



P-ISSN2349-8528  
E-ISSN 2321-4902  
IJCS 2016; 4(5): 52-55  
© 2016 JEZS  
Received: 10-07-2016  
Accepted: 11-08-2016

**AFG Masud Rezaa**  
Assistant Professor, Department  
of Chemistry, National  
University, Gazipur, Bangladesh

**Dr. Mohd. Amirul Islam**  
Associate Professor, Open  
School, Bangladesh Open  
University Gazipur-1705,  
Bangladesh.

## Mild condition synthesis of $\alpha, \beta$ -Unsaturated esters derivatives through copper catalyst

**AFG Masud Rezaa and Dr. Mohd. Amirul Islam**

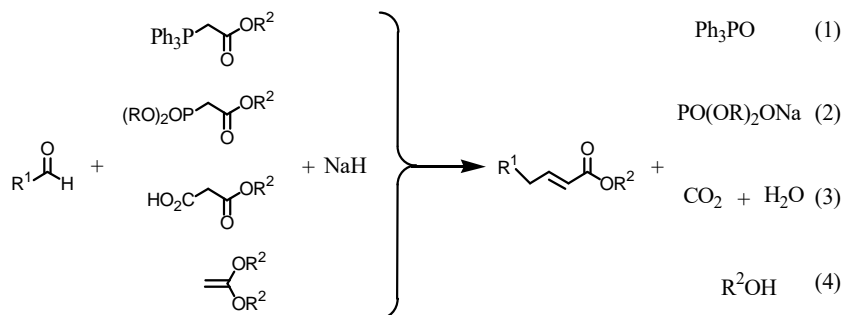
### Abstract

Copper (II) triflate catalyzed reactions of ethylene diazo acetate with aldehyde derivatives are presented in this report. Based on modification of the Wittig reaction, a practical and highly efficient synthesis of  $\alpha, \beta$ -unsaturated esters with good to excellent yields were obtained. A variety of substituted aromatic aldehydes were smoothly converted to the corresponding derivatives of acrylic acid with ethyl ester for the reaction of ethyl diazoacetate using Cu (II) triflate as catalyst in the presence of triphenylphosphine as a reducing agent. Yields of the products obtained were found to be good to excellent, under mild reaction conditions and in a narrow range of solvents.

**Keywords:**  $\alpha, \beta$ -unsaturated esters, Olefination, Wittig reactions, Cu (II) triflate, triphenylphosphine

### Introduction

Catalyst can be used to enhance the reactivity and selectivity of specific chemical transformations, as well as decreasing the amount of energy consumed by these processes. Most catalytic reactions fulfill the criteria for a sustainable transformation on the macroscopic scale, and a wide variety of efficient catalytic systems have been developed in both industry and academia that are capable of affecting a broad range of chemical transformations. Unfortunately, however, most of the popular and frequently used catalysts are based on precious metals such as copper, palladium, rhodium, ruthenium, iridium, and osmium, which are becoming increasingly expensive because they are derived from dwindling resources. Catalytic asymmetric multi-component reactions (CAMCRs), in which three or more reactants are combined in a single chemical step to stereoselectivity products have received considerable attention [1a]. The synthesis of  $\alpha, \beta$ -unsaturated esters from aldehydes is very common carbon-carbon bond forming reaction, especially Wittig reaction variants are widely used [1b]. But almost in every case the problem with these approaches is their unsatisfactory atom economy resulting in significant by-product formation. Alternative approaches have been suggested by different research groups, e.g., modified Horner-Wadsworth-Emmons reaction [2]. An alternative yet rarely used methodology for the synthesis of  $\alpha, \beta$ -unsaturated esters from aldehydes is the decarboxylative Knoevenagel reaction using malonate half esters which leads to the formation of  $H_2O$  &  $CO_2$  as the only by-product [3] (Benjamin *et al.*, 1945). Benjamin *et al* explored the formation of  $\alpha, \beta$ -unsaturated esters from malonate half esters with aldehyde which leads to the formation of  $H_2O$  &  $CO_2$  as the only by-product (scheme 1) [3].



