

Electronic Supplementary Information

Validation of GC methods for quantifying 3,4-dihydro-2H-pyran, benzaldehyde, 2-ethoxy-tetrahydro-2H-pyran and phenylmethylene diacetate

3,4-Dihydro-2H-pyran (2.5302 g) benzaldehyde (2.5251 g) 2-ethoxy-tetrahydro-2H-pyran (2.5036 g) phenylmethylene diacetate (2.4968 g) were weighed into 100 ml volumetric flasks, and made up to volume with absolute ethanol, and designated as stock solutions (A-D). Multi-compound standards were made up from 0.1 g/L to 100 g/L. Detector response curves are shown below, per mol/L (Figure 1), and per g/L (Figure 2). The final response factors obtained were [2-ethoxy-tetrahydro-2H-pyran]/[3,4-Dihydro-2H-pyran] = 1.17 and [phenylmethylene diacetate]/[benzaldehyde] = 1.30.

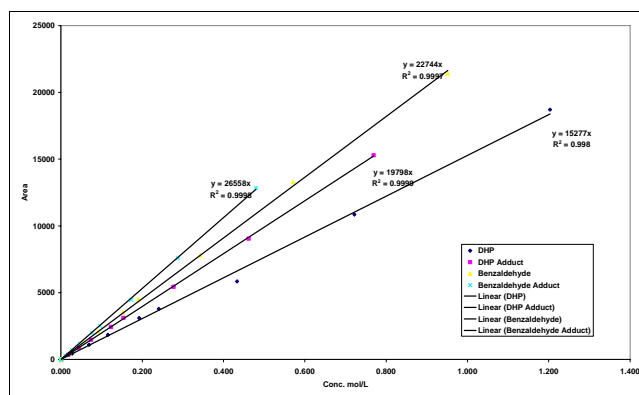


Fig. 1 Detector response per mol/L of compound for DHP, DHP adduct, BA and BA adduct.

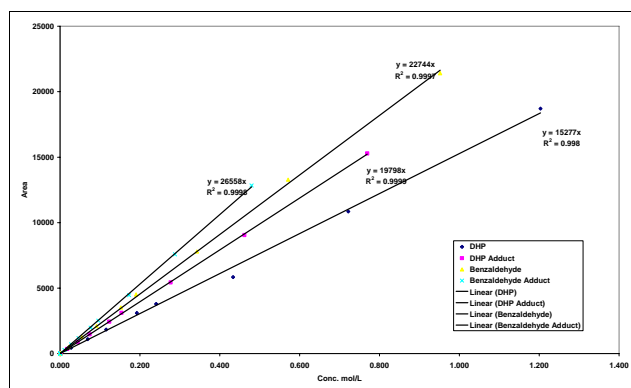


Fig. 2 Detector response per g/L of compound for DHP, DHP adduct, BA and BA adduct.

Inductively coupled plasma – optical emission spectroscopy (ICP-OES) of supernatants from acid-treatment of K-10

Supernatants of acid-treatments were analysed by ICP-OES at the ASIRC laboratories, Monash University Gippsland Campus. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was carried out using a Varian VistaPro ICP-OES with simultaneous CCD and axial view

torch detectors. Elements analysed included Ti, Na, Mg, K, Fe, Ca and Al. Standards were made from 1000 ppm solutions of each element, with standards bracketing every 20 samples. Results are shown below (Table 1).

Table 1 Concentration of analysed elements in acid-treatment supernatants, as determined by ICP-OES (with average deviation in parentheses)

Element (wavelength)	K-10A1 (mg/L)	K-10A2 (mg/L)	K-10A3 (mg/L)	K-10A4 (mg/L)
Al (av 237/396)	3.26 (0.59)	20.23 (0.33)	58.79 (5.24)	541.73 (12.43)
Ca 422.673	124.35 (12.35)	153.25 (1.05)	152.40 (1.50)	299.85 (7.85)
Fe 259.940	5.62 (0.95)	17.72 (0.18)	65.48 (2.64)	281.55 (0.65)
K 769.897	6.84 (0.34)	9.61 (0.59)	12.30 (0.65)	23.65 (0.21)
Mg 280.270	53.86 (4.07)	62.92 (0.34)	62.20 (0.54)	193.20 (1.00)
Na 568.821	10.78 (1.15)	14.25 (0.07)	13.95 (0.19)	23.95 (0.49)
Ti 336.122	0.00 (0.00)	0.24 (0.00)	1.14 (0.08)	4.85 (0.16)

