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Short Communication

Synthesis of Acryclic Acid Ethyl Ester from Aldehydes Catalyzed by Copper Triflates

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Abstract

A variety of substituted aromatic aldehydes were smoothly converted to the corresponding acryclic acid ethyl ester with the reaction of ethyldiazoacetate using Cu(II) triflate as catalyst in the presence of triphenylphosphine as reducing agent. Yields of the products obtained were found to be good to excellent.

Keywords: Acryclic acid ethyl ester; Aromatic aldehyde; Cu(II) triflate; Triphenylphosphine.

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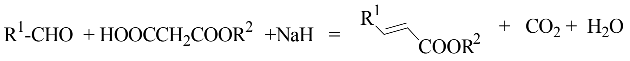
1. Introduction

The synthesis of α, β-unsaturated esters from aldehydes is very common carbon-carbon bond forming reaction, especially Wittig reaction variants are widely used [1]. But almost in every case the problem with these approaches is their unsatisfactory atom economy resulting in significant bye-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 α, β-unsaturated esters from aldehydes is the decarboxylative Knoevenagel reaction using malonate half esters which leads to the formation of water and CO_2 as the only by product [3] (scheme 1).



Scheme 1

Moreover, half-esters of malonates are as inexpensive as the corresponding phosphorous based reagents and can also be obtained from inexpensive dialkylmalonates. In addition, by this method (*E*) vs (*Z*) selectivity varies and, most importantly, in the

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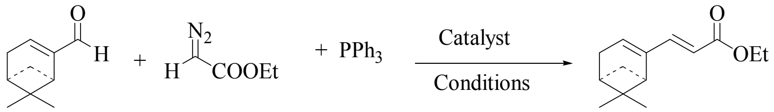
reaction with enolizable aldehydes, not α, β-unsaturated esters (or their mixtures) are commonly obtained [4]. In this context Benjamin et. al explored the formation of α, β-unsaturated esters from malonate half esters with aldehyde and carried out the reaction in the presence of catalytic amount of 4-dimethylaminopyridine (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 [$Cu(OTf)_2$], plays an indispensable role in the discovery of novel and improved reaction process. [$Cu(OTf)_2$], has long been known to promote elimination reactions, oxidative coupling reactions and reactions of diazocompounds [14]. In the present study, we report the formation of α, β-unsaturated esters from aldehydes by using copper triflates as catalyst in the reaction between ethyl diazoacetate (EDA) and carbonyl compounds especially various aromatic aldehydes.

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.

2. Experiments, Results and Discussion

Initially we tested a variety of reaction conditions in presence of copper (II) triflate, employing different solvents such as chloroform, dichloromethane, tetrahydrofuran with different aldehyde at room temperature to elevated temperature. But the best results were obtained when the reaction was carried out in chloroform at 70^0 C (scheme 2). The reaction of aldehyde and ethylene diazoacetate gave the corresponding conjugated ester derivatives 10-18 (entry 1-9; Table 1).



Scheme 2

The reaction was also examined at this temperature with other Cu catalysts available in the laboratory (Table 2). The percent of yield is not satisfactory in those cases (yield 50-55%). The best results were obtained using 0.3 equivalents of the catalyst; a lower loading resulted in no reaction to lower yields, while a higher loading decomposed the reaction in most cases. Moreover an excellent functional group compatibility was observed, as different substituents were not affected under the olefination reaction conditions (entries 6-9). In all cases, the corresponding conjugated ester was obtained in good yields.

Table 1.

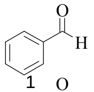
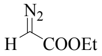
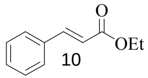
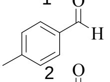
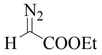
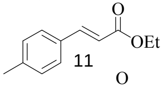
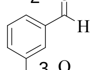
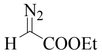
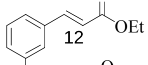
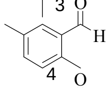
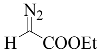
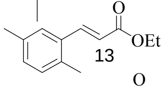
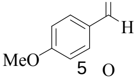
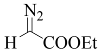
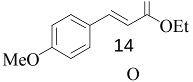
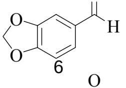
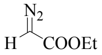
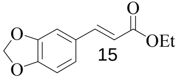
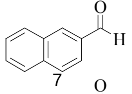
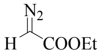
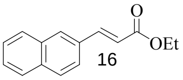
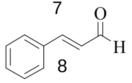
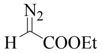
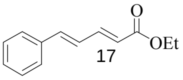
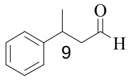
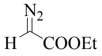
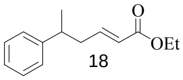
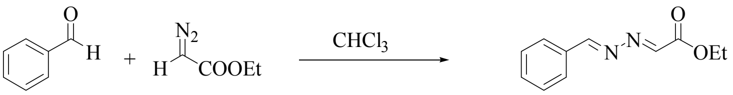
Entry	Aldehyde	Ethyl Diazoacetate	Unsaturated Ester	Yields (%)
1.				60
2				75
3				84
4				85
5				78
6				83
7				84
8				49
9				30

Table 2. Yields of products with different Cu-catalysts.

