SHORT PAPER

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A convenient and improved montmorillonite K-10 catalysed Friedel–Crafts benzylation and allylation with activated esters

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Benzyl benzoate and cinnamyl acetate has been effectively used respectively as alkylating and allylating substrates in Friedel–Crafts reaction catalysed by montmorillonite K-10 clay.

Keywords: montmorillonite K-10 clay, Friedel–Crafts reaction, activated esters

Recent decades have witnessed exponential growth in the application of heterogeneous catalysis to carry out synthetic transformations as a consequence of its significance in terms of enviro-economical and practical aspects.[1,2] In particular, the scenario of Friedel–Crafts alkylation/allylation reaction, a versatile tool for substituting aromatic rings,[3-6] has undergone a dramatic change with the advent of heterogeneous catalysis.[7-9] The attribute of heterogeneous catalyst has led to the development of montmorillonite K-10 clay as an efficient catalyst for variety of environmentally benign organic reactions.[10-12]

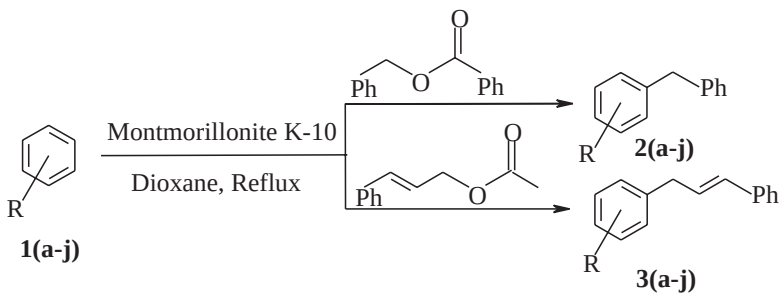
The "demonstrative use" of montmorillanite K-10 for Friedel–Crafts reactions with different alcohols leads to mixture of products.[13] Although cinnamyl acetate and benzyl benzoate are very attractive alkylating substrates compared to the corresponding alkyl halides, their use in conventional Friedel–Crafts reactions is not widespread. In continuation of our interest[14] in Montmorillonite K-10, herein we wish to report its use in the benzylation and allylation of aromatic compounds with benzyl benzoate and cinnamyl acetate respectively (Scheme 1).

The reaction of anisole with benzyl benzoate in dioxane was chosen as a model reaction for our study. The reaction stops with monobenzylation and does not proceed for formation of di or poly-alkylated products.

Having succeeded with benzyl benzoate, the reaction was investigated for cinnamyl acetate for allylation with activated arenes (Scheme 1). As anticipated, allylated products were obtained but in the moderate yields.

In order to study the general attributes of this methodology, several substituted benzenes were subjected to benzylation and allylation reaction. The results are summarised in Table 1. The electron density on aromatic ring was shown to have considerable effect on the yield and time of reaction. Highly activated methoxybenzenes undergo benzylation and allylation reactions with shorter reaction time in good yields compared to alkyl benzenes. In both cases, there is no formation of polyalkylation/allylation products. However, a mixture of *ortho* and *para* substituted products are formed in the case of mono-substituted arenes (entry a, d, i). No side products were obtained from isomerisation of double bond in allylation reaction. It is remarkable that phenols (entry i–j) undergo nuclear allylation/benzylation rather than O-alkylation under the reaction conditions to give *para*-allylation product in major yield, which is in contrast to the previously reported method.[5] In comparison to the conventional catalysts such as $AlCl_3$, BF_3, HF and conc. H_2SO_4 catalysed Friedel–Crafts reactions, the extent of the formation of undesired products from side reactions such as polyalkylation, polymerisation, isomerisation, *etc*. was found to be minimum with the montmorillonite K-10 catalysed reaction.[15]

In conclusion, Friedel-Crafts reactions mediated by montmorillonite K-10 using unconventional alkylating substrates like benzyl benzoate and cinnamyl acetate provide a viable route to synthesise valuable fine chemicals. Furthermore this method is advantageous because of easy separation, consistent yield and minimum environmental effects.



