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SUPPORTING INFORMATION

Title: The Chemistry of Alkylstrontium Halide Analogues, Part 2: Barbier-Type Dialkylation of Esters with Alkyl Halides

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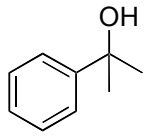
Ref. No.: O200500484

General methods. ^{1}H NMR spectra were recorded with a JEOL EX-90A spectrometer and chemical shifts (δ) were reported in ppm using tetramethylsilane as an internal standard. IR spectra were obtained using a HORIBA FT-IR 210 spectrometer. Commercially available metallic strontium ingot (Kanto Kagaku Co., Ltd., Japan) in liquid paraffin was cut into small pieces with a cutter in preparation for the start of each reaction. Tetrahydrofuran was freshly distilled from sodium diphenylketyl. Preparative thin layer chromatography (TLC) was performed on silica gel (Wakogel B-5F). All reagents were commercially available and used without further purification.

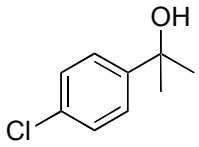
A typical procedure: Under an argon atmosphere, methyl benzoate (134 mg, 1.02 mmol), and methyl iodide (396 mg, 2.79 mmol) were added successively to a THF (5 ml) suspension of metallic strontium (219 mg, 2.50 mmol) at room temperature. After stirring for 30 min, the reaction mixture was quenched with an aqueous solution of 0.2 M hydrochloric acid (10 ml) (1 M = 1 mol dm^{-3}). The organic materials were extracted with diethyl ether (30 ml × 3), and the combined organic layers were washed with with 5% $NaHSO_3$ aqueous solution, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by thin layer chromatography on silica gel (hexane:ethyl acetate=4:1) to give the corresponding alkylated product, 2-phenylpropan-2-ol (136 mg, 96% yield) as yellow oil.



2-phenylpropan-2-ol (96% yield);

^{1}H-NMR (90MHz, $CDCl_3$) δ 1.56 (6H, s), 2.01 (1H, brs), 7.25-7.44 (5H, m)

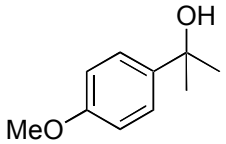
IR (neat) 3392, 3060, 3028, 2976, 2929, 1495, 1446, 1365, 1257, 1174, 1155, 1142, 1074, 1030, 910, 862, 764, 734, 700 cm^{-1}



2-(4-chlorophenyl)propan-2-ol (90% yield);

^{1}H-NMR (90MHz, $CDCl_3$) δ 1.55 (6H, s) , 1.90 (brs,1H) , 7.27 (2H, d, J=9.0Hz), 7.43 (2H, d, J=9.0Hz)

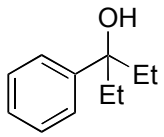
IR (neat) 3354, 2976, 2930, 2872, 1599, 1487, 1400, 1364, 1168, 1141, 1097, 1013, 957, 862, 829 cm^{-1}



2-(4-methoxyphenyl)propan-2-ol (52% yield);

^{1}H-NMR (90MHz, $CDCl_3$) δ 1.54 (6H, s), 2.06 (1H, brs), 3.77 (3H, s), 6.84 (2H, d, J=9.0Hz), 7.39 (2H, d, J=9.0Hz))

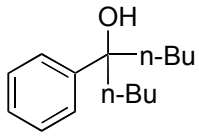
IR (neat) 3385, 2972, 2934, 2835, 1612, 1512, 1464, 1364, 1244, 1178, 1148, 1034, 955, 864, 831, 797, 731 cm^{-1}



3-phenylpentan-3-ol (80% yield);

^{1}H-NMR (90MHz, $CDCl_3$) δ 0.76 (6H, t, J=7.5Hz), 1.74 (1H, brs), 1.85 (4H, q, J=7.5Hz) 7.23-7.40 (5H, m)

