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Direct and efficient synthesis of unsymmetrical ethers from alcohols catalyzed by $Fe(HSO_4)_3$ under solvent-free conditions

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Abstract Highly efficient $Fe(HSO_4)_3$ catalyzed etherification of primary, secondary and tertiary benzylic alcohols with primary and secondary aliphatic alcohols is reported. The reaction affords unsymmetrical benzyl ethers in good to excellent yields under solvent-free conditions.

Keywords Etherification · Ferric hydrogen sulphate [$Fe(HSO_4)_3$] · Alcohols · Unsymmetrical ethers

Introduction

Ethers are essential compounds in organic chemistry, serving as products and important precursors in organic synthesis. Ether bond formation has a fundamentally important and central position in organic chemistry, and there are many synthetic routes for practical preparation of ethers. The Williamson ether synthesis is still the best general method for the preparation of symmetrical and unsymmetrical ethers [1–7]. This method generally involves the preparation of halides, followed by their substitution with alkoxides under strong basic conditions, which cause undesired side reactions such as elimination of the alkylating agent and the generation of large amounts of waste that leads to reduction of both selectivity and yield. However, the Williamson ether synthesis is impractical because the starting halide compounds are not easily available or they are too expensive. Alternatively,

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the direct preparation of ethers from alcohols is more environmentally friendly, and has attracted much attention because of its advantages, such as easy work-up procedures, low costs and the formation of water as the only by-product [8–38]. The dehydration of alcohols using many homogeneous catalysts such as Brønsted acid or Lewis acid have been reported in the etherification of alcohols [8–29]. Ethers are also prepared through hydroalkoxylation of alkenes, [39–41] alcoholysis of epoxides, and [42–44] reductive etherification of carbonyl compounds with triethylsilane and alkoxytrimethylsilane [45–50].

Today, because of strict environmental legislation, heterogeneous catalysis has become attractive in view of their isolation and separation from the reaction media. The reported heterogeneous catalysts have been mostly applied to the synthesis of symmetrical ethers, while the heterogeneous catalysts for the synthesis of unsymmetrical ethers are still rare [16–18].

Under this purview, we have been motivated to develop a convenient and efficient protocol for the synthesis of a wide range of unsymmetrical ethers using heterogeneous catalysts.

Experimental

General

The products were purified by column chromatography. The purity determinations of the products were accomplished by TLC on silica gel polygram STL G/UV 254 plates. The melting points of products were determined with an Electrothermal Type 9100 melting point apparatus. The FT-IR spectra were recorded on an Avatar 370 FT-IR Therma Nicolet spectrometer. The NMR spectra were provided on Brucker Avance 400 MHz instruments in $CDCl_3$. Mass spectra were recorded with a Shimadzu GC–MS-QP5050 and CH7A Varianmat Bremem instruments at 70 eV; in *m/z* (rel %). All the products were characterized by IR, ^{1}H NMR spectroscopy, mass spectrometry and comparison of their melting points (or those of the derivatives) with authentic samples. The catalyst were prepared and purified by the method described in the literature [51].

Preparation of 1-(1-butoxyethyl) benzene in the presence of $Fe(HSO_4)_3$

To a mixture of 1-butanol (0.074 g, 1 mmol) and $Fe(HSO_4)_3$ (0.024 g, 7 mol%) taken into a round-bottomed flask at room temperature, 1-phenyl ethanol (0.122 g, 1 mmol) was added dropwise. The mixture was stirred and heated in an oil bath at 90 °C for the given period of time (45 min). After completion of the reaction (TLC monitoring), the reaction mixture was cooled to room temperature. EtOAc (15 mL) was added to the reaction mixture, stirred for a while, and filtered. The filtrate was washed with saturated $NaHCO_3$ (2 × 10 mL) and H_2O (3 × 10 mL). The organic phase was dried over anhydrous Na_2SO_4, and concentrated in vacuo to give the crude product which was then purified by thin layer chromatography using *n*-hexane/EtOAc (20/1) to afford 1-(1-butoxyethyl) benzene(0.169 g, 95 %).

1-(1-Ethoxyethyl)benzene [52] *(Table 2, entry 1)* Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 3083, 3062, 3028, 2974, 2928, 2867, 1949, 1878, 1809, 1750, 1603, 1492, 1450, 1368, 1350, 1304, 1282, 1206, 1093 (C–O), 1027, 947, 911, 854, 760, 700, 632, 542; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.40–7.28 (m, 5H, Ph), 4.44 (q, J = 6.5 Hz, 1H, CH), 3.39 (q, J = 7.0 Hz, 2H, CH_2), 1.48 (d, J = 6.4 Hz, 3H, CH_3), 1.22 (t, J = 6.8 Hz, 3H, CH_3); MS(EI): *m/z* (%) 150(5)$[M]^+$, 121(87), 105(100), 77(75), 29(70).

1-(1-Butoxyethyl)benzene [52] *(Table 2, entry 2)* Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 3084, 3062, 3028, 2960, 2930, 2868, 2765, 2603, 1947, 1876, 1807, 1751, 1602, 1492, 1451, 1369, 1350, 1302, 1281, 1206, 1102 (C–O), 1030, 971, 948, 910, 841, 760, 700, 632, 610, 557, 542; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.38–7.29 (m, 5H, Ph), 4.42 (q, J = 6.4 Hz, 1H, CH), 3.34 (t, J = 10.0 Hz, 2H, O-CH_2), 1.61–1.56 (m, 2H, CH_2), 1.55 (d, J = 6.4 Hz, 3H, CH_3), 1.44–1.31 (m, 2H, CH_2), 0.91 (t, J = 7.2 Hz, 3H, CH_3); MS(EI): *m/z* (%) 178(37)$[M]^+$, 163(90), 105(27), 73(20), 57(60), 15(7).

