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A LiCl-Mediated Br/Mg-Exchange Reaction for the Preparation of Functionalized Aryl and Heteroaryl Magnesium Compounds Starting from Organic Bromides

Arkady Krasovskiy and Paul Knochel
Ludwig-Maximilians-Universität München, Department Chemie
Butenandtstrasse 5-13, Haus F, 81377 München (Germany)
Fax: (+49) 089 21 80 776 80
e-mail: paul.knochel@cup.uni-muenchen.de

General All reactions were carried out under an nitrogen atmosphere in dried glassware. All starting materials were purchased from commercial sources and used without further purification. THF was continously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Yields refer to isolated yields of compounds estimated to be > 95 % pure as determined by ^{1}H-NMR, capillary GC and combustion analysis (new compounds).

Preparation of the reagent *i*-PrMgCl·LiCl:

Magnesium turnings (110 mmol) and anhydrous LiCl (100 mmol) were placed in an Ar-flushed flask and THF (50 mL) was added. A solution of *i*-PrCl (100 mmol) in THF (50 mL) was slowly added at rt. The reaction starts within a few minutes. After addition, the reaction mixture was stirred for 12 h at rt. The grey solution of *i*-PrMgCl·LiCl was cannulated to an other flask under Ar and removed in this way from excess of magnesium. A yield of ca. 95-98% of *i*-PrMgCl·LiCl is obtained.

General Procedure for the Br/Mg-Exchange

A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgCl·LiCl (1 mL, 1.05 M in THF, 1.05 mmol). The neat aryl bromide (1 mmol) was added at apropriate temperature (as stated in the experiment). The reaction mixture was stirred at the same or plus 5°C temperature, and the completion of the Br/Mg exchange was checked by GC-analysis using tetradecane as internal standard.[1]

General Procedure for Copper Catalyzed Allylations

The freshly prepared magnesium reagent was cooled to -10 °C and the corresponding allyl bromide (1.2 mmol, 1.2 equiv.) was added, followed by addition of one drop of CuCN·2LiCl (a 1.0 M solution in THF was used, ca. 0.02 mmol, 0.02 equiv.). The mixture was stirred for 1 h at 0°C. The consumption of the magnesium reagent was checked by GC-analysis, using tetradecane as internal standard.[1] After the reaction was completed, sat. NH_4Cl solution was added and the mixture was extracted three times with Et_2O. The solvent was evaporated and the product was purified by flash chromatography (SiO_2).

General Procedure for Copper Catalyzed Acylations

The freshly prepared magnesium reagent was cooled to -10 °C and the corresponding acid chloride (1.2 mmol, 1.2 equiv.) was added, followed by dropwise addition of CuCN·2LiCl (a 1.0 M solution in THF was used, 0.2 mmol, 0.2 equiv.). The mixture was stirred for 2 h at room temperature. The consumption of the magnesium reagent was checked by GC-analysis, using tetradecane as internal standard.[1] After the reaction was completed, sat. NH_4Cl solution was added and the mixture was extracted three times with Et_2O. The solvent was evaporated and the product was purified by flash chromatography (SiO_2).

General Procedure for the reaction with aldehydes

The freshly prepared magnesium reagent was cooled to -10 °C and the corresponding aldehyde (1.05 mmol, 1.05 equiv.) was added. The mixture was stirred for 2O min at 0°C. The consumption of the magnesium reagent was checked by GC-analysis, using tetradecane as internal standard.[1] After the reaction was completed, sat. NH_4Cl solution was added and the mixture was extracted three times with Et_2O. The solvent was evaporated and the product was purified by flash chromatography (SiO_2).

