

ELECTRONIC SUPPLEMENTARY INFORMATION
(SPECTRAL DATA)

Manuscript No.: B304178F

Manuscript Title: Perchloric Acid Adsorbed on Silica Gel as a New, Highly Efficient, and Versatile Catalyst for Acetylation of Phenols, Thiols, Alcohols, and Amines

Authors: Asit K. Chakraborti* and Rajesh Gulhane

Address: Department of Medicinal Chemistry, National Institute of Pharmaceutical Education and Research (NIPER), Sector 67, S. A. S. Nagar 160 062, Punjab, India.

* Corresponding Author: akchakraborti@niper.ac.in

General details

Melting points were carried out on V Scientific melting point apparatus and are uncorrected. All anhydrous reactions were performed under an atmosphere of dry nitrogen. Proton nuclear magnetic resonance (^1H NMR) experiments were recorded on a Avance DPX 300, Bruker (300 MHz) spectrophotometer. Carbon-13 nuclear magnetic resonance (^{13}C NMR) were recorded on a Avance DPX 300, Bruker (300 MHz) spectrometer with tetramethylsilane (TMS) as the internal standard. All chemical shifts are quoted in parts per million (ppm) relative to TMS using deuterated solvent. Coupling constants (J) are given in hertz (Hz). Signal splitting are described as singlets (s), doublets (d), double doublet (dd), triplet (t), quartets (q), and multiplets (m). Gas chromatography coupled with mass spectrophotometer was done on Shimadzu QP-5000 instrument and mass recorded in EI and CI mode. Infra-red (IR) spectra were recorded on Nicolet Impact-410 FTIR spectrometer either as neat samples or using KBr for preparing pellets for solid samples. Absorption maxima are quoted in wavenumbers (cm^{-1}) and only structurally significant peaks are listed. Elemental analysis of new compound was done on Elementa, Vario elemental analyzer. The phenols, thiols, amines, alcohols, anhydrides and carboxylic acids are available commercially. The solvents used, if any, were distilled prior to use.

Spectral Data

2-Naphthyl acetate (Table 1, entry 1): mp 70-72°C; IR (KBr) 1755 cm⁻¹; ¹H NMR (CDCl₃) δ 2.36 (s, 3H), 7.24 (d, *J* = 8.85 Hz, 1H), 7.47 (m, 2H), 7.56 (s, 1H), 7.78 (m, 3H); ¹³C NMR (CDCl₃) δ 21.19, 118.53, 121.13, 125.71, 126.56, 127.64, 127.76, 129.41, 131.47, 133.75, 148.33, 169.65; EIMS (m/z) 186 (M⁺), 144 (100).

4-Methoxyphenyl acetate (Table 1, entry 2): IR (KBr) 1761 cm⁻¹; ¹H NMR (CDCl₃) δ 2.27 (s, 3H), 3.79 (s, 3H), 6.88 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 9.0 Hz, 2H); ¹³C (CDCl₃) δ 20.58, 55.12, 114.11, 122.03, 143.92, 156.95, 169.61; EIMS (m/z) 166 (M⁺), 124 (100).

2,6-Di-*tert*-butyl-4-methyl phenyl acetate (Table 1, entry 3): mp 70-74°C; IR (KBr) 1763 cm⁻¹; ¹H NMR (CDCl₃) δ 1.33 (s, 18H), 2.31 (s, 3H), 2.33 (s, 3H), 7.11 (s, 2H); ¹³C (CDCl₃) δ 21.56, 22.72, 31.49, 35.25, 127.11, 134.60, 141.93, 171.41; EIMS (m/z) 262 (M⁺), 43 (100).

2,4,6-Trimethylphenyl acetate (Table 1, entry 4): IR (neat) 1759 cm⁻¹; ¹H NMR (CDCl₃) δ 2.10 (s, 6H), 2.25 (s, 3H), 2.31 (s, 3H), 6.86 (s, 2H); ¹³C (CDCl₃) δ 16.14, 20.38, 20.70, 129.16, 129.57, 136.26, 145.87, 169.01; EIMS (m/z) 178 (M⁺), 43 (100).

4-Bromophenyl acetate (Table 1, entry 5): IR (neat) 1760 cm⁻¹; ¹H NMR (CDCl₃) δ 2.29 (s, 3H), 6.97 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H); ¹³C (CDCl₃) δ 20.99, 118.82, 123.34, 132.39, 149.63, 169.02; EIMS (m/z) 216(M⁺), 172(100).

