SHORT PAPER

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Knoevenagel condensation in the heterogeneous phase using KF-montmorillonite as a new catalyst†

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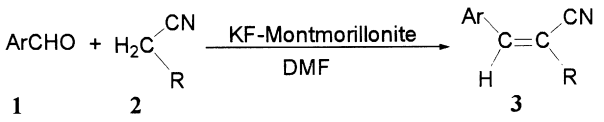
The Knoevenagel condensation of aromatic aldehydes was carried out in DMF as solvent on KF-Montmorillonite catalyst, using malononitrile and ethyl cyanoacetate as the acidic methylene reagents. Only the *e* isomers of the products were obtained and confirmed by X-ray analysis.

Keywords: Knoevenagel condensation, KF-montmorillonite

The Knoevenagel condensation of carbonyl compounds with acidic methylene compounds is one of the most important synthetic methods for substituted alkenes. Reactions are generally catalysed by base or Lewis acids.[1] Recently, inorganic solid supports as catalysts, resulting in higher selectivity, milder conditions and easier work-up have been reported as useful catalysts for Knoevenagel reaction. Thus, aluminium oxide[2], potassium *t*-butoxide–xonotlites,[3] $AlPO_4$-Al_2O_3,[4] KF-Al_2O_3,[5] K10-$ZnCl_2$[6] and cadmium iodide[7] have been reported. We now describe the application of the KF-montmorillonite solid system as the basic catalyst for Knoevenagel condensation in the heterogeneous phase.

When aromatic aldehydes (**1**), malononitrile or ethyl cyanoacetate (**2**) and KF-montmorillonite were kept at 80°C for 3h in DMF(Scheme 1), the desired substituted alkenes (**3**) were obtained in good yields.



Scheme 1

Table 1 Yields of the products

Entry	Ar	R	Isolated yield/%
3a	4–Cl–C_6H_4	COOEt	86
3b	4–$O_2NC_6H_4$	COOEt	89
3c	3,4–$(CH_3O)_2C_6H_3$	COOEt	88
3d	3,4–$OCH_2OC_6H_3$	COOEt	90
3e	2–furyl	COOEt	74
3f	4–ClC_6H_4	CN	86
3g	3,4–$OCH_2OC_6H_3$	CN	92
3h	4–$CH_3C_6H_4$	CN	73
3l	4–$CH_3OC_6H_4$	CN	85
3j	2–ClC_6H_4	CN	73

When the ethyl cyanoacetate was used as the acidic methylene reagents, Only the *E* isomers of the products were obtained. The configuration of **3c** was confirmed by X-ray analysis.[8] Thus the Knoevenagel condensation catalysed by KF-montmorillonite was stereoselective.

Experimental

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a FT IR-8101 spectrometer. ^{1}H NMR spectra were measured on a JEOL FX-90Q spectrometer using TMS as internal standard. Microanalyses were carried out using Carlo Erba 1110 analyzer. X-ray diffraction were measured on a Siemens P4 diffractometer.

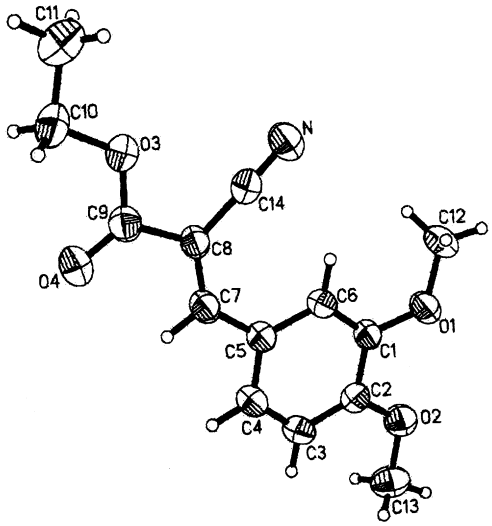


Fig. 1 X-ray crystal structure of **3c**.

General procedure for preparation of KF-montmorillonite: To a solution of KF (58g) in water (100ml) was added montmorillonite (100g) with stirring. The mixture was stirred for 1 hour at 80°C, then the solvent was evaporated and the solid was dried for 4 hour at 120°C to give KF-montmorillonite.

General procedure for synthesis substituted alkenes **3**: A dry 100-ml flask was charged with aromatic aldehydes (**1**) (5mmol), malononitrile or ethyl cyanoacetate (**2**) (5mmol), KF-montmorillonite and DMF (20ml). The mixture was stirred at 80°C for 3h. Then cooled to room temperature, the solid material was filtered off and was washed with DMF. The filterate was poured into 200ml water. The white solid was filtered off, then washed with water. The crude solid was purified by recrystallisation from 95% EtOH to give (**3**).

3a: m.p. 92–94°C; (Lit. [4] m.p. 90°C);IR (KBr, ν, cm^{-1}): 3030, 2990, 2225, 1725, 1610, 1590, 1490, 1265, 1205, 1080, 830; ^{1}H NMR ($CDCl_3$, δ, ppm): 1.40(3 H, t, *J*=7Hz, CH_3), 4.38 (2 H, q, *J*=7Hz, CH_2O), 7.46 (2 H, d, *J*=8Hz, ArH) 7.93 (2 H, d, *J*=8Hz, ArH), 8.18 (1 H, s, -CH=).

3b: m.p. 171–172°C; (Lit. [4] mp 168°C);IR (KBr, ν, cm^{-1}): 3040, 2980, 2220, 1720, 1590, 1510, 1350, 1265, 1205, 860; ^{1}H NMR ($CDCl_3$, δ, ppm): 1.41(3 H, t, *J*=7Hz, CH_3), 4.42 (2 H, q, *J*=7Hz, CH_2O), 8.09–8.40 (5 H, d, *J*=8Hz, ArH and –CH=).