(4-Methoxyphenyl)(phenyl)methanol (3a): A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was

charged with *i*-PrMgCl·LiCl (1 mL, 1.05 M in THF, 1.05 mmol). 4-Bromoanisol (187 mg, 1.0 mmol) was added dropwise. The Br/Mg-exchange was completed after 3 days at rt. The reaction mixture was cooled to -10 °C and PhCHO (1.05 mmol, 1.05 equiv.) was added. The mixture was stirred for 20 min at 0°C and was quenched with sat. aqueous NH_4Cl solution (2 mL). The aqueous phase was extracted with ether (3 x 4 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography (CH_2Cl_2) yielding the (4-methoxyphenyl) (phenyl)methanol **3a** (150 mg, 70%) as a white solid, (mp.: 68 – 69 °C). Analytical data was found to match literature data.[2]

(3-Fluorophenyl)(phenyl)methanol (3b): A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgCl·LiCl (1 mL, 1.05 M in THF, 1.05 mmol). 1-Bromo-3-fluorobenzene (175 mg, 1.0 mmol) was added at rt. The Br/Mg-exchange was completed after 3 h. The reaction mixture was cooled to -10 °C and PhCHO (1.05 mmol, 1.05 equiv.) was added. The mixture was stirred for 20 min at 0°C and was quenched with sat. aqueous NH_4Cl solution (2 mL). The aqueous phase was extracted with ether (3 x 4 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography (CH_2Cl_2) yielding the (3-fluorophenyl)(phenyl)methanol **3b** (172 mg, 85%) as a colourless oil. Analytical data was found to match literature data.[3]

(6-Bromopyridin-2-yl)(phenyl)methanol (3c): A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgCl·LiCl (1 mL, 1.05 M in THF, 1.05 mmol). 2,6-Dibromopyridine (237 mg, 1.0 mmol) was added at 0°C. The Br/Mg-exchange was completed after 3 h. The reaction mixture was cooled to -10 °C and PhCHO (1.05 mmol, 1.05 equiv.) was added. The mixture was stirred for 20 min at 0°C and was quenched with sat. aqueous NH_4Cl solution (2 mL). The aqueous phase was extracted with ether (3 x 4 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography (CH_2Cl_2) yielding the (6-bromopyridin-2-

yl)(phenyl)methanol **3c** (235 mg, 89%) as a white solid, (mp.: 50 – 52 °C). Analytical data was found to match literature data.[4]

4-[Hydroxy(phenyl)methyl]benzonitrile (3d): A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgCl·LiCl (1 mL, 1.05 M in THF, 1.05 mmol). 4-Bromobenzonitrile (182 mg, 1.0 mmol) was added at 0°C. The Br/Mg-exchange was completed after 2 h. The reaction mixture was cooled to -10 °C and PhCHO (1.05 mmol, 1.05 equiv.) was added. The mixture was stirred for 20 min at 0°C and was quenched with sat. aqueous NH_4Cl solution (2 mL). The aqueous phase was extracted with ether (3 x 4 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography (CH_2Cl_2) yielding the 4-[hydroxy(phenyl)methyl]benzonitrile **3d** (170 mg, 81%) as a white solid, (mp.: 68 – 70 °C). Analytical data was found to match literature data.[5]

2-Benzoylbenzonitrile (3e): A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgCl·LiCl (1 mL, 1.05 M in THF, 1.05 mmol). 2-Bromobenzonitrile (182 mg, 1.0 mmol) was added at 0°C. The Br/Mg-exchange was completed after 1 h. The reaction mixture was cooled to -10 °C and PhCOCl (1.2 mmol, 1.2 equiv.) was added, followed by dropwise addition of CuCN·2LiCl (a 1.0 M solution in THF was used, 0.2 mmol, 0.2 equiv.). The mixture was stirred for 2 h at room temperature and was quenched with sat. aqueous NH_4Cl solution (2 mL). The aqueous phase was extracted with ether (3 x 4 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography (CH_2Cl_2) yielding the 2-benzoylbenzonitrile **3e** (180 mg, 87%) as a white solid, (mp.: 85 – 86 °C). Analytical data was found to match literature data.[6]

3-Benzoylbenzonitrile (3f): A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgCl·LiCl (1 mL, 1.05 M in THF, 1.05 mmol). 3-Bromobenzonitrile (182 mg, 1.0 mmol) was added at 0°C. The Br/Mg-exchange was

completed after 3 h. The reaction mixture was cooled to -10 °C and PhCOCl (1.2 mmol, 1.2 equiv.) was added, followed by dropwise addition of CuCN·2LiCl (a 1.0 M solution in THF was used, 0.2 mmol, 0.2 equiv.). The mixture was stirred for 2 h at room temperature and was quenched with sat. aqueous NH_4Cl solution (2 mL). The aqueous phase was extracted with ether (3 x 4 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography (CH_2Cl_2) yielding the 3-benzoylbenzonitrile **3f** (182 mg, 88%) as a white solid, (mp.: 90 – 91 °C). Analytical data was found to match literature data.[7]