4-Acetylphenyl acetate (Table 1, entry 6): IR (KBr) 1764, 1684 cm⁻¹; ¹H NMR (CDCl₃) δ 2.33 (s, 3H), 2.60 (s, 3H), 7.20 (d, *J* = 8.6 Hz, 2H), 8.00 (d, *J* = 8.6 Hz, 2H); ¹³C (CDCl₃) δ 20.70, 26.17, 121.46, 129.57, 134.32, 154.06, 168.47, 196.51; EIMS (m/z) 178 (M⁺), 121(100).

Methyl-(4-acetyl) benzoate (Table 1, entry 7): IR (KBr) 1756, 1716 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.32 (s, 3H), 3.92 (s, 3H), 7.18 (d, $J = 9$ Hz, 2H), 8.08 (d, $J = 9$ Hz, 2H); ^{13}C (CDCl_3) δ 21.03, 52.09, 121.52, 127.63, 131.06, 154.23, 166.20, 168.74; EIMS (m/z) 194 (M^+), 121(100).

4-Cyanophenyl acetate (Table 1, entry 8): IR (KBr) 2229, 1768 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.33 (s, 3H), 7.25 (d, $J = 8.5$ Hz, 2H), 7.70 (d, $J = 8.5$ Hz, 2H); ^{13}C (CDCl_3) δ 20.04, 118.18, 122.70, 133.62, 153.87, 168.47; EIMS (m/z) 161 (M^+), 43 (100).

4-Nitrophenyl acetate (Table 1, entry 9): IR (KBr) 1762 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.36 (s, 3H), 7.29 (d, $J = 8.8$ Hz, 2H), 8.28 (d, $J = 9.2$ Hz, 2H); ^{13}C (CDCl_3) δ 20.79, 122.30, 124.92, 145.03, 155.21, 168.34; EIMS (m/z) 181 (M^+), 43 (100).

Benzene-1,4-diyl diacetate (Table 1, entry 10): IR (KBr) 1762 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.29 (s, 6H), 7.10 (s, 4H); ^{13}C (CDCl_3) δ 21.07, 122.42, 148.07, 169.32; EIMS (m/z) 194 (M^+), 110 (100).

Benzene-1,3-diyl diacetate (Table 1, entry 12): IR (neat) 1768, 1601 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.28 (s, 6H), 6.92 (s, 1H), 6.98 (d, $J = 6.28$ Hz, 2H), 7.37 (t, $J = 8.16$ Hz, 1H); ^{13}C (CDCl_3) δ 20.51, 115.22, 118.71, 129.41, 150.86, 168.71; EIMS (m/z) 194 (M^+), 43 (100).

Benzene-1,2-diyl diacetate (Table 1, entry 11): IR (neat) 1772 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.25 (s, 6H), 7.19 (m, 4H); ^{13}C (CDCl_3) δ 20.41, 123.30, 126.45, 142.00, 168.13; EIMS (m/z) 194 (M^+), 43(100).

Benzene-1,2,3-triyl diacetate (Table 1, entry 13): IR (KBr) 1765, 1608 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.27 (s, 9H), 7.11 (d, $J = 8.03$ Hz, 2H), 7.25 (t, $J = 7.50$ Hz, 1H); ^{13}C (CDCl_3) δ 20.11, 20.59, 120.68, 125.91, 127.27, 134.62, 143.46, 166.98, 167.87; EIMS (m/z) 252 (M^+), 43(100).

S-Phenyl thioacetate (Table 1, entry 14): IR (neat) 1707 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.40 (s, 3H), 7.40 (m, 5H); ^{13}C (CDCl_3) δ 30.12, 127.85, 129.14, 129.37, 134.38, 193.97; EIMS (m/z) 152 (M^+), 43 (100).

S-(4-Methyl)phenyl thioacetate (Table 1, entry 15): IR (neat) 1708 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.35 (s, 3H), 2.38 (s, 3H), 7.20 (d, $J = 8.0$ Hz, 2H,), 7.28 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 21.30, 30.04, 124.45, 130.01, 134.39, 139.66, 194.48; EIMS (m/z) 166 (M^+), 43(100).

S-(4-Methoxy)phenyl thioacetate (Table 1, entry 16): IR (neat) 1705 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.38 (s, 3H), 3.84 (s, 3H), 6.93 (d, $J = 8.57$ Hz, 2H), 7.31 (d, $J = 8.57$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 29.51, 54.90, 114.50, 118.36, 135.72, 160.30, 194.58; EIMS (m/z) 182 (M^+), 43 (100).

S-Benzyl thioacetate (Table 1, entry 17): IR (neat) 1691 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.33 (s, 3H), 4.11 (s, 2H), 7.26 (m, 5H); ^{13}C (CDCl_3) δ 30.09, 33.23, 127.08, 128.44, 128.63, 137.46, 194.74; EIMS (m/z) 166 (M^+), 43 (100).