**Scheme 1.**

**Correspondence**  
**Dr. Mohd. Amirul Islam**  
Associate Professor, Open  
School, Bangladesh Open  
University Gazipur-1705,  
Bangladesh.

Moreover, half-esters of malonates are as inexpensive as the corresponding phosphorous based reagents and can also be obtained from inexpensive diethyl malonate. In addition, by this method (E) vs (Z) selectivity varies and, most importantly, in the reaction with enolizable aldehydes, not  $\alpha$ ,  $\beta$ -unsaturated esters (or their mixtures) are commonly obtained [4]. Benjamin *et al* reported the formation of  $\alpha$ ,  $\beta$ -unsaturated esters from malonate half esters with aldehyde and the reaction was carried out in the presence of catalytic amount of 4-dimethylaminopyridine (4-DMAP, 10 mol %) at room temperature which provided the corresponding unsaturated esters with the remarkable result [5]. A number of transition metal complexes derived from Mo, [6] Re, [7] Fe, [8] Ru, [9] Co, [10] and Ir [11] are known to catalyze the olefination of carbonyl compounds [12] with diazo reagents, in most cases, diazoacetate derivatives. Recently, a research group reported the formation of esters from the reaction of carbonyl compounds with diazoacetate using lanthanide triflates as catalyst [13]. Among the various metal triflates, copper (II) triflate [Cu(OTf)<sub>2</sub>], plays an indispensable role in the discovery of novel and improved reaction process. Copper (II) triflate has been known to promote elimination reactions, oxidative coupling reactions and reactions of diazo-compounds [14]. In the present letter we wish to report Cu(OTf)<sub>2</sub> efficiently catalyses the olefination of variety of aromatic aldehydes with ethyl diazoacetate (EDA) the presence of triphenylphosphine (Ph<sub>3</sub>P) under mild conditions and was obtained in good to excellent yield.

As a part of our ongoing studies to search for new carbon-carbon bond formation processes using diazo compounds our future studies will focus on exploring the full scope of this reaction to other carbonyl compounds.

## Experimental Section

### General method

<sup>1</sup>H NMR was recorded in CDCl<sub>3</sub> solution on a Bruker AC 200 spectrometer operating at 300 MHz, in the Fourier transform mode. IR spectra was recorded in (cm<sup>-1</sup>) JASCO 5300 Spectrometer as KBr pellet or sodium chloride plate in the Fourier transform mode. Column chromatography was used for the separation using Merck Silica gel 7734 and ethyl acetate/hexane. Ethyl diazoacetate, Cu(OTf)<sub>2</sub> were purchased from Aldrich and used without further purification.

### General Procedure

A mixture of aldehyde (1.0 mmol) and EDA (2.0 mmol) in the presence of Cu(OTf)<sub>2</sub> (0.3 mmol) and chloroform (7.0 mL) was stirred at 70 °C for 7-10h. After completion of the reaction (TLC-checked), the solvent was removed under reduced pressure to obtain the crude product. Then the crude product was purified by column chromatography (hexane-EtOAc) on silica gel to give corresponding  $\alpha$ ,  $\beta$ -unsaturated ester.

### General procedure for the preparation of $\alpha$ , $\beta$ -unsaturated ester

A mixture of aldehyde (1.0 mmol) and EDA (2.0 mmol) in the presence of Cu(OTf)<sub>2</sub> (0.3 mmol) and chloroform (7.0 ml) was stirred at 70 °C for 7-10 h. After completion of the reaction (TLC-checked), the solvent was removed under reduced pressure to obtain the crude product. Then, the crude product was purified by column chromatography (hexane-EtOAc) on silica gel to give corresponding  $\alpha$ ,  $\beta$ -unsaturated ester.

