SHORT PAPER

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Cellulose supported tetraethylenepentamine as a catalyst for the Knoevenagel condensation

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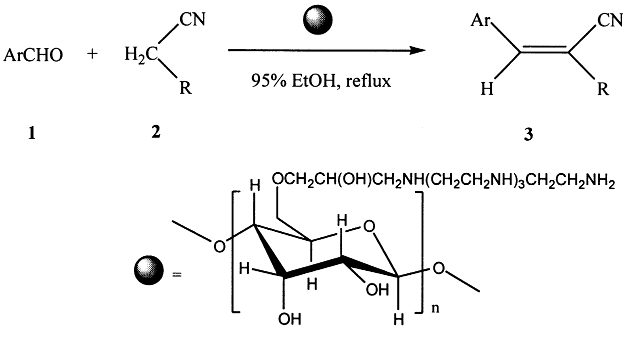
The Knoevenagel condensation of carbonyl substrates with active methylene compounds proceeds smoothly in commercial 95% ethanol and catalysed by cellulose supported tetraethylenepentamine to afford the desired products of good purity in moderate to excellent yields.

Keywords: cellulose supported tetraethylenepentamine, catalysis, Knoevenagel condensation

The knoevenagel condensation is one of the most important preparative methods for substituted alkenes. It may be carried out under either homogenous or heterogenous conditions. The usual catalysts are organic bases (primary, secondary and tertiary amines, ammonia and ammonium salts).[1] Subsequently the use of $AlPO_4$-Al_2O_3,[2] $ZnCl_2$,[3] K10-$ZnCl_2$,[4] KF,[5] LiCl,[6] polystyrene supported piperidine catalyst,[7] K_3PO_4,[8] H_2O/CTMA[9] and TEBA[10] *etc.* has been proven to be an efficient method for the Knoevenagel condensation.

Polymer supported reagents used as catalysts have gained wide interest in recent years. This is primarily because polymeric reagents provide convenience of work-up and product purification, lower the environmental hazards, and in most case provide for the reuse of polymer supported reagent without or after regeneration. But the main drawbacks with the resins currently employed are that they are based on petrochemicals and as such are not only hydrophobic, but also are prepared from non-renewable oil resources and most of them are non-biodegradable. Therefore we selected cellulose as an alternative matrix to prepare the polymer support reagent. This can be prepared from a renewable resource and moreover is biodegradable and benign to the environment.[11] Herein we reported the cellulose supported tetraethenepentamine catalysed a rapid, convenient and general synthesis of alkenes from aldehydes and active methylene (Scheme 1).



Scheme 1

The Knoevenagel condensation is performed under reflux in the presence of small amounts of the catalyst and gives the desired E-isomer products in excellent yields. After five times of repeated use, no decrease in the activity of the catalyst was observed. The results are summarised in Table 1.

Table 1 Knoevenagel reaction of aldehydes and active methylene compounds catalysed by cellulose supported tertlenetriamine

Entry	Ar (1)	R (2)	Time h	m.p. °C	Lit. m.p. °C	Yields[a] %
a	4-MeO–C_6H_4	CO_2Et	1	78–80	79–81[8]	79
b	4-HO–C_6H_4	CO_2Et	1	171–172	172.5–173[9]	89
c	4-HO–3-MeO-C_6H_3	CO_2Et	1	109–111	111–112[5]	91
d	4-Me_2N–C_6H_4	CO_2Et	1	124–125	124–126[5]	85
e	C_6H_5	CO_2Et	1	50–52	50–51[8]	81
f	4-Cl–C_6H_4	CO_2Et	1	91–93	92–94[8]	89
g	4-MeO–C_6H_4	CN	0.5	114–115	115–116[8]	86
h	4-HO–C_6H_4	CN	0.5	187–189	187–188[9]	87
i	4-HO–3-MeO-C_6H_3	CN	0.5	132–134	132[3]	78
j	4-Me_2N–C_6H_4	CN	0.5	178–179	179–180[9]	77
k	C_6H_5	CN	0.5	82–84	82–84[8]	83
l	4-Cl–C_6H_4	CN	0.5	160–162	161–163[8]	88

[a]isolated yields

In conclusion, the Knoevenagel condensation reported here is an attractive addition to existing methodologies since the reaction is rapid, the yields are excellent, the procedure is simple and the polymeric catalyst can be recovered and moreover it is benign to the environment.

Experimental

Melting points were uncorrected. ^1H NMR spectra were recorded in $CDCl_3$ on a DRX-400 MHz instrument with TMS as an internal standard. Benzaldehyde was purified by distillation. All other chemicals used were of commercial grade without further purification. The catalyst used here was prepared according to the literature.[12] The capacity of tetraethenepentamine was found to be 0.8 mmol/g of dry catalyst by microanalysis.

General procedure for the Knoevenagel condensations: A mixture of the aldehyde (10 mmol), active methylene compound (10 mmol) and catalyst (1.0 g) was stirred under reflux in commercial 95% aqueous ethanol (20 ml) for the specified time in table 1. After completion of the reaction, the catalyst was filtered off and washed with acetone for several times by suction. The filtrate was poured into water and the solid materials were filtered off and treated with 3% aqueous alcohol. The products were obtained in good purity without need of further recrystallisation.

