Effective Gold(III)–$CuCl_2$-catalyzed addition of alcohols to alkenes

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Experimental details

Catalytic testing was performed in a closed glass reactor (2.5 mL, SUPELCO) equipped with a micro-syringe through which can take a sample to analysis. For each reaction, the gold catalyst (0.10 mmol) and/or a proper amount (without specified, the amount is two equal mole of gold, i.e., 0.20 mmol) of $CuCl_2$ was added into 1.5 mL of the mixtures of alcohol and alkene (1.21 mmol). Then the reactor was closed tightly and the reactants mixed in the room temperature. The reaction was assumed to start when the reactor was put into the oil bath at 120 ^oC (unless otherwise specified) and stirred extensively. At a desired reaction time, the reaction product was taken and analyzed with a GC.

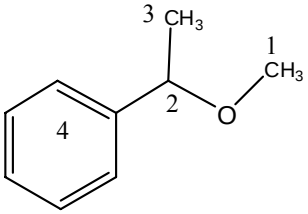
Commercially available reagents including $AuCl_3$ (99.99%), $HAuCl_4 \cdot 3H_2O$ (99.9+%), AuCl (99.9+%), $PdCl_2$ (99.9%) were purchased from Sigma-Aldrich. $CuCl_2 \cdot 2H_2O$ (98%, Panreac), methanol (99.9+%, Merck), ethanol (99.9%, Scharlau), 1-propanol (99.5+%, Sigma-Aldrich), 2-propanol (99.9%, Scharlau), 1-butanol (99.4+%, Sigma-Aldrich), 2-butanol (99%, Aldrich), tert-butyl alcohol (99+%, Aldrich) were used as received without further purification.

GC/MS and ^{1}H-NMR Analysis

GC/MS analyses were performed on a Agilent 5973N spectrometer equipped with the same column and in the same conditions as GC.

Flash column chromatograph was performed over silica gel (0.04−0.06 mm, Scharlau) using the mixtures of hexane and ethyl acetate (hexane/ethyl acetate = 95: 1) as effluent. ^{1}H-NMR spectra were recorded in $CDCl_3$ (or CD_3OD) with TMS as an internal standard at ambient temperature on a Bruker Avance 300 operating at 300 MHz.

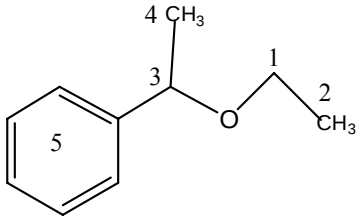
1-methoxyethylbenzene



^{1}H-NMR δ: 7.2 (m, 5H, C_6H_5), 4.3 (q, 1H, C2-H), 3.2 (s, 3H, C1-H), 1.5 (d, 3H, C3-H)

MS (80 eV): m/z (%) = 136 (3) (M^+), 121 (100), 105 (29), 77 (20), 51(10), 91(10)

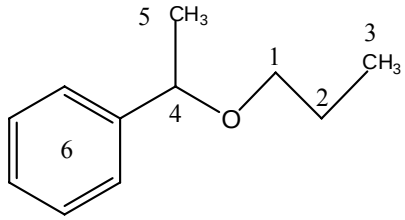
1-ethoxyethylbenzene



^{1}H-NMR δ: 7.3 (m, 5H, C_6H_5), 4.2−4.4 (q, 1H, C3-H), 3.1−3.3 (q, 2H, C1-H), 1.5 (d, 3H, C4-H), 1.1 (t, 3H, C2-H)

MS (80 eV): m/z (%) = 150 (2) (M^+), 135 (100), 105 (100), 77 (55), 79(47), 43(29)

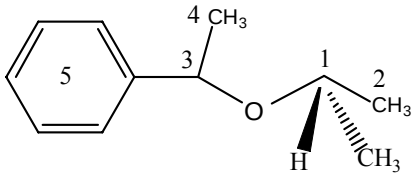
1-propoxyethylbenzene



^{1}H-NMR δ: 7.3 (m, 5H, C_6H_5), 4.2−4.4(q, 1H, C4-H), 3.1−3.3 (t, 2H, C1-H), 1.5 (d, 3H, C5-H), 1.2−1.3 (m, 2H, C2-H), 0.8 (t, 3H, C3-H)

MS (80 eV): m/z (%) = 164 (0.5) (M^+), 107 (100), 105 (88), 149 (73), 79(38), 43(29)

1-(2-methyl-ethoxyethyl)-benzene

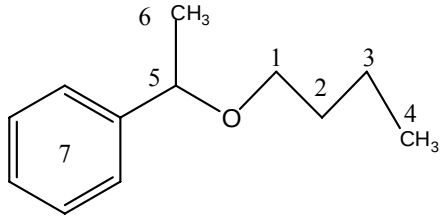


(Contain diastereomeric pairs)

^{1}H-NMR δ: 7.2 (m, 5H, C_6H_5), 4.3−4.4(q, 1H, C3-H), 3.2−3.3 (q, 1H, C1-H), 1.5 (d, 3H, C4-H), 1.2 (d, 3H, C2-H)