### 3-Phenyl-acrylic acid ethyl ester (10)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.67 (d,  $J$  = 16.0Hz, =CH, 1H), 7.52-7.48 (m, 2H), 7.38-7.34 (m, 3H), 6.43 (d,  $J$  = 16.0Hz, =CH, 1H), 4.25 (q,  $J$  = 7.1Hz, -CH<sub>2</sub>, 2H), 1.32 (t,  $J$  = 7.1Hz, CH<sub>3</sub>, 3H).

IR (neat): 2928, 2855, 1721, 1640, 1451, 1368, 1300, 1262, 1177, 1038, 980, 828 cm<sup>-1</sup>.

### 3-*p*-Tolyl-acrylic acid ethyl ester (11)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 (d,  $J$  = 16.0Hz, 1H), 7.40 (d,  $J$  = 8.1Hz, 2H), 7.17 (d,  $J$  = 8.1Hz, 2H), 6.37 (d,  $J$  = 16.0Hz, 1H), 4.24 (q,  $J$  = 7.1Hz, 2H), 2.35 (s, 3H), 1.34 (t,  $J$  = 7.1Hz, 3H).

IR (neat): 2982, 1713, 1638, 1609, 1514, 1368, 1312, 1267, 1206, 1175, 1038, 984, 814 cm<sup>-1</sup>.

### 3-*m*-Tolyl-acrylic acid ethyl ester (12)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 (d,  $J$  = 16.0Hz, 1H), 7.31 (d,  $J$  = 6.1Hz, 2H), 7.25

(t,  $J$  = 7.4Hz, 1H), 7.18 (d,  $J$  = 7.4Hz, 1H), 6.40 (d,  $J$  = 16.0Hz, 1H), 4.24 (q,  $J$  = 7.1Hz, 2H), 2.35 (s, 3H), 1.32 (t,  $J$  = 7.1Hz, 3H).

IR (neat): 2982, 1713, 1640, 1447, 1368, 1312, 1265, 1236, 1179, 1038, 984, 787 cm<sup>-1</sup>.

### 3-(2,5-Dimethyl-phenyl)-acrylic acid ethyl ester (13)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (d,  $J$  = 15.9Hz, 1H), 7.35 (s, 1H), 7.07 (d,  $J$  = 1.0Hz, 2H), 6.33 (d,  $J$  = 15.9Hz, 1H), 4.24 (q,  $J$  = 29 7.1Hz, 2H), 2.37 (s, 3H), 2.30 (s, 3H), 1.32 (t,  $J$  = 7.1Hz, 3H).

IR (neat): 2980, 2928, 1715, 1636, 1497, 1449, 1368, 1314, 1177, 1038, 982, 814 cm<sup>-1</sup>.

### 3-(4-Methoxy-phenyl)-acrylic acid ethyl ester (14)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.62 (d,  $J$  = 16.0Hz, 1H), 7.45 (dq,  $J$  = 8.8Hz, 2.9Hz, 2H),

6.88 (dq,  $J$  = 8.8, 2.9Hz, 2H), 6.28 (d,  $J$  = 16.0Hz, 1H), 4.23 (q,  $J$  = 7.1Hz, 2H), 3.28 (s, 3H), 1.31 (t,  $J$  = 7.1Hz, 3H).

IR (neat): 2982, 1709, 1634, 1605, 1514, 1464, 1304, 1254, 1206, 1173, 1032, 984, 829 cm<sup>-1</sup>.

### 3-Benzo [1,3]dioxol-5-yl-acrylic acid ethyl ester (15)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.56 ( $J$  = 15.9Hz, 1H), 7.01-6.96 (m, 2H), 6.79 (d,  $J$  = 7.9Hz, 1H), 6.24 (d,  $J$  = 15.9Hz, 1H), 5.98 (s, 2H), 4.22 (q,  $J$  = 7.1Hz, 2H), 1.30 (t,  $J$  = 7.1Hz, 3H).

