Design of Polyaromatic Hydrocarbon-Supported Tin Reagents: a New Family of Tin Reagents Easily Removable from Reaction Mixtures

Didier Stien^{a} and Stéphane Gastaldi^{b*}*

^a CNRS-UPS 2561, 16 avenue André Aron, 97300 Cayenne, French Guiana, France, and LAPP-UMR 5810, Université de Montpellier 2, 34095 Montpellier cedex 5, France

^b LCMO-UMR 6517, Université d'Aix-Marseille III, Avenue Escadrille Normandie-Niemen, 13397 Marseille cedex 20, France

stien@univ-montp2.fr ; stephane.gastaldi@univ.u-3mrs.fr

Table of Contents for the Supporting Information Section

Procedures **Pg S1**

¹H and ¹³C NMR spectra **Pg S9**

General Remarks: ¹H NMR spectra were recorded at 200, 250 or 300 MHz and ¹³C NMR spectra at 75.5 or 100.6 MHz as indicated. Chemical shifts (δ) are in ppm downfield from tetramethylsilane, and coupling constants (*J*) are in Hz. s stands for singlet, d for doublet, t for triplet, q for quadruplet, quint for quintuplet, hex for hexuplet and m for multiplet. Satellite signals in NMR refer to distinguishable

signals obtained for ^{117}Sn and ^{119}Sn (spin = 1/2), which natural abundance is 7.7 and 8.6% respectively. All solvents were dried and distilled by standard techniques.

1-Pyrenemethanol [24463-15-8], methyl α -bromophenylacetate [3042-81-7], 1-bromododecane [143-15-7], α -bromo- α -methyl- γ -butyrolactone [33693-67-3], 4-cyanobenzaldehyde [105-07-7], 4-iodoanisole [696-62-8], 3-iodophenol [626-02-8] and 2-iodonitrobenzene [609-73-4] are commercially available. 17*H*-Tetrabenzo[*a,c,g,i*]fluorene (Tbf),¹ allyl-(2-iodophenyl)-ether² and (4-iodobutyl)-phenyl ether³ were prepared accordingly to literature procedures.

10-(17*H*-Tetrabenzo[*a,c,g,i*]fluoren-17-yl)-dec-1-ene (1a). A solution of Tbf (218 mg, 0.6 mmol) in 1,4-dioxane (9 mL) was degassed with argon. The reaction was then heated at 95°C, and 40% aq. Bu₄NOH (382 μL , 0.58 mmol) was added to it. After cooling, the yellow ammonium salt was filtered off under argon and washed with degassed dioxane (2x2 mL) and degassed ether (2x5mL). The ammonium salt was suspended in degassed dioxane (11 mL) again, 10-bromo-dec-1-ene (129 μL , 0.58 mmol) was added, and the mixture was heated at 95°C overnight. Solvent was removed, the residue was triturated three times with ether and the organic fractions were collected by filtration. Evaporation and column chromatography (hexane/CH₂Cl₂ (95/5 to 90/10)) allowed to isolate the desired product (230 mg, 80%); ¹H NMR (CDCl₃, 250 MHz): δ 0.37 (m, 2H), 0.70-1.25 (m, 6H), 1.81 (broad q, 2H, *J* = 7.0), 2.61 (m, 2H), 4.81-4.90 (m, 2H), 5.07 (t, 1H, *J* = 4.4), 5.67 (qt, 1H, *J* = 10.3 and 6.8), 7.60-7.74 (m, 8H), 8.28 (m, 2H), 8.70 (dd, 2H, *J* = 7.9 and 1.2), 8.78-8.83 (m, 4H); ¹³C NMR (CDCl₃, 100.6 MHz): δ 22.8, 29.2, 29.3, 29.4, 29.6, 30.0, 34.1, 34.2, 47.7, 114.5, 124.0, 124.1, 125.0, 125.5, 126.2, 126.4, 127.3, 128.1, 128.6, 129.4, 131.0, 131.9, 137.3, 139.8, 145.0.