3-Allyl-5-bromopyridine (3g): A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgCl·LiCl (1 mL, 1.05 M in THF, 1.05 mmol). The reaction mixture was cooled to -15°C and 3,5-dibromopyridine (237 mg, 1.0 mmol) was added in one portion. The reaction temperature was increased to -10°C and the Br/Mg-exchange was completed after 15 min. Allyl bromide (133 mg, 1.1 mmol) was added, followed by addition of one drop of CuCN·2LiCl (a 1.0 M solution in THF was used, ca. 0.02 mmol, 0.02 equiv.). The reaction mixture was stirred for 1 h at 0°C and was quenched with sat. aqueous NH_4Cl solution (2 mL). The aqueous phase was extracted with ether (3 x 4 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography (CH_2Cl_2) yielding the 3-allyl-5-bromopyridine **3g** (184 mg, 93%) as a colourless oil.

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 8.48 (d, *J* = 2.2 Hz, 1 H); 8.32 (d, *J* = 1.6 Hz, 1 H); 7.61 (dd, *J* = 2.2 Hz, *J* = 1.6 Hz, 1 H); 5.89 – 5.68 (m, 1 H); 5.08-5.01 (m, 1 H); 3.32 (brd, *J* = 6.8 Hz, 1 H).

^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 149.0; 148.5; 139.6; 139.1; 137.5; 121.0; 118.0; 37.1.

IR (KBr): ν/cm^{-1} = 2989 (w); 1714 (s); 1594 (m); 1517 (s); 1446 (w); 1349 (s); 1286 (s); 1248 (m); 1133 (m); 857 (m); 770 (m); 752 (m); 698 (m).

MS (EI, 70 eV): m/z (%) = 197 (M^+, 51); 196 (43); 118 (37); 117 (77); 97 (37); 91 (49); 85 (48); 83 (35); 71 (68); 69 (42); 57 (100); 55 (55); 43 (63); 41 (51).

HR-MS: **(C_8H_8BrN) calculated 196.9840 found 196.9843**

Phenyl(3-thienyl)methanol (3h): A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgCl·LiCl (1 mL, 1.05 M in THF, 1.05 mmol). 3-Bromothiophene (163 mg, 1.0 mmol) was added dropwise. The Br/Mg-exchange was completed after 30 min at rt. The reaction mixture was cooled to -10 °C and PhCHO (1.05 mmol, 1.05 equiv.) was added. The mixture was stirred for 20 min at 0°C and was quenched with sat. aqueous NH_4Cl solution (2 mL). The aqueous phase was extracted with ether (3 x 4 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography (CH_2Cl_2) yielding the phenyl(3-thienyl)methanol **3h** (171 mg, 90%) as a white solid, (mp.: 89 – 90 °C). Analytical data was found to match literature data.[8]

Phenyl(1,3-thiazol-2-yl)methanol (3i): A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgCl·LiCl (1 mL, 1.05 M in THF, 1.05 mmol). 2-Bromothiazole (164 mg, 1.0 mmol) was added dropwise. The Br/Mg-exchange was completed after 30 min at rt. The reaction mixture was cooled to -10 °C and PhCHO (1.05 mmol, 1.05 equiv.) was added. The mixture was stirred for 20 min at 0°C and was quenched with sat. aqueous NH_4Cl solution (2 mL). The aqueous phase was extracted with ether (3 x 4 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography (CH_2Cl_2) yielding the phenyl(1,3-thiazol-2-yl)methanol **3i** (166 mg, 87%) as a white solid, (mp.: 107 – 109 °C). Analytical data was found to match literature data.[4]