IR (neat): 2990, 2905, 1703, 1642, 1611, 1491, 1449, 1369, 1246, 1175, 1098, 1034, 930, 806 cm<sup>-1</sup>.

### 3-Naphthalen-2-yl-acrylic acid ethyl ester (16)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.91 (s, 1H), 7.86 -7.80 (m, 4H), 7.65 (dd,  $J$  = 8.6 Hz,

1.7Hz, 1H), 7.52-7.44 (m, 2H), 6.53 (d,  $J$  = 16.0 Hz, 1H), 4.27 (q,  $J$  = 7.1 Hz, 2H), 1.34 (t,  $J$  = 7.1 Hz, 3H).

IR (neat): 2980, 1709, 1634, 1370, 1298, 1262, 1200, 1175, 1038, 990, 860, 822, 752 cm<sup>-1</sup>.

### 5-Phenyl-penta-2,4-dienoic acid ethyl ester (17)

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.46 (q,  $J$  = 2.1Hz, 1H), 7.43-7.28 (m, 5H), 6.88-6.80 (m, 2H), 5.98 (d,  $J$  = 15.2Hz, 1H), 4.21 (q,  $J$  = 7.1Hz, 2H), 1.30 (t,  $J$  = 7.1Hz, 3H).

IR (neat): 2982, 1709, 1626, 1449, 1368, 1298, 1240, 1134, 1038, 1001, 756, 691 cm<sup>-1</sup>.

**4-Phenyl-pent-2-enoic acid ethyl ester (18)**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J = 7.4\text{Hz}$ , 1H), 7.07 (dd,  $J = 15.7, 7.4\text{Hz}$ , 1H), 5.78 (dd,  $J = 15.7, 1.6\text{Hz}$ , 1H), 4.23 (q,  $J = 7.1\text{Hz}$ , 2H), 2.59 (2H, s), 1.30 (t,  $J = 7.1\text{Hz}$ , 3H).  
IR (neat): 2982, 1723, 1688, 1451, 1368, 1300, 1265, 1157, 1036, 762, 692  $\text{cm}^{-1}$ .

**Results and discussion**

In our initial experiment, the reaction of EDA with aldehyde was carried out under various conditions to find optimum conditions (Table 1). As shown in Table 1, the best results were obtained when the reaction was carried out using  $\text{Cu}(\text{OTf})_2$  as a catalyst in the presence of  $\text{Ph}_3\text{P}$  in  $\text{CHCl}_3$  at  $70^\circ\text{C}$  temperature.

**Table 1.** Reaction of EDA with aldehydes under various conditions


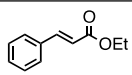

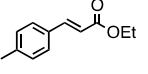

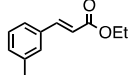

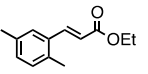
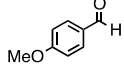
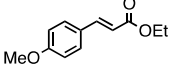
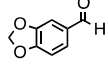
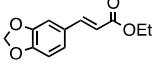
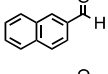
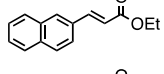
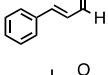
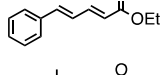
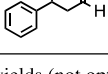
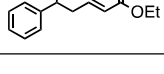
Entry	Catalyst (equiv)	Condition	Yield <sup>b</sup> (%)
1	$\text{Ag}_2\text{O}$ (1.0)	$\text{CHCl}_3$ , $70^\circ\text{C}$	0
2	$\text{Cu}_2\text{O}$ (0.3)	$\text{CHCl}_3$ , $70^\circ\text{C}$	0
3	$\text{CuOAc}$ (1.0)	$\text{CHCl}_3$ , $70^\circ\text{C}$	52
4	$\text{CuBr}$ (1.0)	$\text{CHCl}_3$ , $70^\circ\text{C}$	52
5	$\text{Cu}(\text{OTf})_2$ (0.3)	$\text{CH}_2\text{Cl}_2$ , rt	0
6	$\text{Cu}(\text{OTf})_2$ (0.3)	$\text{CHCl}_3$ , rt	0
7	$\text{Cu}(\text{OTf})_2$ (0.3)	THF, rt	0
8	$\text{Cu}(\text{OTf})_2$ (0.3)	$\text{CHCl}_3$ , $70^\circ\text{C}$	73

