Tetrahedron Letters, Vol.31, No.10, pp 1485-1486, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

COBALT(II) CHLORIDE CATALYSED CONDENSATION OF ACETOACETATE WITH VINYLETHERS

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Summary : Cobalt(II) chloride catalyses the diastereoselective condensation of methylacetoacetate with vinyl ethers to give β-alkoxy carbonyl compounds or α, β-unsaturated compounds in excellent yields.

Metal promoted addition[1] of 1,3-dicarbonyl compounds to olefins is now a very well established method for a new carbon-carbon bond formation. The reaction between vinyl ethers[1d] and acetoacetates in presence of manganese(III) acetate leads to the formation of dihydrofurans in high yields. This reaction requires 2 equivalent of manganese(III) acetate and is believed to proceed via an oxidative free radical cyclisation process. In an attempt to conduct this reaction under catalysis by metal, we explored the possibility of effecting such transformation with Cobalt(II) complexes[1h]. Interestingly, we found that the reaction between methylacetoacetate and vinylethers in presence of catalytic quantity of Cobalt(II) chloride leads to the formation of β-alkoxy carbonyl compounds. A preliminary account of these findings are given below.

Methyl or ethylacetoacetate (10 mmol) and vinyl ethers (15 mmol) in dry acetonitrile (10 ml) are added dropwise to a stirring solution of dry Cobalt(II) chloride (≃ 30 mg) in dry acetonitrile (50 ml). The resulting mixture is stirred at ambient temperature (20°C) under nitrogen for 8-12 hours. Removal of acetonitrile yielded a residue which is taken into ether (80 ml) and the ether layer washed successively with saturated sodium bicarbonate solution and water. Drying ($MgSO_4$) and evaporation of ether gave a liquid which on column chromatography (SiO_2) yielded the β-alkoxy carbonyl compounds. The results are compiled in table. A variety of vinyl ethers are capable of reacting under these conditions to give excellent yield of β-alkoxy carbonyl compounds. In some cases these compounds readily undergo elimination to yield α, β-unsaturated compounds (table, entry 1,2 and 4). However, the yield of the elimination product can be enhanced by prolonging the reaction time (table, entry 1). This reaction is diastereoselective as the trans diastereomer is formed as a major product in all the cases. The method described here is superior to a recently published[2] acid mediated condensation of acetoacetates with dihydrofurans and pyrans. We are currently pursuing its application to organic synthesis.

Reference and Notes :

1.(a) E.I. Heiba, R.M. Dessau and R.M. Koehl, J. Am. Chem. Soc., 5905, **90**, (1968);
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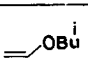
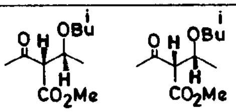
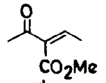
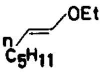
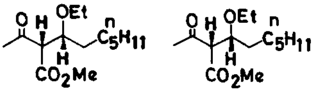
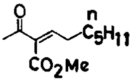
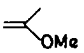
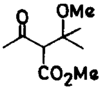
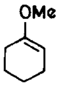
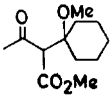
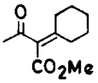
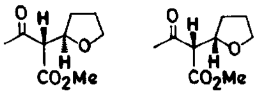
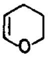
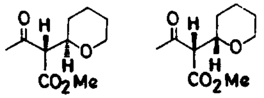
Table : Cobalt(II) chloride catalysed condensation of methylacetoacetate with vinyl ethers

entry	vinyl ether	Product (s) (yield %)^a ^{b}ratio^c	
		condensation	elimination
1		 (50)^d 3:1	 (42)^d (85)^e
2		 (63) 3.1:1	 (28)
3		 (87)^f	—
4		 (72)	 (15)
5		 (67) 2 : 1	—
6		 (78)^f 3 : 1	—

(a) Yield of the isolated product (b) All products had satisfactory ^{1}H NMR, IR and elemental analysis (c) The ratio of diastereomer where determined by ^{1}H NMR (300 MHz) (d) This yield is obtained by running the reaction for 12 hours (e) This yield is obtained by running the reaction for 20 hours (f) These products are obtained by distillation on Kugelrohr.

(c) E.J. Corey and A.W. Gross, Tetrahedron Lett., 4291, **26**, (1985);
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2.R. Bihovsky, M.U. Kumar, S. Ding and A. Goyal, J. Org. Chem., 4291, **54**, (1989).

(Received in UK 4 January 1990)