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ZINC CHLORIDE AS A NEW CATALYST FOR KNOEVENAGEL CONDENSATION+

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ABSTRACT: The knoevenagel condensation of carbonyl substrates with acidic methylene reagents proceeds smoothly in presence of zinc chloride, without the need for solvent, to produce products of good purity in high yield.

Knoevenagel condensation is a base catalysed reaction of importance in organic synthesis. It may be carried out either in homogeneous or heterogeneous phase. The usual catalysts are ammonia and ammonium salts, primary and secondary amines and their salts[1]. Subsequently the use of $TiCl_4$ and base[2], aluminium oxide[3] and $AlPO_4$-Al_2O_3[4] have been reported. Recently silica gel functionalised with amine groups has been used under heterogeneous catalysis conditions[5].

Surprisingly the potentiality of zinc chloride as a catalyst has not been tried so far. We have found that this common reagent can perform the reaction in a matter of minutes to produce the olefinic products in good purity and high yields (82-97.8%). The maximum yield reported in reference 4 is 80%. In the present work yields of the corresponding products are better than that in reference 5. This communication reports on the results of the reactions of malononitrile, cyanoacetamide, ethylcyanoacetate with a variety of aromatic aldehydes that proceeded smoothly without solvent, in presence of zinc chloride as catalyst (Table). Only E isomers were produced.

The general procedure is as follows: To a mixture of 0.01 mol of aldehyde and 0.01 mol of active methylene compound, zinc chloride (0.001 mol) was added and kept at 100° with constant stirring for the specified time (Table). Then the mixture was cooled to room temperature and treated with a solution of 1% aqueous alcohol to obtain the product in good purity. It was filtered and dried. Recrystallisation is not necessary.

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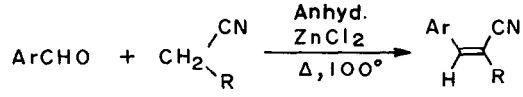
TABLE



Entry	Ar	R	Reaction time, min.	m.p. °C	Yield %
1	C_6H_5-	CN	10	88	90.9
2	4-$CH_3OC_6H_4$-	CN	10	119	97.4
3	4-ClC_6H_4-	CN	10	165	91.0
4	3-CH_3O-4-OHC_6H_3-	CN	10	132	95.0
5	C_6H_5-CH=CH-(E)	CN	10	130	97.2
6	C_6H_5-	$CONH_2$	20	121	93.0
7	4-$CH_3OC_6H_4$-	$CONH_2$	20	216	94.0
8	4-ClC_6H_4-	$CONH_2$	10	210	97.0
9	3-CH_3O-4-OHC_6H_3-	$CONH_2$	20	205	82.0
10	C_6H_5-CH=CH-(E)	$CONH_2$	20	142	96.0
11	C_6H_5-	COOEt	90	50	85.6
12	4-$CH_3OC_6H_4$-	COOEt	90	89	86.5
13	4-ClC_6H_4-	COOEt	25	93	97.8
14	3-CH_3O-4-OHC_6H_3-	COOEt	90	112	85.0
15	C_6H_5-CH=CH-(E)	COOEt	90	115	92.0

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References:

1. Jones, G. Organic Reactions, Wiley, New York, **1967**; Vol. 15, p.204.
2. Lehnert, W. Tetrahedron Letts., **1970**, 54, 4723.
3. Texier-Boullet, F.; Foucaud, A. Tetrahedron Letts., **1982**, 23, 4927.
4. Cabello, J.A.; Campelo, J.M.; Garcia, A.; Luna, D.; Marinas, J.M. J. Org. Chem., **1984**, 49, 5195.
5. Angeletti, I.; Canepa, C.; Martinetti, G.; Venturello, P. Tetrahedron Letts., **1988**, 29, 2261 and references therein.

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