Transacetalisation of pantolactone with methyl-2,3-dideoxy-4,6-O-methylene- α -D-erythro-hex-enopyranoside

Pantolactone (~0.450 g) and methyl-2,3-dideoxy-4,6-O-methylene- α -D-erythro-hex-enopyranoside (~0.200 g) were dissolved in dry toluene (5 mL) followed by the addition of 1) K-10A 2) K-10B 3) 1.0 M HCl K-10A 4) 10 M HCl K-10A 5) silica gel 6) 0.1 M HCl silica gel (~0.060 g, 30 % wt) and activated 3 Å molecular sieves. The reaction mixture was heated to 75 °C for 1 hour. GC samples were taken at a:15, b:30 and c:60 minutes. Analysis by GC revealed the following conversion results (Figure 3). The ratio of α and β isomers was 2:1.

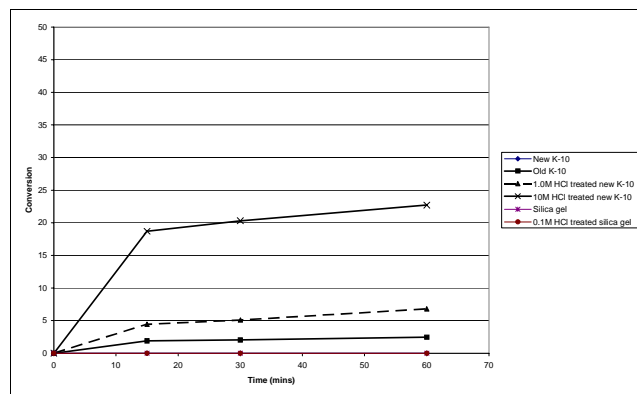


Fig. 3 Transacetalisation of pantolactone, conversion (%) over time.

Powder-XRD comparison of an 'old' batch of K-10 montmorillonite with a 'new' batch of K-10 montmorillonite, and acid-treatment of 'new' K-10

Powder-XRD spectra were obtained for both the 'old' bottle of K-10 (**K-10B**) (28,152-2 batch 11007BI) and the 'new' bottle (**K-10A**) (28,152-2 batch 03412CA). Samples were prepared as pellets in aluminium sample holders, front-loaded. Powder-XRD spectra were collected on a Philips PW1140 diffractometer from 2 – 70° 2 theta with a step size of 0.02° using a copper x-ray source. Slits used were 1° divergence, 1° receiving and 0.2° scatter. The spectra appear below (Figure 5).

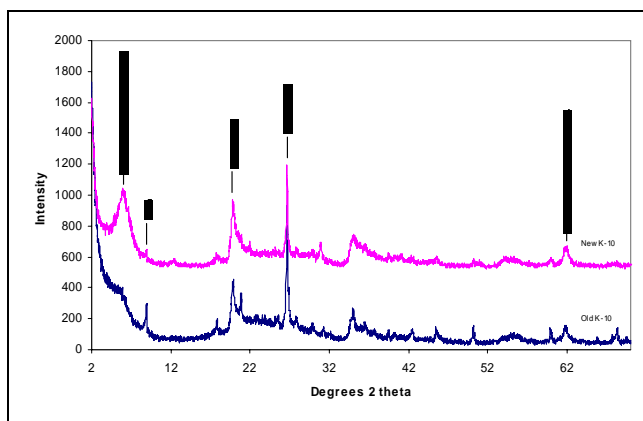
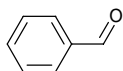


Fig. 5 Powder-XRD spectra of 'old' K-10 (**K-10B**) and 'new' K-10 (**K-10A**) montmorillonite.