Scheme 1

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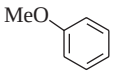
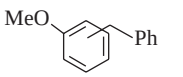
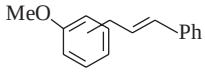
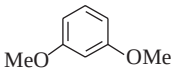
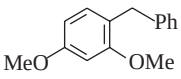
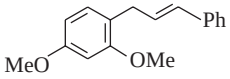
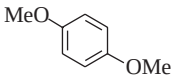
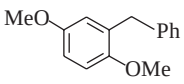
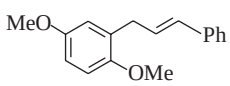
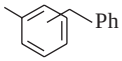
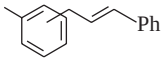
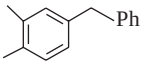
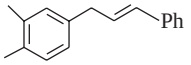
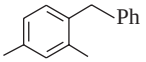
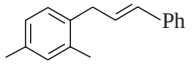
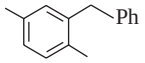
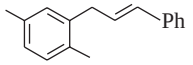
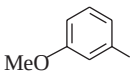
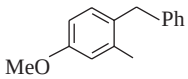
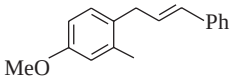
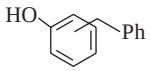
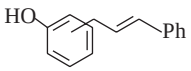
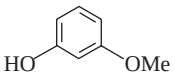
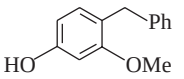
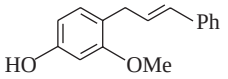
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Benzylation and allylation of arenes catalysed by montmorillonite K-10

Sample no.	Arenes (1)	Benzylation product (2)	Allylation product (3)	Time/h (2)	Time/h (3)	Yield/%[a] (*ortho*:*para*)[b] (2)	Yield/%[a] (*ortho*:*para*)[b] (3)
a				0.5	1.0	88 (1:3)	81 (1:3)
b				0.5	1.0	86	77
c				0.7	1.5	80	73
d				4.0	3.0	74 (1:3)	69 (1:3)
e				3.0	4.0	77	68
f				3.0	3.0	80	71
g				3.0	4.0	76	70
h				1.0	2.0	81	78
i				2.0	3.0	82 (1:3)	75 (1:3)
j				2.0	2.5	83	72

[a] Yield refers to isolated products.
[b] Identified by ^{1}H NMR spectroscopy.

Experimental

Montmorillonite K-10 was purchased from Fluka and dried at 100^{0}C prior to use. All chemicals were of commercial quality from freshly opened container or distilled before use.

IR spectra were recorded on a Perkin-Elmer 137-E spectrometer. The ^{1}H NMR spectra were recorded on a Bruker 300 MHz instrument and the chemical shifts were reported with TMS as an internal standard.

Typical procedure: A mixture of arene (10 mmol), benzyl benzoate (10 mmol) or cinnamyl acetate (10 mmol) and montmorillonite K-10 catalyst (500 mg) in dioxane (20 ml) was refluxed for the time mentioned in Table I. The reaction was monitored by TLC. After completion of reaction, the catalyst was filtered and the filtrate was washed with 10% $NaHCO_3$ solution. The resulting solution was then extracted with CH_2Cl_2 (2 × 15 ml), dried over anhydrous sodium sulfate and purified by column chromatography over silica (95:5, pet ether: ethyl acetate) to give viscous colourless liquid as a final alkylated product.

Representative spectral analysis 4–Benzylanisole[16] **(2a):** ^{1}H NMR: δ 3.41 (3H, s), 4.92 (2H, s), 7.21–7.34 (5H, m), 7.43–7.61 (4H, m). IR (cm^{-1}, Neat) : 3027, 2968, 2936, 1630. 1472, 1248, 840, 753. Anal. Calcd for $C_{14}H_{14}O$: C, 84.84; H, 7.07. Found: C, 84.59; H, 7.16.

3-(4-Methoxyphenyl)-1-phenylpropene[17] **(3a)**: ^{1}H NMR: δ 3.39 (3H, s), 4.1 (2H, d, *J* = 6.5), 6.23 (1H, dt, *J* = 15.3, 6.5), 6.31 (1H, d, *J* = 15.3), 7.10–7.21 (5H, m), 7.29–7.41 (4H, m). IR (cm^{-1}, Neat): 3010, 2961, 2915, 1625, 1458, 1210, 823, 720. Anal. Calcd for $C_{16}H_{16}O$: C, 85.71; H, 7.14. Found: C, 85.68; H, 7.08.

3-Methoxy-4-benzylanisole **(2b):** ^{1}H NMR: δ 3.12 (3H, s), 3.31 (3H, s) 4.67 (2H, s), 6.84–7.31 (5H, m), 7.72–7.89 (3H, m). IR (cm^{-1}, Neat): 3014, 2954, 2928, 1638, 1410, 1248, 828, 752. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.94; H, 7.01. Found: C, 78.92; H, 7.23.

