Supporting Information

Formation of Grignard reagents from aryl halides : effective radical probes hint at a non participation of dianions in the mechanism.

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Procedure for synthesis of radical probes 2a and 2b

General :

All reactions were conducted under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring. THF and Et_2O were dried over and distilled from sodium metal. Acetone was dried over and distilled from K_2CO_3. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as internal standard. Magnesium turning (99%), 2-bromobenzyl bromide (98%), 2-bromophenol (98%) and cinnamyl bromide (97%) were purchased from Aldrich.

2-(4-phenyl-3-butenyl)-1-bromobenzene (2a) :

In a three necked flask equipped with a condenser and a dropping funnel are introduced : magnesium (0.389 g; 15.8 mmol), Et_2O (12 mL) and one crystal of I_2. From the dropping funnel was added slowly (a small part and when the reaction started all the solution) 2-bromobenzyl bromide (2.988 g; 11.7 mmol) dissolved in Et_2O (12 mL). The mixture was refluxed for 1h 15 min. Under nitrogen, the Grignard reagent was transferred with a canula to a solution of cinnamyl bromide (2.400 g; 11.8 mmol) in THF (12 mL). After refluxing 2 h 45 min, the reaction mixture was hydrolysed (HCl 10%), and extracted with Et_2O. The combined extracts were washed with water, dried ($MgSO_4$) and concentrated. A first column chromatography on silica-gel (petroleum ether 40-65°C and 3% ethyl acetate in petroleum ether as eluants) removed the bulk of impurities. The most polar fraction containing **2a** and colored impurities was purified in the same way. We obtained a mixture of **2a** and probably a product resulting from the SN_2' reaction. A last column chromatography on silica-gel impregnated with silver nitrate[a] (petroleum ether 40-65°C as eluant) gave 0.788 g (23%) of **2a** as a colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ 2.52 (m, 2H); 2.90 (m, 2H); 6.26 (dt, 6.4 Hz, 16.1 Hz, 1H); 6.42 (d, 16.1 Hz, 1H); 7.01-7.11 (m, 1H); 7.15-7.37 (m, 7H); 7.54 (d, 7.8 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 33.3, 36.2, 124.6, 126.1, 127.1, 127.5, 127.8, 128.6, 129.6, 130.5, 130.7, 132.9, 137.7, 141.0. Anal. Calcd for $C_{16}H_{15}Br$: C, 66.91; H, 5.26; Br, 27.82. Found: C, 66.69; H, 5.28; Br, 26.65.

2-bromophenyl-3-phenylprop-2-enyl ether (2b) :

In a two necked flask equipped with a condenser are introduced : cinnamyl bromide (2.000 g; 9.84 mmol), 2-bromophenol (1.750 g; 9.91 mmol) and acetone (15 mL). Under nitrogen, K_2CO_3 (2.000 g; 14.5 mmol) was added, and the reaction mixture was refluxed for 15 h. Then the reaction mixture was hydrolysed with water and the products were extracted with Et_2O. The combined extracts were

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[a] Silica-gel impregnated with silver nitrate: in a 1 litre flask equipped with a magnetic stirrer was introduced silver nitrate (4.08 g) and acetonitrile (244 mL). After stirring in the dark (10 min) silica-gel (81.3 g; 230-400 mesh) was added. The mixture was stirred 2 hours in the dark and then the solvent was evaporated. Drying was achieved overnight in an oven. This silica-gel can be stored 1 week in the dark. For successful, the column has to be performed in the dark.

washed with aqueous NaOH (10%) and brine, dried ($MgSO_4$) and concentrated. The resulting solid was recrystallised in EtOH to give 1.730 g (61%) of **2b** as a yellow solid. mp 46-51°C. ^1H NMR (200 MHz, $CDCl_3$) δ 4.75 (dd, 1.4 Hz, 5.5 Hz, 2H); 6.40 (dt, 5.5 Hz, 16.1 Hz, 1H); 6.77 (d, 16.1 Hz, 1H); 6.79-6.96 (m, 2H); 7.19-7.43 (m, 6H); 7.54 (dd, 1.7 Hz, 7.9 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 69.8, 112.5, 113.9, 122.2, 124.0, 126.7, 128.1, 128.5, 128.7, 133.2, 133.6, 136.5, 155.1. Anal. Calcd for $C_{15}H_{13}OBr$: C, 62.30; H, 4.53. Found: C, 62.49; H, 4.58.

Procedure for Grignard reagent formation

General :

All reactions were conducted under an atmosphere of purified argon in oven-dried glassware with magnetic stirring. THF was dried over and distilled from sodium metal. Before use, glassware was purged by four cycles vacuum/ argon. The solution of halide in THF (0.03-0.04 M) was degassed by the freeze-pump-thaw method (three cycles). All reactions were carried out by standard Schlenk techniques using Mg* slurries stored in a Schlenk.

General procedure :

A determined amount of Mg* was transferred with a canula in a Schlenk. To this was added within 1 minute the solution of halide in THF. After the reaction time, Mg* excess was removed off by filtration under purified argon, and the solution introduced in a flask containing 1-2 mg of 1,10-phenanthroline. Titration to the colorless end-point with 1-BuOH in xylene (0.5 M) gave the yield of Grignard reagents. Reaction mixture was washed with aqueous NH_4Cl solution, brine, and dried ($MgSO_4$). Organic layer was analysed by gas chromatography. Products were identified by NMR, co-injection of authentic samples and GC-MS.