1-(2-(1-Phenylethoxy)ethyl)benzene [53] (Table 2, entry 3) Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 3084, 3062, 3027, 2975, 2928, 2863, 2765, 1947, 1877, 1807, 1753, 1603, 1545, 1494, 1452, 1391, 1369, 1351, 1323, 1304, 1282, 1206, 1177, 1102 (C–O), 1029, 1006, 994, 911, 829, 759, 699, 611, 587, 552, 506; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.40–7.10 (m, 10 H, Ph), 4.42 (q, J = 6.3 Hz, 1H, CH), 3.52 (t, J = 7.5 Hz, 2H, αCH_2), 2.90 (m, 2H, βCH_2), 1.48 (t, J = 6.3 Hz, 3H, CH_3); MS(EI): *m/z* (%) 226(97)$[M]^+$, 211(5), 121(40), 105(80), 15(7).

1-(1-Hexan-2-yloxy)ethyl)benzene (Table 2, entry 4) Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 3084, 3063, 3028, 2972, 2929, 2870, 1948, 1876, 1807, 1753, 1602, 1492, 1451, 1370, 1350, 1303, 1281, 1206, 1142, 1091 (C–O), 1029, 948, 910, 857, 759, 699, 632, 613, 542, 514; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.40–7.20 (m, 5H, Ph), 4.42 (q, J = 6.4 Hz, 1H, O(CH)Ph), 3.49 (m, 1H, O(CH)CH_2), 1.60–1.25 (m, 9H, $3CH_2$ and CH_3), 1.19 (d, J = 6.4 Hz, 3H, CH_3), 0.88 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.2, 128.3, 127.1, 126.3, 75.2, 74.4, 69.5, 36.3, 27.8, 22.7, 19.6, 14.1; MS(EI): *m/z* (%) 206(7)$[M]^+$, 121(25), 105(100), 101(10), 85(20).

Butoxydiphenylmethane [54] *(Table 2, entry 5)* Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 3086, 3062, 3028, 2957, 2931, 2869, 1600, 1493, 1452, 1343, 1303, 1185, 1095 (C–O), 1029, 763, 740, 699, 653, 612; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.40–7.20 (m, 10H, Ph), 5.40 (s, 1H, CH), 3.51 (t, J = 7.0 Hz, 2H, αCH_2), 1.70–1.60 (m, 2H, βCH_2), 1.50–1.40 (m, 2H, γCH_2), 0.95 (t, J = 7.0 Hz, 3H, CH_3); MS(EI): *m/z* (%) 240(7)$[M]^+$, 183(15), 167(90), 163(25), 77(87), 57(5).

(3-Phenylpropoxy)diphenylmethane [55] (Table 2, entry 6) Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 3085, 3061, 3026, 2941, 2859, 2771, 1949, 1889, 1807, 1738, 1601, 1585, 1494, 1452, 1396, 1343, 1303, 1263, 1184, 1155, 1100 (C–O), 1074, 1028, 922, 833, 746, 697, 653, 613, 583, 557, 492, 466; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.46–7.25 (m 15H, 3Ph), 5.45 (s, 1H, CH), 3.57 (t, J = 7.0 Hz, 2H, αCH_2), 2.84 (t, J = 7.0 Hz, 2H, γCH_2), 2.10–2.03 (m, 2H, βCH_2);

MS(EI): *m/z* (%) 302(12)$[M]^+$, 225(10), 183(70), 167(100), 135(25), 119(40), 77(70).

(Phenethyloxy)diphenylmethane [55] (Table 2, entry 7) Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 3084, 3061, 3027, 2939, 2861, 2764, 1949, 1889, 1807, 1748, 1601, 1544, 1493, 1451, 1391, 1344, 1304, 1264, 1183, 1156, 1096 (C–O), 1075, 1028, 913, 870, 834, 741, 699, 654, 614, 583, 544, 504, 469, 404; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.37–7.20 (m, 15H, 3Ph), 5.37 (s, 1H, CH), 3.69 (t, J = 8.0 Hz, 2H, αCH_2), 2.99 (t, J = 8.0 Hz, 2H, βCH_2); MS(EI)[3]: *m/z* (%) 288(5)$[M]^+$, 211(5), 183(15), 167(80), 121(5), 105(100), 77(25).

(Isopentyloxy)diphenylmethane [34] (Table 2, entry 8) Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 3086, 3062, 3028, 2955, 2926, 2867, 1492, 1452, 1384, 1345, 1303, 1184, 1095 (C–O), 1075, 1027, 1004, 756, 739, 699, 653, 614; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.40–7.20 (m, 10H, 2Ph), 5.4 (s, 1H, CH), 3.54 (t, J = 6.4 Hz, 2H, αCH_2), 1.87 (sept, J = 5.7 Hz, 1H, $CH(CH3)_2$), 1.64–1.59 (m, 2H, βCH_2), 0.99 (d, J = 6.7 Hz, 6H, $2CH_3$); MS(EI): *m/z* (%) 254(2)$[M]^+$, 183(15), 177(10), 167(90), 87(10), 77(60).