(4-Chloro-3-methoxyphenyl)(diphenyl)phosphine oxide (3j): A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgCl·LiCl (1 mL, 1.05 M in THF, 1.05 mmol). 4-Bromo-1-chloro-2-methoxybenzene (222 mg, 1.0 mmol) was added. The Br/Mg-exchange was completed after 36 h at rt. The reaction mixture was cooled to -10 °C and Ph_2PCl (1.1 mmol, 1.1 equiv.) was added. The mixture was stirred for 20 min at 0°C and was quenched with 30% solution of H_2O_2 in water (5 mL). The

aqueous phase was extracted with ether (3 x 4 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography (CH_2Cl_2) yielding the (4-chloro-3-methoxyphenyl)(diphenyl)phosphine oxide **3j** (291 mg, 85%) as a white solid, (mp.: 105 – 107 °C). Analytical data was found to match literature data.[9]

(2,6-Dichlorophenyl)(phenyl)methanol (3k): A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgCl·LiCl (1 mL, 1.05 M in THF, 1.05 mmol). 2-Bromo-1,3-dichlorobenzene (226 mg, 1.0 mmol) was added. The Br/Mg-exchange was completed after 1 h at rt. The reaction mixture was cooled to -10 °C and PhCHO (1.05 mmol, 1.05 equiv.) was added. The mixture was stirred for 20 min at 0°C and was quenched with sat. aqueous NH_4Cl solution (2 mL). The aqueous phase was extracted with ether (3 x 4 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography (CH_2Cl_2) yielding the (2,6-dichlorophenyl)(phenyl)methanol **3k** (210 mg, 83%) as a white solid, (mp.: 55°C). Analytical data was found to match literature data.[10]

Biphenyl-2-yl(phenyl)methanol (3l): A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgCl·LiCl (1 mL, 1.05 M in THF, 1.05 mmol). 2-Bromobiphenyl (233 mg, 1.0 mmol) was added at rt. The Br/Mg-exchange was completed after 24 h at rt. The reaction mixture was cooled to -10 °C and PhCHO (1.05 mmol, 1.05 equiv.) was added. The mixture was stirred for 20 min at 0°C and was quenched with sat. aqueous NH_4Cl solution (2 mL). The aqueous phase was extracted with ether (3 x 4 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography (CH_2Cl_2) yielding the biphenyl-2-yl(phenyl)methanol **3l** (234 mg, 90%) as a white solid, (mp.: 68-70°C). Analytical data was found to match literature data.[11]

Ethyl 4-(9-phenanthryl)butanoate (3m): A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was

charged with *i*-PrMgCl·LiCl (1 mL, 1.05 M in THF, 1.05 mmol). 9-Bromophenanthrene (257 mg, 1.0 mmol) was added at 0°C. The Br/Mg-exchange was completed after 3 h. The reaction mixture was cooled to -10 °C and $I(CH_2)_3CO_2Et$ (1.2 mmol, 1.2 equiv.) was added, followed by dropwise addition of CuCN·2LiCl (a 1.0 M solution in THF was used, 0.2 mmol, 0.2 equiv.). The mixture was stirred for 12 h at 0°C and was quenched with sat. aqueous NH_4Cl solution (2 mL). The aqueous phase was extracted with ether (3 x 4 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography (CH_2Cl_2) yielding the ethyl 4-(9-phenanthryl)butanoate **3m** (237 mg, 81%) as a colourless oil.

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 8.67 – 8.53 (m, 2 H), 8.09 – 8.00 (m, 1 H), 7.83 – 7.70 (m, 1 H), 7.59 – 7.45 (m, 5 H), 4.06 (q, *J* = 7.1 Hz, 2 H); 3.07 (t, *J* = 7.6 Hz, 2 H), 2.36 (t, *J* = 7.3 Hz, 2 H); 2.13 – 2.01 (m, 2 H), 1.18 (t, *J* = 7.1 Hz, 3 H).

^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 173.9; 136.0; 132.2; 131.5; 131.2; 130.2; 128.5; 127.0; 126.9; 126.6; 126.5; 124.8; 124.5; 123.6; 122.8; 60.7; 34.4; 33.2; 25.7; 14.7.

IR (KBr): ν/cm^{-1} = 2989 (w); 1714 (s); 1594 (m); 1517 (s); 1446 (w); 1349 (s); 1286 (s); 1248 (m); 1133 (m); 857 (m); 770 (m); 752 (m); 698 (m).

