

A Novel Synthesis of Diethyl Malonate

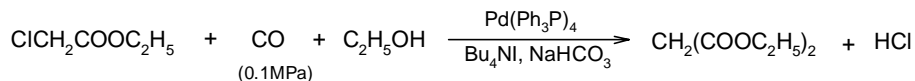
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Abstract: A green synthesis route of diethyl malonate by palladium catalyzed carbonylation of ethyl chloroacetate in the presence of phase transfer agent is carried out under mild conditions in good yield. The effects of reaction temperature and different bases on the yield of diethyl malonate are also discussed.

Keywords: Diethyl malonate, phase transfer agent, carbonylation.

Diethyl malonate (DEM) is an important starting material in pharmaceutical and agricultural chemical industries. Traditional synthetic method by reaction mono chloroacetic acid with sodium cyanide¹ is unfriendly to environment and involves complicated procedures. Therefore, green synthesis routes of diethyl malonate were investigated actively in past decade. There have been proposed various processes for preparing DEM by carbonylation of ethyl chloroacetate catalyzed by $\text{Co}_2(\text{CO})_8$ ^{2, 3}. However, $\text{Co}_2(\text{CO})_8$ must be prepared under high pressure, moreover the synthetic conditions of DEM were severe since EtONa was used as the base and the yield of DEM was not high. In this paper, palladium complex $\text{Pd}(\text{Ph}_3\text{P})_4$, which was easy to prepared⁴, was firstly employed as a catalyst for carbonylation of ethyl chloroacetate in the presence of phase transfer agent (Bu_4NI) and diethyl malonate was obtained under mild conditions in high conversion and very good selectivity.



Experimental

A three necked RB flask (100ml) fitted with a condenser was charged with $\text{Pd}(\text{Ph}_3\text{P})_4$ (0.107g, 0.093mmol), Bu_4NI (0.4576g, 1.24mmol) and NaHCO_3 (1.56g, 18.6mmol). It was flushed with CO for 15 min. then a mixture of $\text{C}_2\text{H}_5\text{OH}$ (18ml) and $\text{ClCH}_2\text{COOC}_2\text{H}_5$ (2ml, 18.6mmol) was added to the flask. Under CO flow (30ml/min), the reaction mixture was heated on water bath with stirring for 6 h. The reaction progress was monitored by G.C.- FID with a column of PEG-20M, then the reaction mixture was filtered. The product was purified by PLC on silica gel eluting with ethyl acetate/hexane=1:3 and identified by HP5973(GC/MS). All experiments were carried out under atmospheric pressure.

Result and Discussion

The effects of reaction temperature on the yield of diethyl malonate presented in **Table 1**. The results showed that the yield of DEM was increased with elevating temperature, when the temperature continued to rise to 80°C, it was decreased. The reason probably related to the evaporation of solvent.

Table 1. The effect of reaction temperature on the yield of DEM

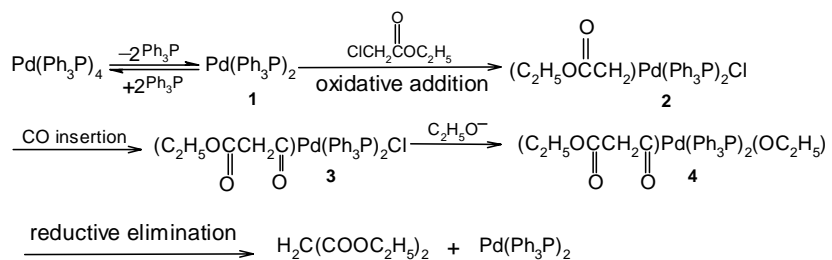
Temperature(°C)	55	65	70	80
Conversion. (%)	46	85	95	99
Yield (%)	27.6	72.3	93	67.6
Selectivity (%)	60	85	98	68.3

Alkaline reagents were necessary as a scavenger of hydrogen chloride which was formed during the reaction. We have tried different kinds of bases (**Table 2**) and found that NaHCO₃ was the best one.

Table 2. The effect of different kinds of bases on the yield of DEM

Base	Na ₂ CO ₃	NaHCO ₃	K ₂ CO ₃	NaOH	Et ₃ N
Conversion. (%)	85	95	80	100	0
Yield (%)	58.5	93	51	0	0
Selectivity (%)	68.8	98	62.8	0	0

The possible reaction mechanism was proposed as follows:



Pd(Ph₃P)₄ released two Ph₃P ligand groups in solvent to form complex **1** which possessed two vacancies, it was oxidized by ethyl chloroacetate to give compound **2**, this maybe a rate determined step, then CO inserted Pd-C bond to form acyl metal complex **3** which interacted with C₂H₅OH to obtain complex **4**, after reductive elimination, compound **4** converted to diethyl malonate and regenerate catalyst compound **1**.

The kinetic data and detail mechanism of this reaction are under further studies.

References

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