(Hexan-2-yloxy)diphenylmethane (Table 2, entry 9) Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 3086, 3062, 3027, 2959, 2930, 2860, 1947, 1891, 1806, 1600, 1492, 1451, 1376, 1337, 1302, 1260, 1218, 1184, 1136, 1115, 1086 (C–O), 1060, 1028, 983, 923, 879, 842, 755, 740, 699, 653, 612, 571; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.40–7.20 (m, 10H, 2Ph), 5.60 (s, 1H, $CH(Ph)_2$), 3.70–3.40 (sept, 1H, $CH(CH_3)(CH_2)$), 1.80–1.30 (m, 6H, $3CH_2$), 1.34 (d, J = 7.0 Hz, 3H, CH_3), 0.81 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142. 9, 128.3, 127.4, 126.3, 80.5, 72.7, 36.6, 27.7, 22.9, 19.8, 14.2; MS(EI): *m/z* (%) 268(2)$[M]^+$, 191(5), 183(20), 167(95), 101(5), 85(10), 77(65).

1-(Butoxymethyl)-4-methoxybenzene [36] (Table 2, entry 10) Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 2999, 2957, 2932, 2863, 1612, 1585, 1513, 1462, 1361, 1300, 1247, 1175, 1096 (C–O), 1037, 821, 754, 578, 515; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.30 (d, J = 4 Hz, 2H, Ph), 6.90 (d, J = 4 Hz, 2H, Ph), 4.42 (s, 2H, CH_2), 3.80 (s, 3H, OCH_3), 3.40 (t, J = 6.4 Hz, 2H, αCH_2), 1.60–1.50 (m, 2H, βCH_2), 1.40–1.30 (m, 2H, γCH_2), 0.90 (t, J = 7.0 Hz, 3H, CH_3); MS(EI): *m/z* (%) 194(10)$[M]^+$, 163(5), 137(20), 121(100), 57(25).

1-3-(4-Methoxybenzyloxy)propyl)benzene [20] (Table 2, entry 11) Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 3083, 3061, 3026, 3000, 2934, 2857, 2792, 2541, 2059, 1883, 1723, 1612, 1585, 1512, 1454, 1363, 1301, 1248, 1174, 1098 (C–O), 1034, 918, 820, 746, 699, 632, 578, 507; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.30–7.27 (m, 4H, Ph), 7.21–7.18 (m, 3H, Ph), 6.90–6.80 (m, 2H, Ph), 4.46 (s, 2H, CH_2(O)(Ph)), 3.84 (s, 3H, OCH_3), 3.49 (t, J = 6.6 Hz, 2H, αCH_2), 2.72 (t, J = 7.3 Hz, 2H, γCH_2), 1.94 (m, 2H, βCH_2); MS(EI): *m/z* (%) 256(37)$[M]^+$, 225(5), 137(10), 121(100), 119(5), 35(5).

1-(2-(4-Methoxybenzyloxy)ethyl)benzene [56] (Table 2, entry 12) Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 3084, 3062, 3027, 3002, 2934, 2860, 2786, 1944, 1879, 1805, 1736, 1611,

1585, 1513, 1454, 1360, 1300, 1247, 1174, 1090 (C–O), 1034, 955, 822, 747, 699, 604, 575, 514; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.31–7.19 (m, 7H, Ph), 6.88–6.83 (m, 2H, Ph), 4.45 (m, 2H, OCH_2), 3.80 (s, 3H, OCH_3), 2.92 (t, $J = 7.2$ Hz, 2H, αCH_2), 2.85 (t, $J = 7.2$ Hz, 2H, βCH_2); MS(EI): *m/z* (%) 242(10)$[M]^+$, 211(5), 137(5), 121(100), 105(90), 31(25).

1-((Isopentyloxy)methyl)-4-methoxybenzene [28] (Table 2, entry 13) Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 3031, 2999, 2955, 2930, 2867, 2836, 2790, 1612, 1585, 1512, 1464, 1383, 1365, 1301, 1247, 1173, 1095 (C–O), 1036, 943, 820, 756, 578, 514; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.28 (d, $J = 9.0$ Hz, 2H, Ph), 6.90 (d, $J = 9.0$ Hz, 2H, Ph), 4.43 (s, 2H, OCH_2), 3.80 (s, 3H, OCH_3), 3.40 (t, $J = 7.2$ Hz, 2H, αCH_2), 1.70 (m, 1H, $CH(CH_3)_2$), 1.53–1.48 (m, 2H, βCH_2), 0.90 (d, $J = 7.0$ Hz, 6H, $2CH_3$); MS(EI)[7]: *m/z* (%) 208(10)$[M]^+$, 137(20), 121(100), 87(30), 71(45), 31(20).

1-((Cyclohexyloxy)methyl)-4-methoxybenzene [56] *(Table 2, entry 14)* Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 3035, 2998, 2931, 2855, 1612, 1584, 1511, 1450, 1364, 1300, 1246, 1174, 1087 (C–O), 1037, 959, 811, 747, 583, 514; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.27 (d, $J = 9.0$ Hz, 2H, Ph), 6.89 (d, $J = 9.0$ Hz, 2H, Ph), 4.48 (s, 2H, OCH_2), 3.78 (s, 3H, OCH_3), 3.35–3.33 (m, 1H, OCH), 1.96–1.22 (m, 10H, cyclohexyl); MS(EI): *m/z* (%) 220(25)$[M]^+$, 137(20), 121(100), 99(10), 83(70), 31(25).

1-(sec-Butoxymethyl)-4-methoxybenzene [17] (Table 2, entry 15) Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 3064, 3039, 2966, 2932, 2873, 2836, 1612, 1585, 1512, 1463, 1373, 1300, 1247, 1173, 1110, 1067 (C–O), 1036, 902, 820, 743, 579; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.20 (d, $J = 8.6$ Hz, 2H, Ph), 6.80 (d, $J = 8.6$ Hz, 2H, Ph), 4.44 (s, 2H, OCH_2), 3.80 (s, 3H, OCH_3), 3.22–3.21 (m, 1H, OCH), 1.90–1.80 (m, 2H, CH_2), 1.59 (s, 3H, CH_3), 0.93 (t, $J = 7.4$ Hz, 3H, CH_3); MS(EI)[8]: *m/z* (%) 194(20)$[M]^+$, 137(20), 121(100), 73(7), 57(30), 31(25).