Catalyst (eq)	Condition	Yield (%)
Ag_2O (1.0)	$CHCl_3$, 70^0 C	0
Cu_2O (0.3)	$CHCl_3$, 70^0 C	0
CuOAc (1.0)	$CHCl_3$, 70^0 C	52
Cubr (1.0)	$CHCl_3$, 70^0 C	52
$Cu(OTf)_2$ (0.3)	CH_2Cl_2, r.t	0
$Cu(OTf)_2$ (0.3)	$CHCl_3$, r.t	0
$Cu(OTf)_2$ (0.3)	PhF, r.t	0
$Cu(OTf)_2$ (0.3)	$CHCl_3$, 70^0 C	73

Moreover, the reaction did not proceed without PPh_3. In case of the absence or small amount of catalyst, the reaction afforded azine as major product when the reaction mixture was stirred for 2 days (scheme 3).

The proposed structures of the products have been confirmed by the spectral data (IR, ^{1}H-NMR) and elemental analyses. The ^{1}H NMR spectra of the compounds 10-20 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 16Hz, while the other protons appeared in the aromatic and aliphatic region.



Scheme 3

Experimental Section

General method

1H NMR were recorded in $CDCl_3$ solution on a Bruker AC 200 spectrometer operating at 300 MHz, in the Fourier transform mode. IR spectra was recorded in (cm^{-1}) JASCO 5300 Spectrometer as KBr pellet or sodium chloride plate in the Fourier transform mode. Column chromatography was used for the separation by using Merck Silica gel 7734 and ethyl acetate/hexane. Ethyl diazoacetate, $Cu(OTf)_2$ were purchased from Aldrich Chemical Co. and used without any purification.

General Procedure

A mixure of aldehyde (1mmol) and EDA (2mmol) in the presence of $Cu(OTf)_2$ (0.3mmol) and chloroform (7ml) was stirred at 70^0 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 α, β-unsaturated esters 10, 11, 12, 13, 14, 15, 16, 17, 18.

3-Phenyl-acrylic acid ethyl ester (10)
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, J = 16.0Hz, $=C\underline{H}$, 1H), 7.52-7.48 (m, 2H), 7.38-7.34 (m, 3H), 6.43 (d, J =16.0Hz,$=C\underline{H}$, 1H), 4.25 (q, J = 7.1Hz, $-C\underline{H}_2$, 2H), 1.32 (t, J = 7.1Hz, $C\underline{H}_3$, 3H).
IR (neat, $\bar{\nu}$): 2928, 2855, 1721, 1640, 1451, 1368, 1300, 1262, 1177, 1038, 980, 828 cm^{-1}.

3-p-Tolyl-acrylic acid ethyl ester (11)
^{1}H NMR (300 MHz, $CDCl_3$): δ= 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, $\bar{\nu}$): 2982, 1713, 1638, 1609, 1514, 1368, 1312, 1267, 1206, 1175, 1038, 984, 814 cm^{-1}.

3-m-Tolyl-acrylic acid ethyl ester (12)
^{1}H NMR (300 MHz, $CDCl_3$): δ= 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, $\bar{\nu}$): 2982, 1713, 1640, 1447, 1368, 1312, 1265, 1236, 1179, 1038, 984, 787 cm^{-1}.

3-(2,5-Dimethyl-phenyl)-acrylic acid ethyl ester (13)
^{1}H NMR (300 MHz, $CDCl_3$): δ= 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, $\bar{\nu}$): 2980, 2928, 1715, 1636, 1497, 1449, 1368, 1314, 1177, 1038, 982, 814 cm^{-1}.

3-(4-Methoxy-phenyl)-acrylic acid ethyl ester (14)
^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.62 (d, J = 16.0Hz, 1H), 7.45 (dq, J = 8.8, 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^{-1}.

3-Benzo[1,3]dioxol-5-yl-acrylic acid ethyl ester (15)
^{1}H NMR (300 MHz, $CDCl_3$): δ= 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, $\bar{\nu}$): 2990, 2905, 1703, 1642, 1611, 1491, 1449, 1369, 1246, 1175, 1098, 1034, 930, 806 cm^{-1}.

3-Naphthalen-2-yl-acrylic acid ethyl ester (16)
^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.91 (s,1H), 7.86 -7.80 (m, 4H), 7.65 (dd, J = 8.6, 1.7Hz, 1H), 7.52-7.44 (m, 2H), 6.53 (d, J = 16.0Hz, 1H), 4.27 (q, J = 7.1Hz, 2H), 1.34 (t, J = 7.1Hz, 3H).
IR(neat, $\bar{\nu}$): 2980,1709, 1634, 1370, 1298, 1262, 1200, 1175, 1038, 990, 860, 822, 752 cm^{-1}.

5-Phenyl-penta-2,4-dienoic acid ethyl ester (17)
^{1}H NMR (300 MHz, $CDCl_3$): δ= 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, $\bar{\nu}$): 2982, 1709, 1626, 1449, 1368, 1298, 1240, 1134, 1038, 1001, 756, 691 cm^{-1}.

4-Phenyl-pent-2-enoic acid ethyl ester (18)
^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.54 (1H, d, J = 7.4Hz, 1H), 7.07 (1H, dd, J = 15.7, 7.4Hz, 1H), 5.78 (1H, dd, J = 15.7, 1.6Hz, 1H), 4.23 (2H, q, J = 7.1Hz, 2H), 2.59 (2H, s), 1.30 (3H, t, J=7.1Hz, 3H).
IR (neat, $\bar{\nu}$): 2982, 1723, 1688, 1451, 1368, 1300, 1265, 1157, 1036, 762, 692 cm^{-1}.

3. Conclusion

We conclude that copper triflate catalyses the reaction between EDA and carbonyl compounds and proves to be a fairly good catalyst. The desired goal of synthesizing acrylic acid ethyl ester from aldehydes has been achieved using the copper-catalyzed olefination reaction as a key step.

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