Supplementary Information for

A Poly(ethylene glycol)-Supported Quaternary Ammonium Salt: An Efficient, Recoverable, and Recyclable Phase-Transfer Catalyst

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General. All PEG samples (Aldrich) were melted at 80°C in vacuum for 30 min before use to remove traces of moisture. After reaction, product purifcation involved evaporation of the reaction solvent in vacuum and addition of the residue dissolved in a few ml of CH_2Cl_2 to a stirred solution of Et_2O (50 mL/g of polymer) cooled at 0°C. After 20-30 min stirring at 0°C, the obtained suspension was filtered through a sintered glass filter and the solid repeatedly washed on the filter with Et_2O (up 100 mL of Et_2O/g of polymer, overall). ^1H NMR spectra were recorded at 300 MHz on $CDCl_3$ solutions at 25°C; δ are in ppm downfield from TMS.

Yield and Purity Determination of PEG-Supported Compounds.

The yields of the PEG-supported compounds were determined by weight, assuming a M_W of 5000 daltons for the PEG fragment, the M_W of which actually ranges from 4500 to 5500. The indicated yields are for pure compounds. The purity of these compounds was determined by 300 MHz ^1H NMR analysis in $CDCl_3$ with pre-saturation of the methylene signals of the polymer at 3.63 ppm. In recording the NMR spectra, a relaxation delay of 6 sec and an acquisition time of 4 sec were used to ensure complete relaxation and accuracy of integration. The relaxation delay was selected after T_1 measurements. The integrations of the signals of the PEG CH_3OCH_2 fragment at 3.30 and 3.36 ppm were used as internal standards. The estimated integration error is $\pm$ 5%.

Synthesis of Alcohol 2.

To a solution of mesylate **1** [1] (10 g, previously dried under vacuum) in DMF (40 mL, 0.05 M), Cs_2CO_3 (2.0 g, 3.0 equiv) and 4-hydroxybenzyl alcohol (0.75 g, 3.0 equiv) were added. The mixture was stirred for 15 h at 50°C and concentrated under vacuum to half of the original volume. Purification by precipitation in Et_2O gave PEG **2** (10 g, 100%). ^1H NMR : δ 7.27 (A part of AB system, ^3J (H,H) = 8.5 Hz, 2H: H meta to O in O-*Ar*-CH_2OH), 7.12 (A part of AB system, ^3J (H,H) = 8.5 Hz, 2H: H meta to O in O-*Ar*-CH_2), 6.88 (B part of AB system, ^3J (H,H) = 8.5 Hz, 2H: H ortho to O in O-*Ar*-CH_2OH), 6.85 (B part of AB system, ^3J (H,H) = 8.5 Hz, 2H: H ortho to O in O-*Ar*-CH_2), 4.26 (s, 2H: CH_2OH), 4.12 (t, ^3J (H,H) = 5.1 Hz, 2H: PEGCH_2-CH_2-OAr), 3.96 (t, ^3J (H,H) = 6.5 Hz, 2H: CH_2-O-Ar-CH_2OH), 3.87 (t, ^3J (H,H) = 5.1 Hz, 2H: PEGCH_2-CH_2-O-Ar), 3.40 (s, 3H: CH_3O), 2.77 (t, ^3J (H,H) = 6.5 Hz, 2H: ArCH_2), 2.08 (t, ^3J (H,H) = 6.5 Hz, 2H: CH_2-CH_2-CH_2).

Synthesis of Bromide 3.