17-(10-Bromodecanyl)-17*H*-tetrabenzo[*a,c,g,i*]fluorene (1b). A solution of Tbf in dioxane (9 mL) was carefully degassed and placed under argon at 95°C. Aqueous TBAOH (382 μL , 0.58 mmol) was added dropwise. The anion precipitated immediately. The reaction mixture was cooled to room temperature and the anion was collected by filtration under argon. The crystal was successively washed with degassed dioxane (2x2 mL) and degassed ether (2x5 mL). Solid 1,10-dibromodecane (720 mg, 2.4 mmol) was added to the anion, and the mixture was suspended in degassed dioxane (11

mL) and heated over night at 95°C. During this time, the reaction mixture became clear. The solvent was evaporated. Removal of the dioxane was insured by two successive evaporation of ethyl acetate. The residue was then dissolved in methylene chloride and silica was added. Evaporation of the solvent, followed by column chromatography (hexane/CH₂Cl₂ (90/10)) allowed to isolate the desired product as a yellow crystal (210 mg, 62%); ¹H NMR (CDCl₃, 250 MHz): δ 0.32 (m, 2H), 0.61-1.23 (m, 12H), 1.65 (quint, 2H, *J* = 7.0), 2.56 (m, 2H), 3.25 (t, 2H, *J* = 6.9), 5.02 (t, 1H, *J* = 4.4), 7.54-7.69 (m, 8H), 8.22 (m, 2H), 8.64 (dd, 2H, *J* = 7.9 and 1.3), 8.73-8.80 (m, 4H); ¹³C NMR (CDCl₃, 100.6 Mhz): δ 22.7, 28.5, 29.0, 29.2, 29.5, 29.9, 33.3, 34.1, 34.6, 47.7, 124.0, 124.1, 125.0, 125.5, 126.1, 126.4, 127.3, 128.0, 128.6, 129.3, 130.9, 131.8, 137.3, 144.9.

17-(10-Iododecanyl)-17*H*-tetrabenzo[*a,c,g,i*]fluorene (1c). A mixture of alkylbromide **1b** (23.4 mg, 40 μmol) and sodium iodide (90 mg, 0.6 mmol) in acetone was heated under reflux for 12 hours. After cooling, the solvent was evaporated and the residue was dissolved in ethyl acetate (10 mL) and water (10 mL). The aqueous layer was separated and the organic layer was washed with brine, dried (Na₂SO₄) and evaporated. ¹H NMR indicated that 90% of the starting bromide had been transformed into the related iodide. The iodide (24.8 mg, 98%) was used without further purification in the attempted stannylation reactions; ¹H NMR (CDCl₃, 250 MHz): δ 0.36 (m, 2H), 0.64-1.35 (m, 12H), 1.66 (quint, 2H, *J* = 7.1), 2.62 (m, 2H), 3.07 (t, 2H, *J* = 7.1), 5.08 (t, 1H, *J* = 4.4), 7.59-7.74 (m, 8H), 8.28 (m, 2H), 8.69 (dd, 2H, *J* = 7.9 and 1.3), 8.78-8.85 (m, 4H).

10-(Dibutyl-phenyl-stannanyl)-decan-1-ol (2). A solution of dibutyl phenyltin hydride (580 mg, 1.86 mmol) in THF (5 mL) was added over 2 hours to a mixture of alkene (222 μL, 1.24 mmol) and Pd(OH)₂/C (66 mg, 0.12 mmol) in the same solvent (10 mL). 1 hour after the end of the addition, the reaction mixture was filtered on celite and evaporated. Column chromatography (hexane/AcOEt (90/10)) allowed to isolate a fraction of the desired product in pure form (96 mg, 17%); ¹H NMR (C₆D₆, 250 MHz): δ 0.90 (t, 6H, *J* = 7.2), 1.00-1.45 (m, 27H), 1.57-1.72 (m, 4H), 3.37 (broad q, 2H, *J* = 4.3), 7.18-7.31 (m, 3H), 7.48-7.66 (m, 2H).

17-[10-(Dibutyl-phenyl-stannanyl)-decanyl]-17*H*-tetrabenzo[*a,c,g,i*]fluorene (3). Tosyl chloride (47 mg, 0.247 mmol) was added in one portion at 0°C to a solution of alcohol (96 mg, 0.205 mmol) in pyridine (660 μ L, 8.2 mmol). The reaction was left to stand overnight in the refrigerator (at a temperature of 5°C). Excess electrophile was destroyed with water (1h at room temperature) and the reaction mixture was separated between ether (40 mL) and water (20 mL). The aqueous layer was discarded and the organic layer was washed with water, was dried, filtered and evaporated. Remaining pyridine was removed under vacuum. The desired toluene-4-sulfonic acid 10-(dibutyl-phenyl-stannanyl)-decyl ester was obtained pure enough for the alkylation step (112 mg, 88%); ^1H NMR (C_6D_6 , 250 MHz): δ 0.90 (t, 6H, $J = 7.2$), 0.95-1.42 (m, 26H), 1.54-1.70 (m, 4H), 1.81 (s, 3H), 3.83 (t, 2H, $J = 6.5$), 6.69 (d, 2H, $J = 8.0$), 7.15-7.29 (m, 3H), 7.45-7.63 (m, 2H), 7.77 (d, 2H, $J = 8.0$).