MS (EI, 70 eV): m/z (%) = 292 (M^+, 59); 205 (19); 204 (100); 203 (30); 192 (17); 191 (60); 189 (18); 165 (11).

HR-MS: **($C_{20}H_{20}O_2$) calculated 292.1463 found 292.1463**

***tert*-Butyl 2-allylbenzoate (3n):** A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgCl·LiCl (1 mL, 1.05 M in THF, 1.05 mmol). The reaction mixture was cooled to -15°C and *tert*-butyl 2-bromobenzoate (257 mg, 1.0 mmol) was added in one portion. The reaction temperature was increased to –10°C and the Br/Mg-exchange was completed after 3 h. Allyl bromide (133 mg, 1.1 mmol) was added, followed by addition of one drop of CuCN·2LiCl (a 1.0 M solution in THF was used, ca. 0.02 mmol, 0.02 equiv.). The reaction mixture was stirred for 1 h at 0°C and was quenched with sat. aqueous NH_4Cl solution (2 mL). The aqueous phase was extracted with ether (3 x 4 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue

was purified by flash chromatography (CH_2Cl_2) yielding the *tert*-butyl 2-allylbenzoate **3n** (179 mg, 82%) as a colourless oil. Analytical data was found to match literature data.[20]

***tert*-Butyl 4-allylbenzoate (3o):** A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgCl·LiCl (0.5 mL, 2.22 M in THF, 1.11 mmol). The reaction mixture was cooled to -15°C and DMPU (1.5 mL) was added. The reaction mixture was stirred for 20 min at -15°C. The *tert*-butyl 4-bromobenzoate (257 mg, 1.0 mmol) was added dropwise. The reaction temperature was increased to –10°C and the Br/Mg-exchange was completed after 24 h. Allyl bromide (133 mg, 1.1 mmol) was added, followed by addition of one drop of CuCN·2LiCl (a 1.0 M solution in THF was used, ca. 0.02 mmol, 0.02 equiv.). The reaction mixture was stirred for 1 h at 0°C and was quenched with sat. aqueous NH_4Cl solution (2 mL). The aqueous phase was extracted with ether (3 x 4 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography (CH_2Cl_2) yielding the *tert*-butyl 4-allylbenzoate **3o** (192 mg, 88%) as a colourless oil. Analytical data was found to match literature data.[12]

3-Phenyl-2-benzofuran-1(3*H*)-one (3p): A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgCl·LiCl (0.5 mL, 2.22 M in THF, 1.11 mmol). The reaction mixture was cooled to -15°C and DMPU (1.5 mL) was added. The reaction mixture was stirred for 20 min at -15°C. Isopropyl 2-bromobenzoate (243 mg, 1.0 mmol) was added at –15°C. The Br/Mg-exchange was completed after 3 h at –10°C and then PhCHO (1.05 mmol, 1.05 equiv.) was added dropwise. The mixture was stirred for 1 h at rt and was quenched with sat. aqueous NH_4Cl solution (2 mL). The aqueous phase was extracted with ether (3 x 4 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography (CH_2Cl_2) yielding the 3-phenyl-2-benzofuran-1(3*H*)-one **3p** (168 mg, 80%) as a white solid, (mp.: 115-117°C). Analytical data was found to match literature data.[13]

(2-Bromophenyl)(phenyl)methanone (6a): A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgCl·LiCl (1 mL, 1.05 M in THF, 1.05 mmol). 1,2-Dibromobenzene (236 mg, 1.0 mmol) was added at -20°C. The Br/Mg-exchange was completed after 2 h at –15°C and PhCOCl (1.2 mmol, 1.2 equiv.) was added, followed by dropwise addition of CuCN·2LiCl (a 1.0 M solution in THF was used, 0.2 mmol, 0.2 equiv.). The mixture was stirred for 12 h at -10°C and was quenched with sat. aqueous NH_4Cl solution (2 mL). The aqueous phase was extracted with ether (3 x 4 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography (CH_2Cl_2) yielding the (2-bromophenyl)(phenyl)methanone **6a** (219 mg, 84%) as a white solid, (mp.: 42 – 44 °C). Analytical data was found to match literature data.[14]