To a solution of alcohol **2** (10 g) in dichloromethane (40 mL, 0.05 M) cooled at 0°C, PBr_3 (0.57 mL, 3.0 equiv) was added. The mixture was stirred for 5 h at 0°C and then slowly allowed to warm up to RT over the following 10 h. The solvent was concentrated under vacuum to half of the original volume. Purification by precipitation in Et_2O gave PEG **3** (9.6 g, 95%). ^1H NMR: δ 7.27 (A part of AB system, ^3J (H,H) = 8.5 Hz, 2H: H meta to O in O-*Ar*-CH_2Br), 7.09 (A part of AB system, ^3J (H,H) = 8.5 Hz, 2H: H meta to O in O-*Ar*-CH_2), 6.84 (two B parts of two AB systems, ^3J (H,H) = 8.5 Hz, 4H: 2H ortho to O in O-*Ar*-CH_2 and 2H ortho to O in O-*Ar*-CH_2Br), 4.51 (s, 2H: CH_2Br), 4.11 (t, ^3J (H,H) = 5,1 Hz, 2H: PEGCH_2-CH_2-OAr), 3.95 (t, ^3J (H,H) = 6.5 Hz, 2H: CH_2-O-Ar-CH_2Br), 3.87 (t, ^3J (H,H) = 5.1 Hz, 2H: PEGCH_2-CH_2-O-Ar), 3.40 (s, 3H: CH_3-O), 2.74 (t, ^3J (H,H) = 6.5 Hz, 2H: ArCH_2), 2.03 (t, ^3J (H,H) = 6.5 Hz, 2H: CH_2-CH_2 -CH_2).

Synthesis of Ammonium Salt 4.

To a solution of bromide **3** (9.6 g) in toluene (40 mL, 0.05M) kept at 65°C, freshly distilled tri-n-butylamine (4.7 mL,10.0 equiv) was added. The mixture was stirred for 72 h at 65°C. The solvent was then evaporated under vacuum, and the residue was dissolved in dichloromethane and precipitated in Et_2O. The product (8.3 g) was obtained in 85% yield. ^1H NMR: δ 7.44 (A part of AB system, ^3J (H,H) = 8.5 Hz, 2H: H meta to O in O-*Ar*-CH_2N), 7.10 (A part of AB system, ^3J (H,H) = 8.5 Hz, 2H: H meta to O in O-*Ar*-CH_2), 6.94 (B part of AB system, ^3J (H,H) = 8.5 Hz, 2H: ortho to O in O-*Ar*-CH_2N), 6.85 (B part of AB system, ^3J (H,H) = 8.5 Hz, 2H: H ortho to O in O-*Ar*-CH_2), 4.83 (s, 2H: CH_2N), 4.13 (t, ^3J (H,H) = 5.1 Hz, 2H: PEGCH_2-CH_2 -OAr), 3.97 (t, ^3J (H,H) = 6.5 Hz, 2H: CH_2-OAr-CH_2N), 3.87 (t, ^3J (H,H) = 5.1 Hz, 2H: PEGCH_2-CH_2-O-Ar), 3.40 (s, 3H: CH_3-O), 3.30 (m, 6H: N-CH_2-$CH_2CH_2CH_3$), 2.75 (t, ^3J (H,H) = 6.5 Hz, 2H: ArCH_2), 2.07 (t, ^3J (H,H) = 6.5 Hz, 2H: CH_2-CH_2 -CH_2), 1.80 (m, 6H: CH_2-CH_2-CH_2CH_3), 1.46 (m, 6H: CH_2CH_2-CH_2-CH_3), 1.02 (t, ^3J (H,H) = 7.4, 9H: CH_2CH_2CH-CH_3).

Synthesis of Ammonium Salt 5.

This was prepared by a similar reaction sequence starting from MeOPEG mesylate.[1] The alcohol was obtained in 99% yield, the bromide in 95% yield, and **5** in 71% yield, respectively. ^1H NMR: δ 7.46 (A part of AB system, ^3J (H,H) = 8.5 Hz, 2H: H meta to O in O-*Ar*-CH_2N), 7.00 (B part of AB system, ^3J (H,H) = 8.5 Hz, 2H: ortho to O in O-*Ar*-CH_2N), 4.84 (s, 2H: CH_2N), 4.13 (t, ^3J (H,H) = 5.1 Hz, 2H: PEGCH_2-CH_2-O-Ar), 3.87 (t, ^3J (H,H) = 5.1 Hz, 2H: PEGCH_2-CH_2-O-Ar), 3.40 (s, 3H: CH_3-O), 3.30 (m, 6H: N-CH_2-$CH_2CH_2CH_3$), 1.80 (m, 6H: CH_2-CH_2-CH_2CH_3), 1.45 (m, 6H: CH_2CH_2-CH_2-CH_3), 1.00 (t, ^3J (H,H) = 7.4, 9H: $CH_2CH_2CH_2$-CH_3).

