SHORT PAPER

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Potassium phosphate as a catalyst for the Knoevenagel condensation[†]

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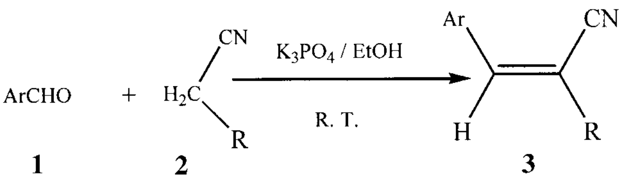
The Knoevenagel condensation of carbonyl compounds with active methylene compounds proceeds smoothly in presence of potassium phosphate in commercial absolute ethanol to afford the desired products of good purity in moderate to excellent yields.

The Knoevenagel condensation is one of the most important preparative methods for substituted alkenes. It may be carried out under either homogenous or heterogeneous conditions. The usual catalysts are organic bases[1] (primary, secondary and tertiary amines, ammonia and ammonium salts). Subsequently the use of $TiCl_4$,[2] Al_2O_3,[3] $AlPO_4$-Al_2O_3,[4] $ZnCl_2$,[5] and Cdl_2[6] *etc*. has been reported. Recently K10-$ZnC1_2$[7], silica gel[8], LiC1[9] and ammonium salts[10] *etc*. coupled with microwave irradiation without a solvent, has been shown to be an efficient method for the Knoevenagel condensation.

Surprisingly the potential of potassium phosphate as a catalyst has not, hitherto, been studied in the Knoevenagel condensation. We have found that this common commercially available reagent can catalyse the reaction to produce the corresponding alkenes in good purity and excellent yields (Table 1).



The results show that only the *E* isomers of the olefinic products were produced. In conclusion, the Knoevenagel condensation reported here is an attractive addition to existing methodologies since the reaction is rapid, the yields are excellent and the procedure is simple.

Experimental

Melting points were uncorrected. Infrared spectra were recorded using KBr pellet on a Perkin Elmer Spectrum One spectrometer. ^1H NMR spectra were recorded in $CDC1_3$ on a Bruker ARX 300 (300MHz) instrument with TMS as an internal standard. Furyl aldehyde was purified by distillation. All other chemicals used were of commercial grade without further purification.

General procedure for the Knoevenagel condensations: A mixture of the aldehyde (5 mmol), active methylene compound (5 mmol) and K_3PO_4 (0.25 mmol) was stirred at room temperature in absolute ethanol (10 ml) for the specified time in Table 1. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was poured into water. The solid materials were filtered off and treated with 1% aqueous alcohol in good purity without need of the further recrystallization.

3a: ^1H NMR($CDC1_3$) δ_H 1.40 (t, *J* 7.1Hz, 3H), 3.91 (s, 3H), 4.38 (q, *J* 7.1Hz, 2H), 7.00 (d, *J* 8.9Hz, 2H), 8.01 (d, *J* 8.9Hz, 2H), 8.12 (s, 1H) ppm; IR(KBr) ν_{max} 2216, 1717, 1586, 1262, 1211, 1185, 838 cm^{-1}.

3b: ^1H NMR($CDC1_3$) δ_H 1.41 (t, *J* 7.2Hz, 3H), 2.44 (s, 3H), 4.37 (q, *J* 7.2Hz, 2H), 7.31 (d, *J* 8.1Hz, 2H), 7.94 (d, *J* 8.1Hz, 2H), 8.23 (s, 1H) ppm; IR(KBr) ν_{max} 2216, 1725, 1594, 1270, 1208, 1188, 815 cm^{-1}.

3c: ^1H NMR($CDC1_3$) δ_H 1.43 (t, *J* 7.1Hz, 3H), 4.41 (q, *J* 7.1Hz, 2H), 7.50~7.59 (m, 3H), 8.00~8.03 (m, 2H), 8.28 (s, 1H) ppm; IR(KBr) ν_{max} 2223, 1726, 1606, 1444, 1256, 1200, 768 cm^{-1}.