1-((Hexan-2-yloxy)methyl)-4-methoxybenzene (Table 2, entry 16) Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 3063, 3031, 3002, 2958, 2932, 2859, 2836, 2059, 1989, 1879, 1612, 1585, 1512, 1464, 1374, 1338, 1300, 1247, 1174, 1113, 1072 (C–O), 1037, 924, 821, 750, 641, 578, 513; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.28 (d, $J = 8.4$ Hz, 2H, Ph), 7.10 (d, $J = 8.4$ Hz, 2H, Ph), 4.51 (d, $J = 12.0$ Hz, 1H, OCH_2), 4.41 (d, $J = 12.0$ Hz, 1H, OCH_2) 3.81 (s, 3H, OCH_3), 3.79–3.74 (m, 1H, OCH), 1.70–1.30 (m, 6H, $3CH_2$), 1.19 (d, $J = 7.2$ Hz, 3H, CH_3), 0.91 (t, $J = 7.5$ Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.0, 131.3, 129.2, 113.8, 74.6, 69.9, 55.2, 36.4, 27.8, 22.8, 19.6, 14.1; MS(EI): *m/z* (%) 222(2)$[M]^+$, 137(5), 121(100), 85(10), 31(15).

1-Methoxy-4-((octan-2-yloxy)methyl)benzene [57] *(Table 2, entry 17)* Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 2957, 2930, 2856, 1613, 1586, 1512, 1464, 1373, 1339, 1301, 1247, 1172, 1119, 1083 (C–O), 1038, 931, 821, 752, 722, 579, 513; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.27 (d, $J = 8.4$ Hz, 2H, Ph), 6.86 (d, $J = 8.4$ Hz, 2H, Ph), 4.50 (d, $J = 11.2$ Hz, 1H, OCH_2) 4.39 (d, $J = 11.2$ Hz, 1H, OCH_2), 3.80 (s, 3H, OCH_3), 3.50–3.46 (m, 1H, OCH), 1.43–1.27 (m, 10H, $5CH_2$), 1.17 (d, $J = 6.0$ Hz, 3H, CH_3), 0.88 (t, $J = 6.8$ Hz, 3H, CH_3); MS(EI): *m/z* (%) 250(5)$[M]^+$, 137(37), 121(100), 113(42).

1-(Butoxymethyl)benzene [30] *(Table 2, entry 18)* Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 2999, 2957, 2932, 2863, 1612, 1585, 1513, 1462, 1361, 1300, 1247 (C–O), 1175, 1096, 1037, 821, 754, 578, 515; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.37–7.25 (m, 5H, Ph), 4.50 (d, J = 6.3 Hz, 2H, OCH_2), 3.48 (t, J = 6.4 Hz, 2H, αCH_2), 1.64–1.57 (m, 2H, βCH_2), 1.45–1.36 (m, 2H, γCH_2), 0.94 (t, J = 7.2 Hz, 3H, CH_3); MS(EI): *m/z* (%) 164(15)$[M]^+$, 107(5), 91(40), 77(5), 73(10), 57(95).

1-((Hexan-2-yloxy)methyl)benzene [58] *(Table 2, entry 19)* Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 2960, 2931, 2860, 1732, 1601, 1491, 1465, 1375, 1339, 1274, 1117, 1086 (C–O), 1015, 923, 807, 739, 673, 481; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.37–7.27 (m, 5H, Ph), 4.58 (d, J = 12.0 Hz, 1H, OCH_2), 4.49 (d, J = 12.0 Hz, 1H, OCH_2), 3.53–3.49 (m, 1H, CH), 1.63–1.30 (m, 6H, $3CH_2$), 1.21 (d, J = 6.0 Hz, 3H, CH_3), 0.91 (t, J = 6.8 Hz, 3H, CH_3); MS(EI): *m/z* (%) 192(2)$[M]^+$, 107(57), 91(100), 77(42), 85(15).

1-(Butoxymethyl)-4-chlorobenzene [30] *(Table 2, entry 20)* Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 3063, 3031, 3002, 2958, 2932, 2859, 2836, 2059, 1989, 1879, 1612, 1585, 1512, 1464, 1374, 1338, 1300, 1247 (C–O), 1174, 1113, 1072, 1037, 924, 821, 750, 641, 578, 513; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.32–7.24 (m, 4H, Ph), 4.46 (s, 2H, OCH_2), 3.47 (t, J = 6.5 Hz, 2H, αCH_2), 1.62–1.56 (m, 2H, βCH_2), 1.45–1.36 (m, 2H, γCH_2), 0.91 (t, J = 7.2 Hz, 3H, CH_3); MS(EI): *m/z* (%) 198(2)$[M]^+$, 141(5), 125(5), 111(10), 57(95).