2-Nitroacetanilide (Table 1, entry 18): IR (KBr) 1701 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.30 (s, 3H), 7.18 (t, $J = 7.86$ Hz, 1H), 7.65 (t, $J = 7.86$ Hz, 1H), 8.22 (d, $J = 8.50$ Hz, 1H), 8.77 (d, $J = 8.50$ Hz, 1H), 10.33 (s, 1H); ^{13}C (CDCl_3) δ 25.54, 122.10, 123.14, 125.63, 134.78, 135.88, 136.26, 168.98; EIMS (m/z) 180 (M^+), 43(100).

2,4-Dinitroacetanilide (Table 1, entry 19): IR (KBr) 1745 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.38 (s, 3H), 8.48 (d, $J = 9.40$ Hz, 1H), 9.09-9.15 (several peaks, 2H), 10.65 (s, 1H); ^{13}C (CDCl_3) δ 25.71, 121.93, 122.23, 130.08, 134.85, 139.70, 141.56, 169.23; EIMS (m/z) 225 (M^+), 43(100).

Benzyl acetate (Table 1, entry 20): IR (neat) 1740 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.10 (s, 3H), 5.10 (s, 2H), 7.35 (m, 5H); ^{13}C (CDCl_3) δ 20.95, 66.29, 128.22, 128.52, 135.84, 170.97; EIMS (m/z) 150 (M^+), 43(100).

2-Phenethyl acetate (Table 1, entry 21): IR (neat) 1740 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.02 (s, 3H), 2.92 (t, $J = 7.09$ Hz, 2H), 4.27 (t, $J = 7.09$ Hz, 2H), 7.29 (m, 5H); ^{13}C (CDCl_3) δ 20.87, 34.98, 64.85, 126.47, 128.41, 128.80, 137.72, 170.95; EIMS (m/z) 104 ($\text{M}-60^+$), 43(100).

1-Phenethyl acetate (Table 1, entry 22): IR (neat) 1744 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.53 (d, $J = 6.6$ Hz, 3H), 2.06 (s, 3H), 5.88 (q, $J = 6.6$ Hz, 1H), 7.30 (m, 5H); ^{13}C (CDCl_3) δ 21.31, 22.17, 72.28, 126.06, 127.83, 128.46, 141.65, 170.29; EIMS (m/z) 104 ($\text{M}-60^+$), 43(100).

2-Acetyl-2-phenylacetophenone (Table 1, entry 23): IR (neat) 1739, 1696 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.21 (s, 3H), 6.86 (s, 1H), 7.34-7.54 (several peaks, 8H), 7.94 (d, $J = 8.69$ Hz, 2H); ^{13}C (CDCl_3) δ 20.13, 77.27, 128.21, 128.30, 128.67, 128.88, 133.06, 133.19, 134.07, 169.93, 193.32; EIMS (m/z) 254 (M^+), 105(100).

1-Acetoxy-1-methyl cyclohexane (Table 1, entry 24): IR (neat) 1732 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.42 (m, 10H), 1.99 (s, 3H), 2.12 (d, $J = 11.39$ Hz, 3H); EIMS (m/z) 125 ($\text{M}-31^+$), 43(100).

Glucose pentacetate (Table 1, entry 25): IR (KBr) 1750, 1649, cm^{-1} ; ^1H NMR (CDCl_3) δ 2.10 (m, 15H), 4.10 (m, 2H), 4.28 (m, 1H), 5.13 (m, 2H), 5.48 (t, $J = 9.87$ Hz, 1H), 6.34 (d, $J = 3.61$ Hz, 1H); ^{13}C (CDCl_3) δ 20.41, 20.54, 20.64, 20.84, 61.45, 67.87, 69.17, 69.80, 76.61, 89.04, 168.78, 169.43, 169.68, 170.25, 170.68; EIMS (m/z) 347 ($\text{M}-43^+$), 43(100).

(1R,2S,5R)-(-)-Menthyl acetate (Table 1, entry 26): IR (neat) 1735 cm^{-1} ; $[\alpha]^{25} = -79.5^\circ$ ($c = 8$, C_6H_6); ^1H NMR (CDCl_3) δ 0.76 (d, $J = 6.58$ Hz, 3H), 0.90 (d, $J = 6.32$ Hz, 6H), 1.01 (m, 4H), 1.36 (m, 1H), 1.50 (m, 1H), 1.67 (m, 2H), 1.88 (m, 1H), 2.04 (s, 3H), 4.66 (m, 1H); ^{13}C

(CDCl₃) δ 16.22, 20.54, 21.05, 21.83, 23.37, 26.17, 31.21, 34.13, 40.79, 46.87, 73.89, 170.32;
EIMS (m/z) 138(M-60⁺), 43(100).