3-(2,4–Dimethoxyphenyl)-l-phenylpropene **(3b):** ^{1}H NMR: δ 3.51 (3H, s), 3.68 (3H,s), 3.95 (2H, d, *J*=7.1), 6.45 (1H, dt, *J*=15.1, 7.1), 6.21 (1H, d, *J* = 15.1), 7.2–7.6 (8H, m). IR (cm^{-1}, Neat): 3028, 2963, 2928, 1642, 1470, 1220, 854, 710. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.31; H, 7.08. Found: C, 80.24; H, 7.23.

4-Methoxy-2-benzylanisole[18] **(2c)**: ^{1}H NMR: δ 3.16 (3H, s), 3.23 (3H, s), 4.82(2H, s), 7.02–7.62 (8H, m). IR (cm^{-1}, Neat): 3023, 2982, 2957, 1617, 1443, 1252, 827, 734. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.94; H, 7.01. Found: C, 78.86; H, 7.18.

3-(2,6-Dimethoxyphenyl)-1-phenylpropene **(3c)**: ^{1}H NMR: δ 3.49 (3H, s), 3.31 (3H, s), 4.12 (2H, d, *J* = 6.9), 6.43 (1H, dt, *J*=15.2, 6.9), 6.23 (1H, d, *J* = 15.2), 7.23–7.61 (8H, m), IR (cm^{-1}, Neat): 3017, 2960, 2928, 1631, 1464, 1246, 842, 769, 721. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.31; H, 7.08. Found: C, 80.32; H, 7.12.

4-Benzyltoluene[19] **(2d)**: ^{1}H NMR: δ 2.21 (3H, s), 4.6 (2H, s), 7.02–7.30 (9H, m). IR (cm^{-1}, Neat): 3018, 2972, 2947, 1629, 1431, 852, 771. Anal. Calcd for $C_{14}H_{14}$: C, 93.33; H, 7.77. Found: C, 93-18; H, 7.65.

3-(4-Methylphenyl)-1-phenylpropene[6] **(3d)**: ^{1}H NMR: δ 2.32 (3H, s), 3.50 (2H, d, *J* = 6.6), 6.34 (1H, dt, *J*=15.8, 6.6), 6.42 (1H, d, *J* = 15.8), 7.03–7.21 (5H, m), δ 7.23–7.36 (4H, m). IR (cm^{-1}, Neat): 3015, 2953, 2927, 1622, 1437, 1257, 820, 773. Anal. Calcd for $C_{16}H_{16}$: C, 92.30; H,7.69. Found: C, 92.27; H, 7.63.

2-Methyl-4-benzyltoluene[19] **(2e):** ^{1}H NMR: δ2.21 (3H, s), 2.46 (3H, s), 4.13(2H, s), 7.02–7.39 (8H, m). IR (cm^{-1}, Neat): 3030, 2986, 2923, 1601, 1503, 1150, 930, 750. Anal. Calcd for $C_{15}H_{16}$: C, 91.83; H, 8.16. Found: C, 91.76; H, 8.19.

3-(3,4-Dimethylphenyl)-1-phenylpropene **(3e)**: ^{1}H NMR: δ 2.17 (3H, s), 2.41 (3H, s), 3.54 (2H, d, *J* = 6.9), 6.27 (1H, dt, *J* = 15.4, 6.9), 6.47 (1H, d, *J* = 15.4), 7.08–7.45 (8H, m). IR (cm^{-1}, Neat): 3010, 2952, 2938, 1633, 1426, 1231, 1024, 872, 653. Anal. Calcd for $C_{17}H_{18}$: C, 91.89; H, 8.10. Found: C, 91.72; H, 8.07.

3-Methyl-4-benzyltoluene[19] **(2f)**: ^{1}H NMR: 2.24 (3H, s), 2.33 (3H, s) 4.57 (2H, s), 7.12–7.59 (8H, m). IR (cm^{-1}, Neat): 3012, 2969, 2897, 1619, 1456, 892, 819, 712. Anal. Calcd. for $C_{15}H_{16}$: C, 91.83 ; H, 8.16. Found: C, 91.87; H, 8.13.

3-(2,4-Dimethylphenyl)-1-phenylpropene **(3f)**: ^{1}H NMR: δ 2.16 (3H, s), 2.27 (3H,s), 3.89 (2H, d, *J* = 7.1), 6.41 (1H, dt, *J*=15.2, 7.1), 6.59 (1H, d, *J* = 15.2), 7.10–7.63 (8H, m). IR (cm^{-1}, Neat): 3014, 2979, 2932, 1623, 1482, 1428, 842, 712. Anal. Calcd for $C_{17}H_{18}$: C, 91.89; H, 8.10. Found: C, 91.81; H, 8.13.