<sup>b</sup> Isolated yields (not optimized)

In order to obtain the further clue, we studied the reaction of EDA (2.0 equiv) with several aldehydes (1.0 equiv) using  $\text{Cu}(\text{OTf})_2$  as a catalyst (0.3 equiv) in the presence of  $\text{Ph}_3\text{P}$  [15]. In

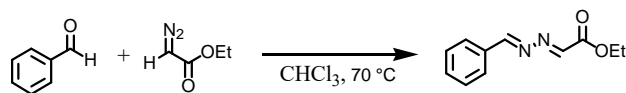
all cases, the corresponding conjugated ester was obtained in good to excellent yields [16]. The results are listed in Table 2.

**Table 2:** Reactions of EDA with aldehydes in the presence of  $\text{Cu}(\text{OTf})_2/\text{Ph}_3\text{P}$

Entry	Aldehyde	Product	Yield <sup>b</sup> (%)
1			60
2			75
3			84
4			85
5			78
6			83
7			84
8			49
9			30

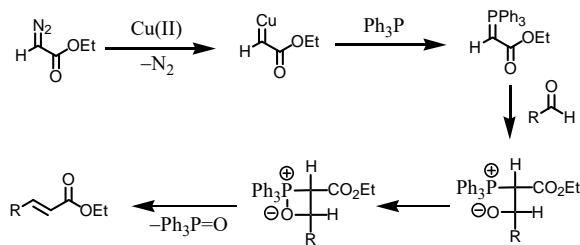
<sup>b</sup> Isolated yields (not optimized)

Next, the reaction was carried out without  $\text{PPh}_3$ , but the olefination did not proceed. In case of small amount or absence of catalyst, the reaction afforded azine as major product when the reaction mixture was stirred for 2 days (Scheme 2)<sup>[16]</sup>.



Scheme 2

The structure of the products has been confirmed by the spectral data (IR,  $^1\text{H-NMR}$ ) and elemental analyses. The  $^1\text{H}$  NMR spectra of the products were not identical, but the characteristic spectra of two double bond hydrogen of those compounds were similar in all cases. Two geminal protons appeared nearly at 7.6 ppm and 6.4 ppm as doublets and the coupling constant was about 16 Hz, while the other protons appeared in the aromatic and aliphatic region. The reaction proceeded smoothly with aromatic aldehydes while alkyl and aryl ketones were found to be practically unreactive. The obtained product also can be confirmed by the following mechanism. The olefination process can be explained by the formation of copper yield firstly and the next step formed phosphorus yield as well as continued the formation of four member ring intermediate by attacking aldehydes.  $\alpha$ ,  $\beta$ -unsaturated compound were obtained as a final products and the very stable phosphine oxide as the bye-product. The probable mechanism for the formation of  $\alpha$ ,  $\beta$ -unsaturated ester will be depicted as shown in Scheme 3.