[(1S)-endo]-(-)Bornyl acetate (Table 1, entry 27): IR (Neat) 1723 cm⁻¹; [α]²⁵ = -38° (neat);
¹H NMR (CDCl₃) δ 0.83 (s, 3H), 0.87 (s, 3H), 0.90 (s, 3H), 1.25 (m, 4H), 1.71 (m, 2H), 2.06
(s, 3H), 2.35 (m, 1H), 4.88 (d, *J* = 9.79 Hz, 1H); ¹³C (CDCl₃) δ 13.42, 18.78, 19.66, 21.23,
27.02, 27.99, 36.71, 44.85, 47.72, 48.64, 79.81, 171.38; EIMS (m/z) 196 (M⁺), 43(100).

1-Adamantanyl acetate (Table 1, entry 28): IR (KBr) 1733 cm⁻¹; ¹H NMR (CDCl₃) δ 1.66
(m, 6H), 1.96 (s, 3H), 2.11 (m, 9H); ¹³C (CDCl₃) δ 22.64, 30.74, 36.15, 41.23, 80.19, 88.44,
170.21; EIMS (m/z) 194 (M⁺), 134 (100).

Geranyl acetate (Table 1, entry 29): IR (neat) 1741 cm⁻¹; ¹H NMR (CDCl₃) δ 1.60 (s, 3H),
1.68 (s, 3H), 1.70 (s, 3H), 2.05 (s, 3H), 2.09 (m, 4H), 4.59 (d, *J* = 7.1 Hz, 2H), 5.08 (m, 1H),
5.34 (t, *J* = 7.1 Hz, 1H); ¹³C (CDCl₃) δ 16.41, 17.64, 21.00, 25.63, 26.27, 39.50, 53.39, 61.36,
118.25, 123.72, 131.21, 142.21, 171.07; EIMS (m/z) 136 (M-60⁺), 43 (100).

Linalyl acetate (Table 1, entry 30): IR (neat) 1730 cm⁻¹; ¹H NMR (CDCl₃) δ 1.48 (m, 9),
1.96-2.06 (several peaks, 4H), 2.05 (s, 3H), 5.13 (m, 3H), 5.93 (m, 1H); ¹³C (CDCl₃) δ 17.53,
22.67, 23.46, 25.55, 27.64, 41.97, 73.24, 111.51, 124.29, 131.59, 144.95, 169.86.

2-Propyne-1-yl acetate (Table 1, entry 31): IR (neat) 1740 cm⁻¹; ¹H NMR (CDCl₃) δ 2.11
(s, 3H), 2.51 (t, *J* = 2.40 Hz, 1H), 4.68 (d, *J* = 2.38 Hz, 2H); ¹³C (CDCl₃) δ 20.55, 51.85,
74.80, 77.51, 170.13.

3-Butyne-2-methyl-2-yl acetate (Table 1, entry 32): IR (neat) 1712 cm⁻¹; ¹H NMR (CDCl₃)
δ 1.67 (s, 6H), 2.03 (s, 3H), 2.55 (s, 1H); ¹³C (CDCl₃) δ 21.70, 28.71, 71.39, 72.18, 84.54,
169.17.

1-Pentyne-3-methyl-3-yl acetate (Table 1, entry 33): IR (neat) 1742 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.03 (t, $J = 7.42$ Hz, 3H), 1.66 (s, 3H), 1.90 (several peaks, 2H), 2.03 (s, 3H), 2.56 (s, 1H); ^{13}C (CDCl_3) δ 8.21, 21.67, 25.70, 34.17, 73.10, 75.12, 83.51, 169.21.

1-Acetoxy-1-ethynyl cyclohexane (Table 1, entry 34): IR (neat) 1744 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.63 (several peaks, 6H), 1.81-1.89 (m, 2H), 2.05 (s, 3H), 2.12 (m, 2H), 2.60 (s, 1H); ^{13}C (CDCl_3) δ 21.87, 22.38, 25.03, 36.84, 74.19, 75.04, 83.58, 169.24; EIMS (m/z) 123 ($\text{M}-43^+$), 43(100).

1-Acetoxy-1-phenyl propane (Table 2, entry 4): IR (neat) 1737 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.87 (t, $J = 7.38$ Hz, 3H), 1.73-1.99 (several peaks, 2H), 2.06 (s, 3H), 5.66 (t, $J = 6.86$ Hz, 1H), 7.28 (m, 5H); ^{13}C (CDCl_3) δ 9.72, 20.99, 29.12, 77.13, 126.38, 127.63, 128.19, 140.39, 170.12; EIMS (m/z) 178 (M^+), 43(100).