MS (80 eV): m/z (%) = 164 (0.3) (M^+), 107 (100), 105 (92), 149 (44), 79(38), 77(30)

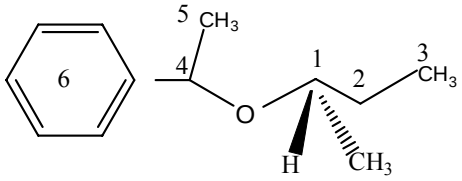
1-butoxyethylbenzene



^{1}H-NMR δ: 7.3 (m, 5H, C_6H_5), 4.3−4.4 (q, 1H, C5-H), 3.2−3.5 (t, 2H, C1-H), 1.5 (d, 3H, C6-H), 1.2 (m, 2H, CH_2 (2-3)), 0.8 (t, 3H, C4-H)

MS (80 eV): m/z (%) = 178 (Tr) (M^+), 107 (100), 105 (88), 163 (74), 79 (28), 77 (21)

1-(2-methyl-propoxyethyl)-benzene

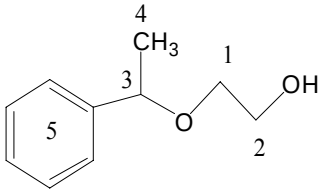


(Contain diastereomeric pairs)

^{1}H-NMR δ: 7.3 (m, 5H, C_6H_5), 4.3−4.4 (q, 1H, C4-H), 3.0 (m, 1H, C1-H), 1.5 (d, 3H, C5-H), 1.2 (d, 3H, C1-CH_3), 1.3−1.4 (q, 2H, C2-H), 0.8 (t, 3H, C3-H)

MS (80 eV): m/z (%) = 178 (Tr) (M^+), 105 (100), 107 (36), 163 (23), 106 (16), 79(13)

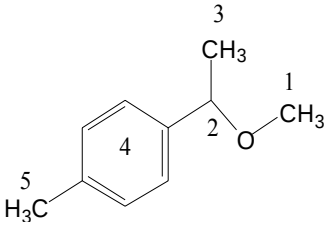
2-(1-phenylethoxy)-ethanol



^{1}H-NMR δ: 7.2 (m, 5H, C_6H_5), 4.3−4.4 (q, 1H, C3-H), 3.4−3.5 (t, 2H, C1-H), 3.2 (s, 1H, C2-OH), 3.7 (t, 2H, C2-H), 1.5 (d, 3H, C4-H)

MS (80 eV): m/z (%) = 166 (13) (M^+), 105 (100), 151 (41), 79 (25), 77 (23), 121 (21)

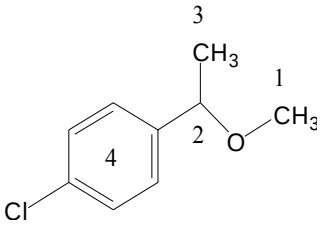
4-methyl-1-methoxyelthylbenzene



^{1}H-NMR δ: 7.1 (m, 5H, C_6H_5), 4.3 (q, 1H, C2-H), 3.2 (s, 3H, C1-H), 1.5 (d, 3H, C3-H), 2.4 (s, 3H, C5-H)

MS (80 eV): m/z (%) = 150 (8) (M^+), 135 (100), 91 (60), 119 (41), 136 (15), 117 (13)

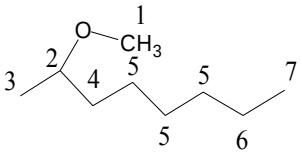
4-chloro-1-methoxyelthylbenzene



^{1}H-NMR δ: 7.1−7.2 (m, 5H, C_6H_5), 4.3 (q, 1H, C2-H), 3.2 (s, 3H, C1-H), 1.5 (d, 3H, C3-H)

MS (80 eV): m/z (%) = 170 (5) (M^+), 155 (100), 157 (33), 139 (26), 91 (25), 103 (24)

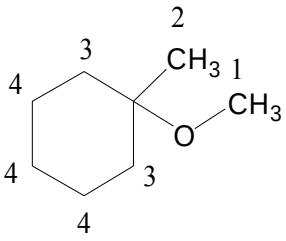
2-methoxyoctane



^{1}H-NMR δ: 3.2 (s, 3H, C1-H), 3.0 (m, 1H, C2-H), 1.4 (q, 2H, C4-H),
1.29 (m, 2H, C5-H), 1.33 (m, 2H, C6-H), 1.2 (d, 3H, C3-H), 1.0 (t, 3H, C7-H)

MS (80 eV): m/z (%) = 144 (Tr) (M^+), 59 (100), 55 (23), 60 (8), 58 (8), 112 (1)

1-methyl-1-methoxycyclohexane



^{1}H-NMR δ: 3.1 (s, 3H, C1-H), 1.5−1.6 (t, 2H, C3-H), 1.2−1.4 (t, 2H, C4-H), 1.1 (s, 3H, C1-H),

MS (80 eV): m/z (%) = 128 (48) (M^{+}), 85 (100), 72 (92), 55 (88), 113 (66), 81 (39)