3c: m.p. 138–140°C; IR (KBr, ν, cm^{-1}): 3010, 2980, 2225, 1725, 1590, 1510, 1450, 1370, 1270, 1240, 1190, 1090, 1030, 850, 830, 760; ^{1}H NMR ($CDCl_3$, δ, ppm): 1.39(3 H, t, *J*=7Hz, CH_3), 3.96(6 H, s, 2×CH_3O), 4.37 (2 H, q, *J*=7Hz, CH_2O), 6.94 (1 H, d, *J*=8Hz, ArH) 7.48 (1 H, dd, *J*=8Hz, *J*'=2Hz, ArH), 7.80(1 H, d, *J*=2Hz, ArH), 8.16 (1 H, s, -CH=), (Found: C, 64.50; H, 5.99; N, 5.24. $C_{14}H_{15}NO_4$ requires C, 64.37; H, 5.79; N, 5.36%).

3d: m.p. 107–108°C; (Lit. [9] m.p. 109–108°C);IR (KBr, ν, cm^{-1}): 3030, 2925, 2225, 1725, 1620, 1590, 1505, 1450, 1370, 1280, 1240, 1190, 1090, 1040, 930, 850, 820, 760; ^{1}H NMR ($CDCl_3$, δ, ppm):

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

1.38(3 H, t, *J*=7Hz, CH_3), 4.36 (2 H, q, *J*=7Hz, CH2O), 6.08 (2 H, s, OCH_2O), 6.89 (1 H, d, *J*=8Hz, ArH) 7.40 (1 H, dd, *J*=8Hz, *J'*=2Hz, ArH), 7.66(1 H, d, *J*=2Hz, ArH), 8.08 (1 H, s, -CH=).

3e: m.p. 90–92°C; (Lit. [4] mp 93°C);IR (KBr, ν, cm^{-1}): 3030, 2990, 2225, 1715, 1610, 1290, 1260, 1210, 1090, 1020, 760; ^{1}H NMR ($CDCl_3$, δ, ppm): 1.38(3 H, t, *J*=7Hz, CH_3), 4.36 (2 H, q, *J*=7Hz, CH_2O), 6.66 (1 H, dd, *J*=4Hz, *J'*=2Hz, ArH), 7.40 (1 H, d, *J*=4Hz, ArH), 7.74 (1 H, d, *J*=2Hz, ArH), 8.01 (1 H, s, -CH=).

3f: m.p. 162–164°C; (Lit. [4] m.p. 161°C);IR (KBr, ν, cm^{-1}): 3030, 2885, 2225, 1580, 1490, 1410, 1290, 1095, 825; ^{1}H NMR ($CDCl_3$, δ, ppm): 7.52 (2 H, d, *J*=8Hz, ArH), 7.78 (2 H, d, *J*=8Hz, ArH), 7.97 (1 H, s, -CH=).

3g: m.p. 198–199°C; IR (KBr, ν, cm^{-1}): 3030, 2850, 2225, 1610, 1570, 1505, 1495, 1460, 1290, 1115, 1035, 925, 850, 815; ^{1}H NMR ($CDCl_3$, δ, ppm): 6.12(2 H, s, OCH_2O), 6.70–7.26 (3 H, m, ArH), 7.61 (1 H, s, -CH=), (Found: C, 66.79; H, 2.93; N, 14.02. $C_{11}H_6N_2O_2$ requires C, 66.66; H, 3.05; N, 14.14%).

3h: m.p. 136–137°C; (Lit. [4] m.p. 134°C);IR (KBr, ν, cm^{-1}): 3030, 2850, 2225, 1605, 1590, 1560, 1510, 1225, 1190, 810, 710; ^{1}H NMR ($CDCl_3$, δ, ppm): 2.47(3 H, s, CH_3), 7.48 (2 H, d, *J*=8Hz, ArH), 7.96 (2 H, d, *J*=8Hz, ArH), 8.30 (1 H, s, -CH=).

3i: m.p. 114–115°C; (Lit. [4] m.p. 113°C);IR (KBr, ν, cm^{-1}): 3030, 2850, 2225, 1605, 1570, 1560, 1520, 1320, 1280, 1180, 1020, 835; ^{1}H NMR ($CDCl_3$, δ, ppm): 3.92 (3 H, s, OCH_3), 7.01 (2 H, d, *J*=9Hz, ArH), 7.75 (2 H, d, *J*=9Hz, ArH), 8.01 (1 H, s, -CH=).

3j: m.p. 95–97°C; IR (KBr, ν, cm^{-1}): 3030, 2880, 2225, 1580, 1560, 1460, 1440, 1220, 1050, 1020, 960, 760; ^{1}H NMR ($CDCl_3$, δ, ppm): 7.14–8.17 (4 H, m, ArH), 8.27 (1 H, s, -CH=), (Found: C, 63.80; H, 2.51; N, 14.62. $C_{11}H_6N_2O_2$ requires C, 63.68; H, 2.67; N, 14.86%).

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8 X-ray crystallography for **3c**: Empirical formula $C_{14}H_{15}NO_4$, F_W =261.27, T=293(2)K, monoclinic, space group P2(1)/n, *a*=13.101(3)Å, *b*=8.032(2)Å, *c*=13.854(2) Å, α=90°, β=114.21(1)°, γ=90°, *V*=1329.6(5)$Å^3$, *Z*=4, *Dc*=1.305Mg/m^3, λ(*MoK*α)= 0.71073Å, μ= 0.096 mm^{-1}, *F(000)*=552. 1.80° < θ < 25.00°, *R*=0.0389, *wR*=0.0816. *S*=0.846, Largest diff. Peak and hole: 0.124 and –0.136 e. $Å^{-3}$.
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