3a: ^1H NMR ($CDCl_3$) δ_H 1.36 (t, 3H, J=7.2 Hz, CH_3), 3.87 (s, 3H, CH_3O), 4.34 (q, 2H, J=7. 2 Hz, CH_2), 6.79 (d, 2H, J=8.8 Hz, Ar-H), 7.98 (d, 2H, J=8.8 Hz, Ar-H), 8.15 (s, 1H,CH=) ppm

3b: ^1H NMR ($CDCl_3$) δ_H 1.38 (t, J=7.2 Hz, 3H, CH_3), 4.36 (q, J=7.2 Hz, 2H, CH_2), 6.26 (s, 1H, OH), 6.95 (d, J=8.8 Hz, 2H, Ar-H), 7.94 (d, J=8.8 Hz, 2H, Ar-H), 8.17 (s, 1H, CH=) ppm

3c: ^1H NMR ($CDCl_3$) δ_H 1.36 (t, J=7.2 Hz, 3H, CH_3), 3.94 (s, 3H, CH_3O-Ar), 4.34 (q, J=7.2 Hz, 2H, CH_2), 6.32 (s, 1H, OH), 6.96 (d, J=8.0 Hz, 1H, Ar-H), 7.37 (d, J=8.0 Hz, 1H, Ar-H), 7.81 (s, 1H, Ar-H), 8.11 (s, 1H, CH=) ppm.

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

3d: ^{1}H NMR ($CDCl_3$) δ_H 1.35 (t, *J*=7.2 Hz, 3H, CH_3), 3.08 (s, 6H, $(CH_3)_2N$), 4.31 (q, *J*=7.2 Hz, 2H, CH_2), 6.67 (d, *J*=9.0 Hz, 2H, Ar-H), 7.90 (d, *J*=9.0 Hz, 2H, Ar-H), 8.03 (s, 1H, CH=) ppm.

3e: ^{1}H NMR ($CDCl_3$) δ_H 1.43 (t, 3H, *J*=7.1 Hz, CH_3), 4.41 (q, 2H, *J*=7.1 Hz, CH_2), 7.50–7.59 (m, 3H, Ar-H), 8.00–8.03 (m, 2H, Ar-H), 8.28 (s, 1H, CH=) ppm.

3f: ^{1}H NMR ($CDCl_3$) δ_H 1.38 (t, 3H, *J*=7.2 Hz, CH_3), 4.36 (q, 2H, *J*=7.2 Hz, CH_2), 7.46 (d, 2H, *J*=8.6 Hz, Ar-H), 7.92 (d, 2H, *J*=8.6 Hz, Ar-H), 8.18 (s, 1H, CH=) ppm.

3g: ^{1}H NMR ($CDCl_3$) δ_H 3.90 (s, 3H, OCH_3), 6.99 (d, 2H, *J*=9.2 Hz, Ar-H), 7.63 (s, 1H, CH=), 7.89 (d, 2H, *J*=9.2 Hz, Ar-H) ppm.

3h: ^{1}H NMR($CDCl_3$) δ_H 5.83 (s, 1H, OH), 6.94 (d, *J*=8.8Hz, 2H, Ar-H), 7.63 (s, 1H, CH=), 7.85 (d, *J*=9.0Hz, 2H, Ar-H) ppm.

3i: ^{1}H NMR ($CDCl_3$) δ_H 3.96 (s, 3H, CH_3O), 6.38 (s, 1H, OH), 6.99 (d, *J*=8.0 Hz, 2H, Ar-H), 7.30 (d, *J*=8.0 Hz, 2H, Ar-H), 7.61 (s, 1H, Ar-H), 7.70 (s, 1H, CH=) ppm.

3j: ^{1}H NMR ($CDCl_3$) δ_H 3.12 (s, 6H, $(CH_3)_2N$), 6.66 (d, *J*=8.8 Hz, 2H, Ar-H), 7.43 (s, 1H, CH=), 7.78 (d, *J*=9.0 Hz, 2H, Ar-H) ppm.

3k: ^{1}H NMR($CDCl_3$) δ_H 7.54–7.56 (m, 2H, Ar-H), 7.64–7.71 (m, 1H, Ar-H), 7.81 (s, 1H, CH=), 7.91–7.94 (m, 2H, Ar-H) ppm.

3l: ^{1}H NMR($CDCl_3$) δ_H 7.49 (d, 2H, *J*=8.4 Hz, Ar-H), 7.71 (s, 1H, CH=), 7.83 (d, 2H, *J*=8.7 Hz, Ar-H) ppm.

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Preparation of catalyst: Commercial cellulose (3g) was swelled in 30% aqueous sodium hydroxide (100cm^3) for 1h. The resin was collected and washed with 8% aqueous sodium hydroxide. Epichlorohydrin (9g) was added and the suspension was stirred for 10h. The resin was filtered, washed with water, acetone and dried at 70°C. The resin (1g) and heated to 40°–50°C for 2h. It was filtered and washed with water and dried at 70°C. The resin contained 0.8mmol/g dry resin of Tetraethylene pentamine.