Scheme 3. Probable mechanism for the formation of  $\alpha$ ,  $\beta$ -unsaturated ester

### Conclusion

In conclusion, we have developed a simple and efficient method to prepare  $\alpha$ ,  $\beta$ -unsaturated esters from aldehyde by the reaction with EDA and  $\text{Ph}_3\text{P}$  in the presence of a catalytic amount of  $\text{Cu}(\text{OTf})_2$  and established Wittig reagents through a one-pote process. By optimizing the reaction conditions, this catalyst proved to be a fairly good catalyst in mild condition with good to excellent yields (85%), also cost effective, and highly selective ( $E > 95\%$ ) compounds. In addition, a salient feature of copper (II) triflate is inherent stable in aqueous solvents that open the way to environmental chemistry. These allow the carbonyl compounds to react under the mild reaction conditions. The desired goal is achieved using the copper-catalyzed olefination reaction as a key step. We are now undergoing to make clear the scope and limitations of the reaction using various carbonyl compounds.

### References

- (a) Guo HC, Ma JA, *Angew. Chem.* 2006, 118, 362;  
(b) Maryanoff BE, Reitz AB. *Chem. Rev.* 1989; 89:863-927.

- Hatsuda M, Kuroda T, Seki M. *Synth. Commun.* 2003; 33:427-434.
- J. Am. Chem. Soc.* 1945; 68:376.
- Carmona T, Fuentes J, Robina I, Rodriguez-Garcia E, Demange R, Vogel P *et al. J. Org. Chem.* 2003; 68:3874-3883.
- Benjamin L, Arno D, Maria T, Hechavarria F, Kthrin W, Hendrik VT, Ramon RT *et al. Commun*, 2005; 347:1558.
- Lu XY, Fang H, Ni ZJJ. *Organomet. Chem.* 1989; 373:77.
- (a) Herrmann WA, Wang M, *Angew. Chem. Int. Ed. Engl.* 1991; 30:1641.  
(b) Herrmann WA, Roesky PW, Wang M, Scherer W. *Organometallics* 1994; 13:4531-4535.
- Herrmann WA, Wang M. *Angew. Chem. Int. Ed. Engl.* 1991; 30:1641.
- (a) Mirafzal GA, Cheng GL, Woo LK. *J. Am. Chem. Soc.* 2002; 124:176.  
(b) Cheng GL, Mirafzal GA, Woo LK. *Organometallics* 2003; 22:1468-1474.  
(c) Chen Y, Huang L, Ranade MA, Zhang XP. *J. Org. Chem.* 2003; 68:3714-3717.
- (a) Fujimura O, Honma T. *Tetrahedron Lett.* 1998; 39:625-626.  
(b) Kuhn FE, Santos AM, Jpgalekar AA, Pedro FM, Rigo P, Baratta WJ. *Catal.* 2004; 227:253.
- (a) Lee MY, Chen Y, Zhang XP. *Organometallics.* 2003; 22:4905-4909.  
(b) Ertuerk E, Demir AS. *Tetrahedron*, 2008; 64:7555-7560.
- Lebel H, Ladjel C. *Organometallics.* 2008; 27:2676-2678.
- Curini M, Epifano F, Marcotullio MC, Rosati O. *Eur. J. Org. Chem.* 2002, 1562-1565.
- Laali KK in: *Encyclopedia of Reagents for Organic synthesis*, L.A. Paquette (Ed.), Wiley, New York, NY and references cited therein. 1995; 2:1380.
- Christian H. *J. Parkt. Chem.* 2000; 342:3.
- (a) Kaori A, Kyohei Y. *Tetrahedron.* 2010; 51:3297-3299.  
(b) Eun YL, Youngkwon K, Jae SL, Jae SL, Jaiwook P. *Eur. J. Org. Chem.* 2009, 2943-2946.  
(c) Helio AS, Jesus MP, Kemilla G, Nicola P, Boniek GV, Marcos NE. *Tetrahedron Lett.* 2009; 50:5589-5595.  
(d) Yangzhou L, Zhiming L, Feng L, Quanrui W, Fenggang T. *Tetrahedron Lett.* 2005; 46:6159-6162.  
(e) Cristau HJ, Taillefer M. *Tetrahedron.* 1998; 54:1507-1522.  
(f) Osamu F, Takashi H. *Tetrahedron Lett.* 1998; 39:625-626.