

Olefination of Aldehydes by Ethyl Diazoacetate Catalyzed by a Ruthenium(II) Complex

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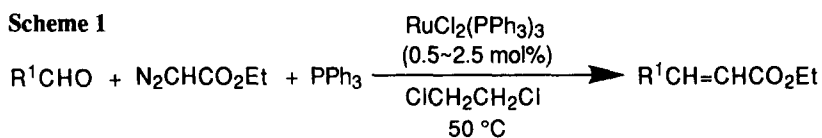
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Abstract: A variety of aldehydes were stereoselectively converted to (*E*)-olefins by the reaction with ethyl diazoacetate and triphenylphosphine in the presence of a catalytic amount of $\text{RuCl}_2(\text{PPh}_3)_3$
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The Wittig reaction and its modified versions are most commonly used methodologies for constructing carbon-carbon double bonds in organic synthesis.¹ Organometallic variants for this transformation have also been investigated and titanium-based systems achieved significant successes.² Another organometallic approach is olefination of aldehydes by diazoacetates in the presence of transition metal catalysts with phosphines or trialkylstibines as reducing agents.³ In the viewpoint of practical synthesis, this approach have several drawbacks such as (1) trialkylstibines are pyrophoric,^{3b} (2) reactivity^{3a} and high stereoselectivity^{3c} is dependent on the choice of substrate aldehydes, (3) requiring high catalyst loading (> 5 mol%).³

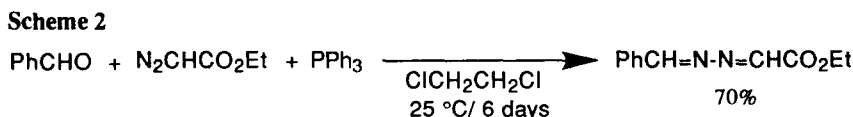
In this letter, we wish to report $\text{RuCl}_2(\text{PPh}_3)_3$ efficiently catalyzes the olefination of variety of aldehydes with ethyl diazoacetate in the presence of triphenylphosphine under very mild conditions (Scheme 1).



It is well known that ruthenium carbene species are generated from $\text{RuCl}_2(\text{PPh}_3)_3$ and diazo compounds by carbene transfer.⁴ We assumed carbene moiety could be further transferred from ruthenium to phosphorus which is capable of olefinating aldehydes.⁵ Thus treatment of the mixture of aldehyde, PPh_3 and catalytic amount of $\text{RuCl}_2(\text{PPh}_3)_3$ in 1,2-dichloroethane with ethyl diazoacetate at 50 °C resulted evolution of N_2 gas and after several hours reaction, gave corresponding olefinated product.

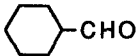
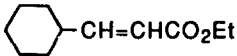
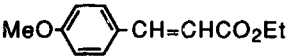
The products 3-substituted acrylic acid esters are obtained in good yields and high (*E*)-selectivity. The results are summarized in Table 1. Reaction proceeded smoothly with aromatic, aliphatic and α,β -unsaturated aldehydes. The catalyst loading can be reduced to 0.5 mol% without causing significant problem. In addition, all the materials are commercially available and can be used without further purification.

The olefination did not proceed without triphenylphosphine. In the case the reaction was performed in the absence of a ruthenium catalyst, azine was obtained as the only product (Scheme 2).



A typical reaction procedure is as follows: To a solution of benzaldehyde (0.11 g, 1.0 mmol), triphenylphosphine (0.29 g, 1.1 mmol) and $\text{RuCl}_2(\text{PPh}_3)_3$ (24 mg, 0.025 mmol) in 1,2-dichloroethane (3 mL) was added a solution of ethyl diazoacetate in 1,2-dichloroethane (1.5 mL, 0.93 M, 1.4 mmol) dropwise at 50 °C under argon. The evolution of N_2 gas was observed. The reaction mixture was stirred for 4 hours at 50 °C and then cooled to 25 °C. The solvent was removed in vacuo. The residue was purified by flash chromatography (EM reagents silica gel 60, 230-400 mesh, Hexane~Hexane/ EtOAc = 10/1) yielded 0.16g (90%) of Ethyl 3-phenyl-2-propenoate. *E/Z* ratio was determined by NMR and gas chromatography (G-100, 40m) to be 97/3.

Table 1. $\text{RuCl}_2(\text{PPh}_3)_3$ Catalyzed Olefination of Aldehydes by Ethyl Diazoacetate with PPh_3 .^a

entry	R^1CHO	temp/time	product	yield(%) ^b	<i>E/Z</i> ^c
1	PhCHO	50 °C/ 4 h	$\text{PhCH=CHCO}_2\text{Et}$	90	97/ 3
2 ^d		50 °C/ 24 h		85	97/ 3
3	$\text{Ph-CH}_2\text{-CH}_2\text{-CHO}$	50 °C/ 5 h	$\text{Ph-CH}_2\text{-CH=CHCO}_2\text{Et}$	90	95/ 5
4		50 °C/ 17 h		82	>99/ 1
5		50 °C/ 12 h		92	97/ 3
6	Ph-CH=CH-CHO	50 °C/ 8 h	$\text{Ph-CH=CH-CH=CHCO}_2\text{Et}$	92	90/ 10

^a The aldehyde (1.0 equiv.) was treated with ethyl diazoacetate (1.4 equiv.), PPh_3 (1.1 equiv.) and $\text{RuCl}_2(\text{PPh}_3)_3$ (0.025 equiv.) in 1,2-dichloroethane.

^b Isolated yields. ^c Determined by gas chromatography. ^d 0.5 mol% catalyst were used.

In conclusion, we demonstrated a variety of aldehydes were stereoselectively converted to (*E*)-olefins by the reaction with ethyl diazoacetate and triphenylphosphine in the presence of a catalytic amount of $\text{RuCl}_2(\text{PPh}_3)_3$.

References and Notes

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