Phase-Transfer Reactions.

General. These were carried out as described in Table 1. To allow a more meaningful comparison between the present data and those reported in the Literature, described procedures were followed as much as possible, replacing the catalyst employed in the reported procedures with compound **4**. 250 mg (approximately 0.04 mmol) of catalyst were generally used, and the amount of substrate was adjusted to this weight in order for the reaction to be carried out either with 4 mol% or 1 mol% of catalyst. The experiments in which the catalyst was recovered and recycled were carried out using 500 mg of catalyst to allow easier recovery by filtration. As mentioned in the text, the catalyst recovered from the first reaction contained a certain amount of NaOH; in this case the weight of the recovered catalyst was 1.0 g. When this catalyst was recovered again, its weight did not increase. The yields were determined on the products isolated by flash chromatography. The products showed ^1H NMR data in agreement with those reported in the Literature.

Bromide/Iodide Exchange.

A round bottom flask was charged with catalyst **4** (0.250 g, 0.04 mmol), CH_2Cl_2 (6 mL), KI (0.830 g, 5 mmol), and 1-bromooctane (0.172 mL, 1 mmol). The resulting slurry was stirred at the temperature and for the time indicated in Table 1. After catalyst precipitation, the crude product was isolated from the Et_2O solution by rotary evaporation under moderate vacuum. The relative amounts of product and unreacted starting material were determined by GC. When this reaction was carried out under liquid/liquid conditions a 5 :1 CH_2Cl_2 : H_2O mixture was used as solvent.

Bromide/Cyanide Exchange.

A round bottom flask was charged with catalyst **4** (0.250 g, 0.04 mmol), H_2O (1 mL), KCN (0.130 g, 2 mmol), and 1-bromooctane (0.172 mL, 1 mmol) or benzylbromide (0.119 mL, 1 mmol). The reaction was stirred at the temperature and for the time indicated in Table 1. After catalyst precipitation, the crude product was isolated from the Et_2O solution by rotary evaporation under moderate vacuum. The relative amounts of product and unreacted starting material were determined by NMR.

Benzylation of Phenol and Pyrrole.

A round bottom flask was charged with NaOH (0.480 g, 12 mmol), the organic substrate (4 mmol), catalyst **4** (0.250 g, 0.04 mmol) , benzyl bromide (0.571 mL, 4.8 mmol), and CH_2Cl_2 (20 mL), added in this order. The resulting slurry was stirred at the temperature and for the time indicated in Table 1. After catalyst precipitation, the crude product was isolated from the Et_2O solution and purified by flash chromatography (hexane : Et_2O 95 : 5 mixture as eluant). When this reaction was carried out under liquid/liquid conditions a 1 :1 CH_2Cl_2 : NaOH 0.1 M in H_2O mixture was used as solvent (6 mL).

Dichlorocyclopropanation of Styrene.

A round bottom flask was charged with styrene (0.114 mL, 1 mmol), $CHCl_3$ (1 ml), catalyst **4** (0.250 g, 0.04 mmol), a 9M solution of NaOH in H_2O (2 mL), and CH_2Cl_2 (0.5 mL).The reaction was stirred at the temperature and for the time indicated in Table 1. After catalyst precipitation, the crude product was isolated from the Et_2O solution and purified by flash chromatography (hexane : Et_2O 90 : 10 mixture as eluant).

References for Supplementary Information.

1) Annunziata, R.; Benaglia, M.; Cinquini, M.; Cozzi, F. *Chem. Eur. J.* **2000**, *6*, 133-138.