3d: ^1H NMR($CDC1_3$) δ_H 1.42 (t, *J* 7.1Hz, 3H), 4.41 (q, *J* 7.1Hz, 2H), 7.68 (d, *J* 8.6Hz, 2H), 7.88 (d, *J* 8.6Hz, 2H), 8.21 (s, 1H) ppm; IR(KBr) ν_{max} 2222, 1723, 1611, 1582, 1265, 1203, 827 cm^{-1}.

3e: ^1H NMR($CDC1_3$) δ_H 1.42 (t, *J* 7.2Hz, 3H), 4.43 (q, *J* 7.2Hz, 2H), 8.14 (d, *J* 8.9Hz, 2H), 8.31 (s, 1H) 8.36 (d, *J* 8.9Hz, 2H) ppm; IR(KBr) ν_{max} 2226, 1721, 1616, 1593, 1515, 1347, 1267, 1202, 859 cm^{-1}.

3f: ^1H NMR($CDC1_3$) δ_H 1.39 (t, *J* 7.1Hz, 3H), 4.38 (q, *J* 7.1Hz, 2H), 6.67 (dd, *J* 1.7Hz, *J* 1.7Hz 1H), 7.40 (d, *J* 3.7Hz, 2H), 7.75 (d, *J* 1.6Hz, 1H), 8.03 (s, 1H) ppm; IR(KBr) ν_{max} 2223, 1716, 1620, 1261, 1212, 1025, 760 cm^{-1}.

3g: ^1H NMR($CDC1_3$) δ_H 3.89 (s, 3H), 7.04 (d, *J* 9.0Hz, 2H), 7.68 (s, 1H), 7.94 (d, *J* 9.0Hz, 2H) ppm; IR(KBr) ν_{max} 2222, 1605, 1571, 1278, 1184, 833 cm^{-1}.

Table 1 Knoevenagel reaction of aldehydes and active methylene compounds catalysed by potassium phosphate in the absolute ethanol

Entry	Ar (1)	R (2)	Reaction time h	m.p. °C	Lit. m.p. °C	Yields %[a]
a	4-MeO-C_6H_5	CO_2Et	1	79~81	79[4]	77
b	4-Me-C_6H_5	CO_2Et	1	90~92	90[4]	89
c	C_6H_5	CO_2Et	1	50~51	50[9]	83
d	4-C1-C_6H_5	CO_2Et	1	92~94	93[5]	85
e	4-NO_2-C_6H_5	CO_2Et	1	168~170	168[9]	91
f	2-Furyl	CO_2Et	0.5	89~91	93[4]	93
g	4-MeO-C_6H_5	CN	0.5	115~116	114[8]	82
h	4-Me-C_6H_5	CN	0.5	138~139	134[4]	70
i	C_6H_5	CN	0.5	82~84	83[6]	78
j	4-C1-C_6H_5	CN	0.5	161~163[4]	161	91
k	4-NO_2-C_6H_5	CN	0.5	159~160	159~160[6]	96

[a] Isolated yields.

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[*] To receive any correspondence.

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

3h: ^{1}H NMR(CDC1$_3$) δ_H 2.46 (s, 3H), 7.34 (d, *J* 8.1Hz, 2H), 7.72 (s, 1H), 7.81 (d, *J* 8.1Hz, 2H) ppm; IR(KBr) ν_{max} 2223, 1587, 1412, 1220, 815 cm^{-1}.

3i: ^{1}H NMR(CDC1$_3$) δ_H 7.54~7.56 (m, 2H), 7.64~7.71 (m, 1H), 7.81 (s, 1H), 7.91~7.94 (m, 2H) ppm; IR(KBr) ν_{max} 2223, 1590, 1566, 1216, 957, 755, 677 cm^{-1}.

3j: ^{1}H NMR(CDC1$_3$) δ_H 7.72 (d, *J* 8.7Hz, 2H), 7.74 (s, 1H), 7.78 (d, *J* 8.7Hz, 2H) ppm; IR(KBr) ν_{max} 2225, 1578, 1074, 823 cm^{-1}.

3k: ^{1}H NMR(CDC1$_3$) δ_H 7.89 (s, 1H), 8.07 (d, *J* 8.8Hz, 2H), 8.39 (d, *J* 8.8Hz, 2H) ppm; IR(KBr) ν_{max} 2230, 1604, 1580, 1521, 1343, 1212, 935, 850, 834 cm^{-1}.

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