1-Chloro-4-((hexan-2-yloxy)methyl)benzene (Table 2, entry 21) Oil; IR (neat): ($\bar{\upsilon}$/cm^{-1}) 3084, 3027, 2960, 2931, 2860, 1896, 1777, 1719, 1598, 1576, 1491, 1464, 1408, 1375, 1338, 1297, 1250, 1205, 1143, 1117, 1087 (C–O), 1015, 922, 807, 729, 668, 482; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.30–7.20 (m, 4H, Ph), 4.52 (d, J = 12.0 Hz, 1H, OCH_2), 4.40 (d, J = 12.0 Hz, 1H, OCH_2), 3.52–3.40 (m, 1H, CH), 1.46–1.29 (m, 6H, $3CH_2$), 1.18 (d, J = 6.0 Hz, 3H, CH_3), 0.90 (t, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.7, 133.0, 128.8, 128.4, 75.2, 69.5, 36.3, 27.7, 22.8, 19.6, 14.1; MS(EI): *m/z* (%) 226(2)$[M]^+$, 141(5), 125(100), 111(7), 101(7), 85(10).

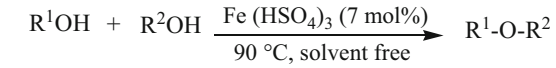
(Phenethyloxy)triphenylmethane [59] *(Table 2, entry 22)* mp 85–87 °C (lit. 87 °C); IR (KBr): ($\bar{\upsilon}$/cm^{-1}) 3057, 3022, 2932, 2873, 1596, 1489, 1445, 1392, 1222, 1193, 1153, 1058 (C–O), 1027, 982, 898, 767, 702, 629, 510, 477; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.38–7.18 (m, 20H, 4Ph), 3.31–3.28 (m, 2H, αCH_2), 2.91–2.87 (m, 2H, βCH_2); MS(EI): *m/z* (%) 364(5)$[M]^+$, 259(2), 243(100), 105(100), 77(75).

(Cyclohexyloxy)triphenylmethane [60] *(Table 2, entry 23)* mp 78–80 °C (lit. 80 °C); IR (KBr): ($\bar{\upsilon}$/cm^{-1}) 3084, 3059, 3025, 2974, 2927, 2878, 1737, 1597, 1492, 1447, 1374, 1266, 1245, 1156, 1115, 1067 (C–O), 1003, 918, 898, 845, 745, 702, 632, 605, 481; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.47–7.10 (m, 15H, 3Ph), 3.10 (m, 1H, OCH), 1.95 (m, 2H, cyclohexyl), 1.76 (m, 2H, cyclohexyl), 1.51–1.23 (m, 6H, cyclohexyl); MS(EI): *m/z* (%) 342(10)$[M]^+$, 259(5), 243(100), 83(5), 77(75).

Results and discussion

Recently, we demonstrated that $Fe(HSO_4)_3$ acted as an efficient solid acid catalyst for *C*-alkylation of 1,3-dicarbonyl compounds [61]. The scope of this article was to study the direct synthesis of unsymmetrical ethers from different classes of alcohols under mild reaction conditions in the presence of Fe $(HSO_4)_3$ as an effective, easily available, cheap, and reusable catalyst (Scheme 1).

Etherification of 1-phenyl ethanol with 1-butanol was chosen as the model reaction to optimize the reaction conditions in the presence of Fe $(HSO_4)_3$ (Table 1). At room temperature, in the absence of any catalyst and solvent, no reaction occurred between 1-phenyl ethanol and 1-butanol (Table 1, entry 1). In the presence of 10 mol% of Fe $(HSO_4)_3$ at ambient temperature, no reaction was observed between 1-phenyl ethanol and 1-butanol (Table 1, entry 2). To improve the efficiency of the catalyst, the effect of temperature was studied in etherification reaction. Temperature has an essential effect on the reaction rate, so at 90 °C the 1-(1-butoxyethyl)benzene was obtained in 45 min (Table 1, entry 3). At the same reaction conditions, using Fe $(HSO_4)_3$/silica leads to the formation of 1-(1-butoxyethyl)benzene in a longer reaction time (Table 1, entry 4). Temperatures over 90 °C were not suitable for etherification reaction in the presence of Fe $(HSO_4)_3$, because of the formation of by-products (Table 1, entry 5). The effect of different solvents was investigated on the etherification reaction by performing the reaction in CH_3CN, 1,4-dioxane, and toluene (Table 1, entries 6–8). As can be seen, in comparison with solvent-free condition, performing the etherification reaction in different solvents does not lead to the formation of 1-(1-butoxyethyl) benzene in a reasonable rate and yield. The effect of different amounts of catalyst was studied on etherification reaction of 1-phenyl ethanol with 1-butanol (Table 1, entries 9–12). Applying 7 mol% of Fe $(HSO_4)_3$ at 100 °C leads to the formation of by-products, whilst applying 7 mol% of catalyst at 90 °C produced the desired product in 45 min without the formation of any by-products (Table 1, entries 9, 10). By performing the reaction in the presence of 5 mol% of Fe $(HSO_4)_3$ at 90 °C, etherification was completed in a longer reaction time (Table 1, entries 11). Additional amounts of catalyst accelerated the etherification reaction but the formation of by-products decreased the yield of the reaction (Table 1, entry 12). A 1/1 molar ratio of 1-phenyl ethanol/1-butanol was the optimized amount of reactants. Treatment of additional amounts of 1-butanol with 1-phenyl ethanol did not increased the reaction rate (Table 1, entries 13).



R^1=PhCHCH$_3$,PhCHPh , *p*-CH$_3$O-PhCH$_2$, PhCH$_2$, *p*-Cl-PhCH$_2$,(Ph)$_3$C.
R^2=CH$_3$CH$_2$,CH$_3$(CH$_2$)$_2$CH$_2$,PhCH$_2$CH$_2$,Ph(CH$_2$)$_2$CH$_2$, (CH$_3$)$_2$CHCH$_2$CH$_2$, CH$_3$CH$_2$CHCH$_3$, CH$_3$(CH$_2$)$_3$CHCH$_3$, CH$_3$(CH$_2$)$_5$CHCH$_3$, (CH$_2$)$_5$CH.

