**2c:** (*E: Z*, 79:21): IR (KBr):  $\nu_{\text{max}}$  1728, 1635, 1512, 1440  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.64, 7.10 (1H, 2s), 7.41–7.22 (4H, m), 4.12, 4.07 (2H, 2q,  $J=7.0$  Hz), 3.82, 3.63 (3H, s), 2.80, 2.71 (2H, 2t,  $J=7.0$  Hz), 2.52, 2.48 (2H, 2t,  $J=7.0$  Hz), 1.25, 1.21 (3H, t,  $J=7.0$  Hz); FABMS:  $m/z$  321, 319 [ $M+\text{Na}$ ] $^+$ .

**2d:** (*E: Z*, 77:23): IR (KBr):  $\nu_{\text{max}}$  1730, 1638, 1587, 1470  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.67, 6.80 (1H, 2s), 7.46, 7.40 (1H, d,  $J=2.0$  Hz), 7.32–7.14 (2H, m), 4.16, 4.10 (2H, 2q,  $J=7.0$  Hz), 3.88, 3.58 (3H, 2s), 2.77, 2.68 (2H, 2q,

$J=7.0$  Hz), 2.58, 2.49 (2H, 2q  $J=7.0$  Hz), 1.23, 1.21 (3H, 2t,  $J=7.0$  Hz); FABMS:  $m/z$  357, 355, 353 [ $M+\text{Na}$ ] $^+$ .

**2j:** IR (KBr):  $\nu_{\text{max}}$  2360, 1732, 1514, 1439  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  7.65 (2H, d,  $J=8.0$  Hz), 7.38 (2H, d,  $J=8.0$  Hz), 6.96 (1H, s), 4.15 (2H, q,  $J=7.0$  Hz), 2.70 (2H, t,  $J=7.0$  Hz), 2.61 (2H, t,  $J=7.0$  Hz), 1.24 (3H, t,  $J=7.0$  Hz); FABMS:  $m/z$  288, 286 [ $M+\text{Na}$ ] $^+$ .

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