Following the characterisation of the 'new' K-10 montmorillonite by powder-XRD, this materials was subjected to acid treatments. 'New' K-10 was weighed out into two ~5 g portions. One portion was subjected to stirring in 100 ml of 1.0 M HCl and the other in 10 M HCl. The suspensions were stirred for 6 hours, and solids recovered by centrifugation, repeated washing until free of halide ions (AgNO_3), and drying in a vacuum oven at 120 °C.

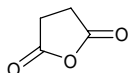
Compound information



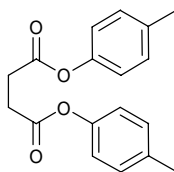
Benzaldehyde $^1\text{H NMR}$ (CDCl_3) δ : 7.56, 2H, m, C(3,5)-H; 7.64, 1H, m, C(4)-H; 7.87, 2H, m, C(2,6)-H; 10.02, 1H, s, C(7)-HO.



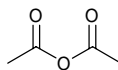
3,4-Dihydro-2H-pyran $^1\text{H NMR}$ (CDCl_3) δ : 1.846, 2H, C(3)-H; 1.984, 2H, C(4)-H; 3.957, 2H, C(2)-H; 4.644, 1H, C(5)-H; 6.342, 1H, C(6)-H.



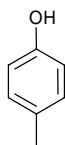
Succinic anhydride $^1\text{H NMR}$ (CDCl_3) δ : 3.006, 4H, s, C(3,4)-H.



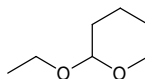
Succinic acid, di-p-tolyl ester $^1\text{H NMR}$ (CDCl_3) δ : 2.247, 6H, s, CH_3 ; 2.892, 4H, s, C(3,4)-H; 6.865 - 7.096, 8H, dd, Ar-H.



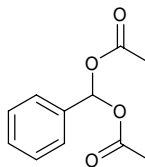
Acetic anhydride IR¹ (liquid film) 3660, 3567, 3025, 2942, 2119, 1827, 1766, 1647, 1542, 1430, 1370, 1226, 1124, 1046, 997, 897, 809, 799, 784, 651, 596, 563, 543, 529 cm^{-1} . $^1\text{H NMR}$ (CDCl_3) δ : 2.219, 6H, s, CH_3 .



p-Cresol (lit² m.p. 35-36 °C). IR¹ (liquid film) 3333, 3322, 3036, 3026, 2948, 2922, 2867, 2736, 2724, 2707, 2694, 2594, 2462, 1876, 1614, 1600, 1514, 1463, 1436, 1361, 1296, 1237, 1172, 1115, 1106, 1042, 1016, 841 cm^{-1} . $^1\text{H NMR}$ (CDCl_3) δ : 2.267, 3H, s, C(7)-H₃; 5.10, 1H, s, C(1)-OH; 6.731, 2H, d, C(2,6)-H; 7.028, 2H, d, C(3,5)-H.



2-Ethoxytetrahydro-2H-pyran $^1\text{H NMR}$ (CDCl_3) δ : 1.246, 3H, t, CH_3 ; 1.529 – 1.568, 6H, m, C(3,4,5)-H; 3.476, 2H, m, C(8)-H; 3.619 – 3.846, 2H, m, C(6)-H; 4.599, 1H, m, C(2)-H.



Phenylmethylene diacetate (lit³ m.p. 44-45 °C). $^1\text{H NMR}$ (CDCl_3) δ : 2.014, 3H, s, CH_3 ; 2.216, 3H, s, CH_3 ; 7.381 – 7.679, 5H, m, Ar-H; 8.032, 1H, s, C(7)-H.

References

- 1 National Institute of Advanced Industrial Science and Technology (AIST), in 'Spectral Database for Organic Compounds', 2006.
- 2 W. Kotlarek, *Pol. J. Chem.*, 1983, **57**, 809-815.
- 3 L. Yin, Z.-H. Zhang, Y.-M. Wang, and M.-L. Pang, *Synlett*, 2004, **10**.