Scheme 1 Etherification of different classes of alcohols by $Fe(HSO_4)_3$

Table 1 Synthesis of 1-(1-butoxyethyl) benzene in the presence of $Fe(HSO_4)_3$ under different reaction conditions

Entry	Molar ratio of 1-phenylethanol/ 1-buthanol	Catalyst (mol%)	Solvent	Temperature (°C)	Time (min)	Isolated Yield (%)
1	1:1	None	None	r.t	24 (h)	0
2	1:1	10	None	r.t	24 (h)	0
3	1:1	10	None	90	45	97
4[a]	1:1	10	None	90	1 (h)	95
5[b]	1:1	10	None	100	25	75
6	1:1	10	CH_3CN	Reflux	36 (h)	90
7	1:1	10	1,4-Dioxane	Reflux	2 (h)	98
8	1:1	10	Toluene	90	4 (h)	98
9[b]	1:1	7	None	100	30	75
10	1:1	7	None	90	45	95
11	1:1	5	None	90	75	95
12[b]	1:1	13	None	90	30	80
13	1:1.2	7	None	90	60	90

[a] The reaction was performed in the presence of $Fe(HSO_4)_3$/silica

[b] The etherification reaction is accompanied with formation of by-products

To show the general application of the protocol and with the optimal conditions at hand (Table 1, entry 10), the substrate scope of the etherification reaction was investigated. We have studied the etherification of primary, secondary and tertiary benzylic alcohols with primary and secondary aliphatic alcohols. All the reactions proceeded well in short reaction times with the production of benzyl alkyl ethers in excellent yields (Table 2). From this Table, it is clear that, in the presence of $Fe(HSO_4)_3$, condensation of tertiary and secondary benzylic alcohols (triphenylmethanol, 1-phenyl ethanol and benzhydrol) with primary aliphatic alcohols was completed faster than with secondary aliphatic alcohols owing to the steric hindrance (compare entries 1–3, 5–8 and 22 with entries 4 and 9, 23 respectively). Comparatively, the etherification reaction of triphenylmethanol and benzhydrol with aliphatic alcohols was performed in a shorter reaction time than 1-phenyl ethanol (compare entries 5–9 and 22–23 with entries 1–4). This result led us to conclude that the more stable carbocation improved the reaction rate. We also tested the etherification reaction of the highly reactive primary *p*-methoxybenzyl alcohol with primary and secondary aliphatic alcohols in the presence of $Fe(HSO_4)_3$ (Table 2, entries 10–17). Due to the greater stability and also lack of steric hindrance of the corresponding carbocation, the etherification reaction of *p*-methoxybenzyl alcohol was achieved in a high yield and short reaction time. The catalyst was also effective in promoting the reaction of benzyl alcohol and *p*-chloro benzyl alcohol with the primary and secondary aliphatic alcohols (Table 2, entries 18–22). The corresponding ethers were obtained with good yields but in longer reaction times. With effective conditions established for the etherification reaction, we next investigated

Table 2 Etherification of primary, secondary and tertiary benzylic alcohols with primary and secondary aliphatic alcohols in the presence of $Fe(HSO_4)_3$ under solvent free condition

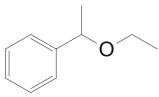
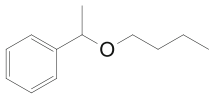
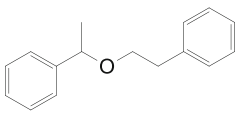
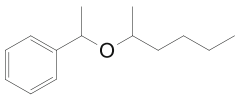
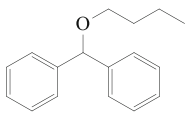
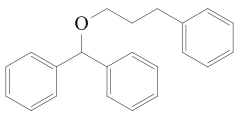
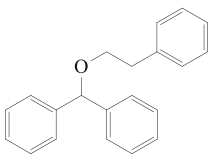
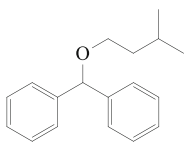
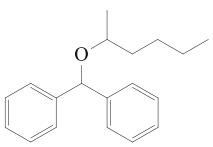
Entry	Alcohol(1)	Alcohol(2)	Product	Time (min)	Isolated Yield%
1	1-phenyl ethanol	Ethanol		45	85
2	1-phenyl ethanol	1-butanol		45	95
3	1-phenyl ethanol	2-phenyl-1-ethanol		45	90
4	1-phenyl ethanol	2-hexanol		60	80
5	benzhydrol	1-butanol		30	95
6	benzhydrol	3-phenyl-l-propanol		30	95
7	benzhydrol	2-phenyl-1-ethanol		30	95
8	benzhydrol	3-methyl-1-butanol		30	90
9	benzhydrol	2-hexanol		45	90

