SUPPORTING INFORMATION

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Heck Vinylation of Aryl Iodides by a Silica Sol-Gel Entrapped Pd(II) Catalyst and its One-Pot Combination with a Photocyclization Process

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Experimental Details

Entrapment of Dichlorobis(triphenylphosphine)palladium in a Silica Sol-Gel Matrix. Five mL (33.9 mmol) of tetrametoxysilane (TMOS) was stirred for 1 h at 25 °C with 4 mL (0.222 mol, r = 6.7) of triply distilled water. To the slurry was added a solution of 30 mg (4.27×10^{-2} mmol) of $PdCl_2(PPh_3)_2$ in 11 mL of THF. The addition of 50 µl of an 0.1 M solution of tetrabutylammonium fluoride induced gelation of the reaction mixture within a few minutes. The gel was left for aging for 16 h, treated for 1 h with 30 mL of boiling toluene, dried for 10 h at 1 mm, sonicated and refluxed for 30 min with 15 mL CH_2Cl_2 and dried again for 3 h at 1 mm to give 2.30 g of the entrapped catalyst. The combined toluene and CH_2Cl_2 washings proved to contain < 1 ppm palladium (measuring limit).

Vinylation and Alkynylation of Aryl Iodides and Bromides. Typically a solution of 4.0 mmol of the unsaturated substrate, 4.0 mmol of the aryl halide and 1.14 mL (6 mmol) of tripropylamine in 15 mL of toluene was refluxed in the presence of a crushed silica sol-gel sample containing 30 mg (4.27×10^{-2} mmol) of $PdCl_2(PPh_3)_2$. After 8-16 h the reaction mixture was cooled and the used catalyst separated by filtration, washed with CH_2Cl_2, dried and stored to await recycling in the second run. The toluene solution was washed (x 3) with 5 mL water, dried ($MgSO_4$) and concentrated. After chromatographic separation the products were compared with authentic samples.

One-Pot Heck and Photocyclization Reactions. A mixture of 4.0 mmol of the alkene, 4.0 mmol of the iodoarene, 1.14 mL (6 mmol) of Pr_3N, silica gel containing 4.27×10^{-2} mmol of $PdCl_2(PPh_3)_2$ and 15 mL toluene was placed in a quartz well. The mixture was refluxed for 12 h under ambient atmosphere, cooled to 25 °C and then irradiated with a 150 W Hanovia medium pressure mercury lamp. After further 3-4 h the catalyst was separated by filtration, washed with water, CH_2Cl_2 and dried before reusing in a second run. The catalyst-free reaction mixture was concentrated and chromatographed on alumina using hexane-benzene mixtures as eluent. The products were compared with authentic samples of phenanthrene and chrysene.

Physical Data of the Isolated Products

Chrysene. Mp 252-4 °C; 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.61-7.74 (m, 4), 7.99-8.03 (m, 4), 8.72 (d, J = 9 Hz, 2), 8,78 (d, J = 8 Hz, 2).

***E*-1-Chloro-4-(2-phenylethenyl)benzene**. Mp 128-129 °C; 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.05 (s, 1), 7.20-7.49 (m, 10).

***E*-1,1′-(1,2-Ethenediyl)bisbenzene.** Mp 127 °C; 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.12 (s, 2), 7.24-7.29 (m, 2), 7.34-7.39 (m, 4), 7.51 (d, J = 7 Hz), 4).

***Z*-1,1′-(1,2-Ethenediyl)bisbenzene.** 300 MHz ^{1}H NMR ($CDCl_3$) δ 6.66 (s, 2), 7.18-7.34 (m, 10).

1,1′-(1,2-Ethynediyl)bisbenzene. Mp 59-61 °C; 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.32-7.40 (m, 6), 7.53-7.58 (m, 4).

***E*-1-Nitro-4-(2-phenylethenyl)benzene.** Mp 155 °C; 400 MHz ^{1}H NMR ($CDCl_3$) δ 7.14 (d, J = 16 Hz, 1), 7.25-7.42 (m, 4), 7.55 (d, J = 7 Hz, 2), 7.93 (ABq, J_{AB} = 9 Hz, 4).

Phenanthrene. Mp 102-103 °C; 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.58-7.69 (m, 4), 7.75 (s, 2), 7.89 (d, J = 7 Hz, 2), 8.69 (d, J = 8 Hz, 2).

***E*-3-Phenyl-2-propenenitrile**. Bp 135 °C (12 mm); 400 MHz ^{1}H NMR ($CDCl_3$) δ 5.77 (d, J = 17 Hz, 1), 7.29-7.37 (m, 6); 100 MHz, ^{13}C NMR ($CDCl_3$) δ 96.22, 118.05, 127.26, 129.00, 131.10, 133.40, 150.48.

***Z*-3-Phenyl-2-propenenitrile**. Bp 108-110 °C (12 mm); 400 MHz ^{1}H NMR ($CDCl_3$) δ 5.35 (d, J = 12 Hz, 1), 7.03 (d, J = 12 Hz, 1), 7.28-7.37 (m, 5); 100 MHz, ^{13}C NMR ($CDCl_3$) δ 94.95, 117.19, 128.45, 128.90, 130.87, 133.48, 148.61.

***E*-3-Phenyl-2-propionic Acid Methyl Ester**. Mp 38 °C; 300 MHz ^{1}H NMR ($CDCl_3$) δ 3.81 (s, 3), 6.40 (d, J = 16 Hz, 1), 7.35-7.39 (m, 3), 7.40-7.53 (m, 2), 7.55 (d, J = 16 Hz, 1).