3-(2-Bromophenyl)cyclohex-2-en-1-one (6b): A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgCl·LiCl (1 mL, 1.05 M in THF, 1.05 mmol). 1,2-Dibromobenzene (236 mg, 1.0 mmol) was added at -20°C. The Br/Mg-exchange was completed after 2 h at –15°C and 3-iodocyclohex-2-en-1-one (1.2 mmol, 1.2 equiv.) was added, followed by dropwise addition of CuCN·2LiCl (a 1.0 M solution in THF was used, 0.2 mmol, 0.2 equiv.). The mixture was stirred for 12 h at -10°C and was quenched with sat. aqueous NH_4Cl solution (2 mL). The aqueous phase was extracted with ether (3 x 4 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography (CH_2Cl_2) yielding the 3-(2-bromophenyl)cyclohex-2-en-1-one **6b** (216 mg, 86%) as a colourless oil.

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 7.62 (dd, *J* = 1.2 Hz, *J* = 8.0 Hz, 1 H); 7.35 (dt, *J* = 1.2 Hz, *J* = 7.5 Hz, 1 H); 7.25 – 7.16 (m, 2 H); 6.04 (s, 1 H); 2.69 (dt, *J* = 1.6 Hz, *J* = 7.0 Hz, 2 H); 2.54 (brt, *J* = 6.7 Hz, 2 H); 2.26-2.15 (m, 2 H).

^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 199.4; 162.5; 141.8; 133.1; 129.7; 129.2; 128.7; 127.5; 120.6; 37.4; 30.6; 23.0.

IR (KBr): ν/cm^{-1} = 2947 (m); 1673 (vs); 1468 (m); 1428 (m); 1344 (m); 1181 (m); 958 (w); 891 (w); 754 (s).

MS (EI, 70 eV): m/z (%) = 250 (M^+, 30); 224 (46); 222 (47); 171 (32); 143 (30); 128 (11); 116 (10); 115 (100).

HR-MS: **($C_{12}H_{11}BrO$) calculated 249.9993 found 250.0015**

1-(2,5-Dibromophenyl)-2,2-dimethylpropan-1-ol (6c): A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgCl·LiCl (1 mL, 1.05 M in THF, 1.05 mmol). 1,2,4-Tribromobenzene (315 mg, 1.0 mmol) was added at -55°C. The Br/Mg-exchange was completed after 2 h at -50°C and *t*-BuCHO (1.1 mmol, 1.1 equiv.) was added. The mixture was stirred for 1 h at -20°C and was quenched with sat. aqueous NH_4Cl solution (2 mL). The aqueous phase was extracted with ether (3 x 4 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography (CH_2Cl_2) yielding the 1-(2,4-dibromophenyl)-2,2-dimethylpropan-1-ol **6c** (287 mg, 89%) as a colouless oil.

^{1}H-NMR ($CDCl_3$, 200 MHz): δ = 7.68 (d, *J* = 2.5 Hz, 1 H); 7.39 (d, *J* = 8.5 Hz, 1 H); 7.25 (dd, *J* = 2.5 Hz, *J* = 8.5 Hz, 1 H); 4.93 (s, CH); 2.02 (brs, OH); 1.01 (brs, $3CH_3$, 9 H).

^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 144.0; 134.2; 133.1; 132.1; 122.9; 121.4; 79.1; 37.5; 26.2.

IR (KBr): ν/cm^{-1} = 2989 (w); 1714 (s); 1594 (m); 1517 (s); 1446 (w); 1349 (s); 1286 (s); 1248 (m); 1133 (m); 857 (m); 770 (m); 752 (m); 698 (m).

MS (EI, 70 eV): m/z (%) = 322 ($M^+(^{81}Br)$, 2); 320 (M^+, 1); 267 (42); 266 (27); 243 (28); 241 (29); 158 (27); 156 (30); 57 (100).

HR-MS: **($C_{11}H_{14}{}^{81}Br_2O$) calculated 321,9411 found 321,9350**

References and Notes:

[1] An aliquot of the reaction mixture was hydrolysed with sat. NH_4Cl solution and the organic compounds were extracted with Et_2O. The organic layer was subsequently subjected to GC-analysis.

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