Table 2 continued

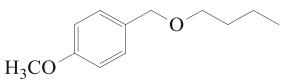
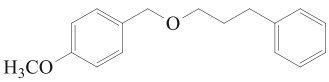
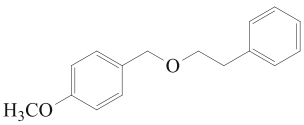
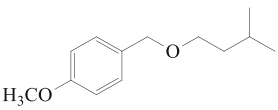
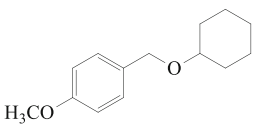
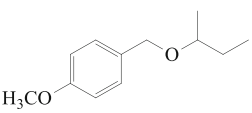
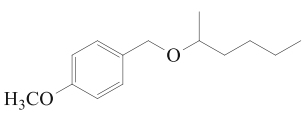
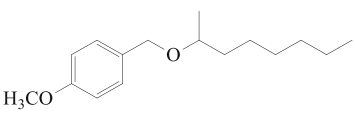
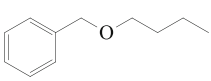
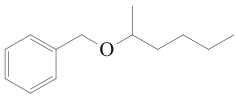
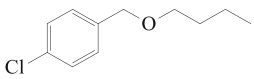
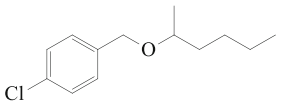
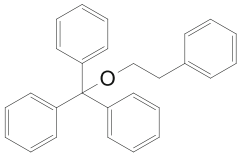
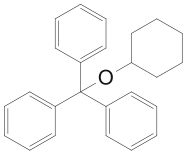
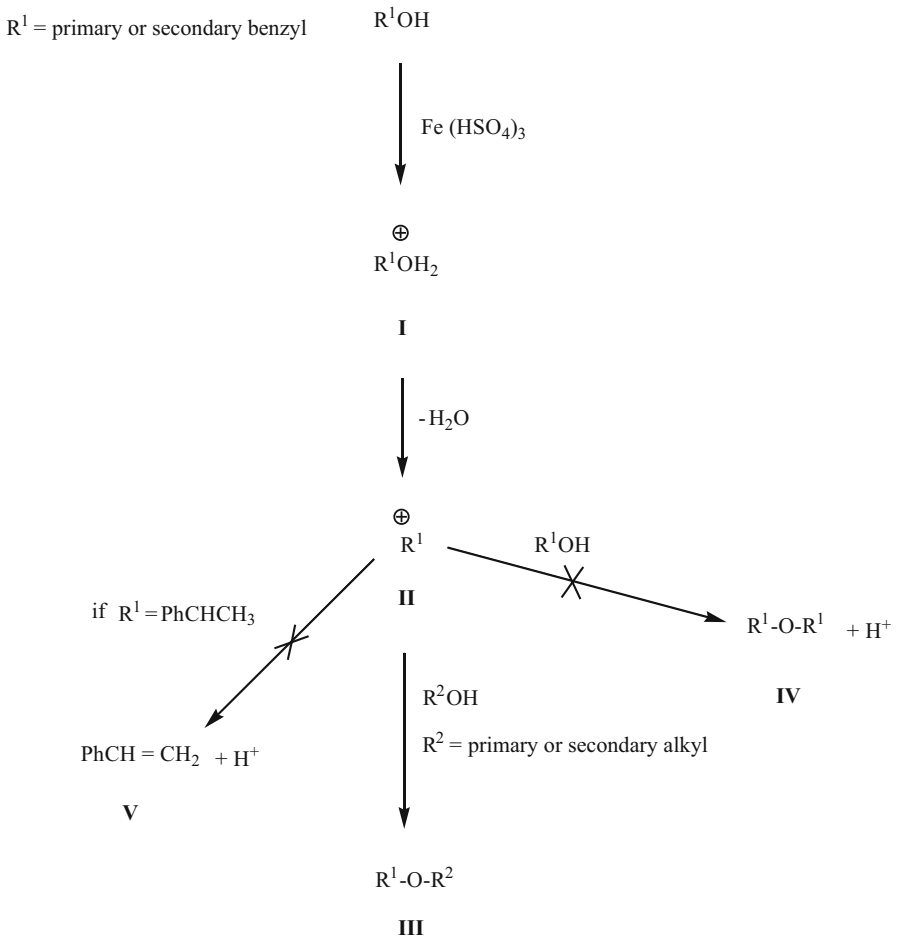
Entry	Alcohol(1)	Alcohol(2)	Product	Time (min)	Isolated Yield%
10	4-methoxy benzyl alcohol	1-butanol		15	97
11	4-methoxy benzyl alcohol	3-phenyl-l-propanol		15	95
12	4-methoxy benzyl alcohol	2-phenyl-l-propanol		15	85
13	4-methoxy benzyl alcohol	3-methyl 1-butanol		15	90
14	4-methoxy benzyl alcohol	cyclohexanol		45	90
15	4-methoxy benzyl alcohol	2-butanol		45	90
16	4-methoxy benzyl alcohol	2-hexanol		45	98
17	4-methoxy benzyl alcohol	2-octanol		45	95
18	benzyl alcohol	1-butanol		4(h)	95

Table 2 continued

Entry	Alcohol(1)	Alcohol(2)	Product	Time (min)	Isolated Yield%
19	benzyl alcohol	2-hexanol		5(h)	90
20	4-chloro benzyl alcohol	1-butanol		5(h)	80
21	4-chloro benzyl alcohol	2-hexanol		7(h)	75
22	triphenyl methanol	2-phenyl-1-ethanol		15	98
23	triphenyl methanol	cyclohexanol		35	98

the ability of $Fe(HSO_4)_3$ to catalyze the formation of unsymmetrical ethers from a series of benzylic alcohol with phenol. After a long period of time, phenol did not react with benzylic alcohol under optimized reaction conditions. Comparatively, low activity of phenol towards benzylic alcohols in the presence of $Fe(HSO_4)_3$ was attributed to the low nucleophilicity of phenols. To test the scope of the reaction further, we attempted an etherification reaction of *t*-butyl alcohol with 2-phenyl-1-ethanol and 2-hexanol. Unfortunately, the catalyst was ineffective in etherification of tertiary aliphatic alcohols with primary and secondary aliphatic alcohols even under forced conditions (10 mol% of catalyst).