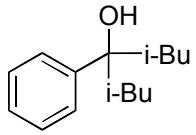
IR (neat) 3446, 3060, 3028, 2970, 2937, 2879, 1494, 1446, 1377, 1155, 1052, 1030, 962, 894, 758, 702 cm^{-1}



5-phenylnonan-5-ol (84% yield);

^{1}H-NMR (90MHz, $CDCl_3$) δ 0.78-1.90 (19H, m) , 7.21-7.45 (5H, m)

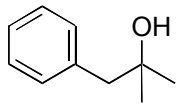
IR (neat) 3475, 3060, 3028, 2935, 2871, 1494, 1468, 1446, 1379, 1149, 1049, 1034, 910, 766, 735, 702 cm^{-1}



2,6-dimethyl-4-phenylheptan-4-ol (96% yield);

^{1}H-NMR (90MHz, $CDCl_3$) δ 0.65 (6H, d, J=6.1Hz), 0.90 (6H, d, J=6.2Hz), 1.47-1.79 (7H, m), 7.22-7.36 (5H, m)

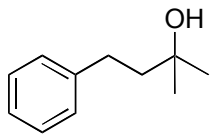
IR (neat) 3504, 3060, 3028, 2952, 2867, 1602, 1496, 1468, 1446, 1365, 1160, 1031, 910, 769, 735, 702 cm^{-1}



2-methyl-1-phenylpropan-2-ol (81% yield);

^{1}H-NMR (90MHz, $CDCl_3$) δ 1.14 (6H, s) , 1.53 (1H, brs) , 2.69 (2H, s), 7.19 (5H, brs)

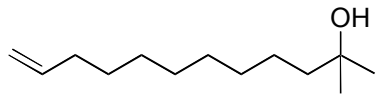
IR (neat) 3400, 3028, 2972, 2931, 1492, 1452, 1375, 1151, 1126, 901, 727, 712, 700 cm^{-1}



3-methyl-1-phenylbutan-3-ol (90% yield);

^{1}H-NMR (90MHz, $CDCl_3$) δ 1.28 (6H, s), 1.50-1.88 (3H, m), 2.60-2.80 (2H, m), 7.22 (5H, m)

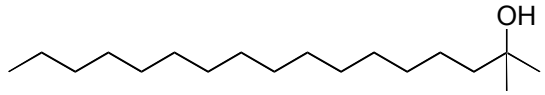
IR (neat) 3384, 3026, 2970, 2864, 1604, 1495, 1468, 1377, 1213, 1151, 1126, 928, 914, 740, 698 cm^{-1}



2-methyl-11-dodecen-2-ol (87% yield);

^{1}H-NMR (90MHz, $CDCl_3$) δ 1.20 (6H, s), 1.28-1.60 (14H, m), 1.95-2.15 (2H, m), 4.87-5.10 (2H, m), 5.59-5.98 (1H, m)

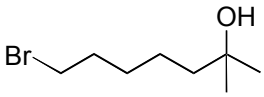
IR (neat) 3352, 2926, 2855, 1641, 1468, 1377, 1151, 991, 908, 735 cm^{-1}



2-methylheptadecan-2-ol (84% yield);

^{1}H-NMR (90MHz, $CDCl_3$) δ 0.85 (3H, m), 1.17 (6H, s), 1.20-1.90 (29H, m)

IR (KBr) 3460, 2966, 2920, 2848, 1471, 1466, 1379, 1157, 1149, 910, 727, 721 cm^{-1}



7-bromo-2-methylheptan-2-ol (84% yield);

^{1}H-NMR (90MHz, $CDCl_3$) δ 1.25 (6H, s), 1.29-2.09 (9H, m), 3.46 (2H, t, J=6.7Hz)

IR (neat) 3383, 2968, 2936, 2862, 1466, 1377, 1238, 1150, 908, 733 cm^{-1}