2-Benzyl-4-methyltoluene[19] **(2g)**: ^{1}H NMR: 2.31 (3H, s), 2.48 (3H, s) 4.12 (2H, s), 7.15–7.47 (8H, m). IR (cm^{-1}, Neat): 3024, 2918, 2859, 1602, 1496, 1110, 840, 730. Anal. Calcd. for $C_{15}H_{16}$: C, 91.83 ; H, 8.16. Found: C, 91.73; H, 8.25.

3-(2,5-Dimethylphenyl)-1-phenylpropene **(3g)**: ^{1}H NMR: δ 2.27 (3H, s), 2.41 (3H,s), 3.47 (2H, d, *J* = 6.8), 6.27 (1H, dt, *J*=15, 6.8), 6.51 (1H, d, *J* = 15), 7.01–7.43 (8H, m). IR (cm^{-1}, Neat): 3010, 2952, 1620, 1439, 1284, 1037, 910, 670. Anal. Calcd for $C_{17}H_{18}$: C, 91.89; H, 8.10. Found: C, 91.82; H, 8.73.

3-Methyl-4benzylanisole **(2h)**: ^{1}H NMR: δ 2.26 (3H, s), 3.21 (3H, s), 4.31 (2H, s), 7.08–7.56 (8H, m). IR (cm^{-1}, Neat): 3026, 2971, 2918, 1609, 1438, 1483, 1262, 858, 769. Anal. Calcd for $C_{15}H_{16}O$: C, 84.90; H, 7.54. Found: C, 84.93; H, 7.51.

3-(2-Methyl-4-methoxyphenyl)-1-phenylpropene **(3h)**: ^{1}H NMR: δ 2.23 (3H, s), 3.27 (3H, s), 3.97 (2H, d, *J* = 7.2), 6.48 (1H, dt, *J* = 14.9, 7.2), 6.71 (1H, d, *J* = 14.9), 7.13–7.59 (8H, m). IR (cm^{-1}, Neat): 3017, 2963, 2918, 1628, 1481, 1434, 1267, 827, 764, 709. Anal. Calcd for $C_{17}H_{18}O$: C, 85.71; H, 7.56. Found: C, 85.78; H, 7.54.

4-Benzylphenol[20] **(2i)**: ^{1}H NMR: δ 4.89 (2H, s), 5.67 (1H, s), 7.13–7.69 (9H, m). IR (cm^{-1}, Neat): 3456, 3010, 2937, 1623, 1484, 1256, 844, 768, 708. Anal. Calcd for $C_{13}H_{12}O$: C, 84.78; H, 6.52. Found: C, 84.86; H, 6.59.

3-(4-Hydroxyphenyl)-1-phenylpropene **(3i)**: ^{1}H NMR: δ 3.81 (2H, d, *J* = 7.1), 5.69 (1H, s), 6.47 (1H, dt, *J* = 15, 7.1), 6.69 (1H, d, *J* = 15), 7.08–7.61 (9H, m). IR (cm^{-1}, Neat): 3471, 3018, 2937, 1619, 1482, 1264, 837, 764, 708. Anal. Calcd for $C_{15}H_{14}O$: C, 85.71; H, 6.66. Found: C, 85.78; H, 6.63.

3-Methoxy–4-benzylphenol **(2j)**: ^{1}H NMR: δ 3.43 (3H,s), 5.89 (1H,s), 5.07 (2H, s), 7.26–7.58 (8H, m). IR (cm^{-1}, Neat): 3408, 30232, 2986, 2934, 1637, 1468, 1234, 856, 740. Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.58; H, 6.54. Found: C, 77.93; H, 6.67.

3–(2-Methoxy–4–hydroxyphenyl)–1–phenylpropene **(3j):** ^{1}H NMR: δ 3.49 (3H, s) 5.68 (1H,s), 4.21 (2H,d, *J* = 6.7), 6.48 (1H, dt, *J* = 15, 6.7), 6.27 (1H, d, *J* = 15), δ 7.31–7.64 (8H, m). IR (cm^{-1}, Neat): 3426, 3030, 2976, 2958, 1632, 1470, 1238, 872, 754. Anal. Calcd for $C_{16}H_{16}O_2$: C, 80; H, 6.06. Found: C, 79.78; H, 6.63.

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