The present protocol, in its entirety, simply involves the addition of a primary/or secondary/or tertiary benzylic alcohol to primary/or secondary aliphatic alcohols in the presence of a catalytic amount of $Fe(HSO_4)_3$, and warming the reaction mixture to afford the corresponding ether. The reactions are reasonably fast, but because of acidic media, to prevent formation of any by-products (symmetrical ethers or alkenes in the case of 1-phenyl ethanol), the addition of benzylic alcohols should be carried out drop by drop, which prolonged the reaction times.



Scheme 2 Mechanism for etherification of alcohols by $Fe(HSO_4)_3$

The final verification of the products' identity which can be achieved spectroscopically (FT-IR, ^{1}H NMR and ^{13}C NMR) are found to be comparable in all respects with pure samples. The melting points and mass spectrometric data also compared favorably with data previously reported in the literature.

Although the mechanism of the present catalytic etherification remains to be elucidated, we are prompted to propose the following mechanism (Scheme 2) for the catalytic etherification of primary, secondary and tertiary benzylic alcohols with primary and secondary aliphatic alcohols in the presence of 7 mol% of $Fe(HSO_4)_3$ at 90 °C. It is seen that the etherification reaction is in fact a Brønsted acid catalyzed reaction with fast generation of the protonated species **I** which subsequently generates the corresponding stable benzylic carbocation **II**. This idea is supported by performing the reaction in the absence of a catalyst. Without any catalyst, the etherification reaction is not performed even after a long period of time (Table 1,

Table 3 Reaction of benzhydrol with 1-butanol in the presence of reused catalyst

Run	Time (min)	Conversion (%)	Isolated yield (%)
1	30	100	95
2	30	100	92
3	30	100	97
4	30	100	98
5	30	100	95
6	30	100	90
7	30	100	90
8	30	100	95
9[a]	30/60	85/100	80/92

[a] The second numbers in the third and fourth columns correspond to conversion and yield after 1 h

Table 4 Etherification of 1-phenyl ethanol with 1-butanol under optimized conditions in the presence of other catalysts

Entry	Catalyst	Time (min)	Isolated Yield (%)
1	$FeCl_3{\cdot}6H_2O$	60	45
2	$Fe(NO_3)_3{\cdot}9H_2O$	105	45
3	$Cu(SO_4)_2{\cdot}5H_2O$	120	0
4	$Cu(OAc)_2{\cdot}H_2O$	120	0
5	$CuCl_2$	120	80
6	$NiCl_2{\cdot}6H_2O$	120	0
7	$AlCl_3$	100	80
8	$ZnBr_2$	60	50
9	$ZnCl_2$	60	50
10	$Fe(HSO_4)_3$	45	95

entries 1). Nucleophilic attack of aliphatic alcohols to **II** affords the desired unsymmetrical ether **III**, H_2O and releases the proton for the next catalytic cycle. As addition of benzylic alcohol to the reaction mixture was performed drop by drop, the formation of any symmetric ether **IV** as by product was prohibited. Also, dehydration of **II**, which leads to alkene **V**, did not happen in the etherification reaction in the presence of $Fe(HSO_4)_3$. Further investigation on the elucidation of the mechanism and scope of this reaction are currently underway in our laboratory.

Recovery of $Fe(HSO_4)_3$ was accomplished by simple filtration followed by washing thoroughly with ethyl acetate (3 × 10) to remove all organic compounds and then dried at 100 °C for 1 h. Using this treatment, the recyclability of the catalyst was evaluated for the reaction of benzhydrol with 1-butanol (Table 3). The recovered catalyst was reused at least 8 times without any decrease in the yield of butoxydiphenyl methane. The 9th run gave 85 % conversion after 30 min, but complete conversion and similar yield was obtained after 1 h.

To show novel catalytic activity of $Fe(HSO_4)_3$ in direct etherification of alcohols, the model reaction in the presence of $Fe(HSO_4)_3$ was compared with various metal catalysts such as $FeCl_3{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Cu(SO_4)_2{\cdot}5H_2O$, $Cu(OAc)_2{\cdot}H_2O$, $CuCl_2$, $NiCl_2{\cdot}6H_2O$, $AlCl_3$, $ZnBr_2$, $ZnCl_2$ (Table 4).

Performing the reaction in the presence of $Cu(SO_4)_2{\cdot}5H_2O$ $Cu(OAc)_2{\cdot}H_2O$ and $NiCl_2{\cdot}6H_2O$ did not produce the desired product in quantitative yield (Table 4, entries 3, 4, 6). Comparatively, direct etherification in the presence of $FeCl_3{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ produced the corresponding ether in low yield after a long reaction time (Table 4, entries 1, 2). Reaction of 1-phenyl ethanol with 1-butanol in the presence of $CuCl_2$, $AlCl_3$, $ZnBr_2$ and $ZnCl_2$ required long reaction times to achieve reasonable yields concomitant with the formation of by-products (Table 4, entries 5, 7, 8, 9).

Conclusions

The present study demonstrates the ability of $Fe(HSO_4)_3$ to act as the simplest and least expensive heterogeneous catalyst for dehydration of two different alcohols to produce unsymmetrical ethers under solvent-free conditions. The significant features of this environmentally benign and cost-effective straightforward protocol for direct conversion of alcohols into unsymmetrical ethers include operational simplicity, low reagent loading, high product yields, short reaction time and mild reaction conditions, which do not require any solvent and distilled and/or dry reagents, and consequently minimizes the generation of toxic waste. We believe the $Fe(HSO_4)_3$-promoted etherification of alcohols is a straightforward exercise that could be easily incorporated into any synthetic methodologies.

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