This reaction was performed at all time under argon and all solvents used were degassed. A suspension of Tbf (95 mg, 0.261 mmol) in dioxane (4 mL) was heated at 95°C. At this temperature, the reaction mixture becomes homogeneous. 40% aqueous tetrabutylammonium hydroxide was added, and after 5 min, the reaction mixture was cooled down to room temperature. The insoluble anion was collected by filtration and was washed abundantly with ether. It was then suspended in dioxane (5 mL) in the presence of the tosylate (157 mg, 0.253 mmol). The reaction mixture was heated at 95°C overnight and was then cooled down to room temperature, diluted with ether and filtered. Solvents were evaporated and the residue was purified by chromatography (hexane/AcOEt (98/2)) to give **3** (94 mg, 46%); ^1H NMR (C_6D_6 , 250 MHz): δ 0.26-1.60 (m, 30H), 0.82 (t, 6H, $J = 7.2$), 2.48-2.56 (m, 2H), 4.73 (t, 1H, $J = 4.2$), 7.10-7.25 (m, 3H), 7.35-7.57 (m, 10H), 8.11 (dd, 2H, $J = 8.0$ and 1.0), 8.60 (d, 4H, $J = 7.9$), 8.76 (dd, 2H, $J = 8.5$ and 1.7).

1-Allyloxymethyl-pyrene (5). 1-Pyrenemethanol (1.46 g, 6.28 mmol) was dissolved in THF (15 mL) and was added to a suspension of NaH (0.38 g, 9.43 mmol) in the same solvent (5 mL). After 1h at room temperature, the reaction mixture was cooled down to -40°C and allyl bromide (0.82 mL, 9.43 mmol) was added in one portion. The reaction was allowed to stand overnight at room temperature, aqueous NH_4Cl was added (caution) and the reaction mixture was diluted with AcOEt (50 mL). The

organic phase was washed with saturated NH_4Cl (20 mL) and brine (20 mL), and was then dried, filtered and evaporated. Column chromatography (hexane/AcOEt (95/5)) allowed to isolate the desired product as a pale yellow oil (1.13 g, 66%). Spectral data were identical to those previously described in the literature (CAS reg. No: 144096-40-2);⁴ ^1H NMR (C_6D_6 , 250 MHz): δ 3.94 (dt, 2H, J = 5.3 and 1.6), 5.02 (s, 2H), 5.10 (dq, 1H, J = 10.5 and 1.6), 5.31 (dq, 1H, J = 17.2 and 1.6), 5.93 (ddt, 1H, J = 17.2, 10.5 and 5.3), 7.78 (t, 1H, J = 7.6), 7.84 (s, 2H), 7.93-8.01 (m, 5H), 8.39 (d, 1H, J = 9.3).

Dibutyl-[3-(pyren-1-ylmethoxy)-propyl]-stannane (6). Dibutyltin hydride (381 μL , 2 mmol) was slowly added to a solution of olefin (547 mg, 2 mmol), AIBN (7 mg, 0.02 mmol) and dibutyltin dichloride (608 mg, 2 mmol) in methylene chloride (1 mL). The reaction was stirred overnight at room temperature. TLC indicated some remaining starting material. More dibutyltin dichloride (608 mg, 2 mmol), AIBN (7 mg, 0.02 mmol) and dibutyltin hydride (381 μL , 2 mmol) were therefore added. After 24 hours, only a minimal amount of SM was left (TLC). The reaction mixture was thus diluted with $t\text{BuOH}$ (15 mL) and NaBH_3CN was added (628 mg, 10 mmol). After being refluxed for half an hour, the solvents were evaporated and the residue was triturated with ether and filtered. The ether was evaporated and the crude oil was purified by FC (hexane/AcOEt (97/3)) to yield the expected tin hydride (570 mg, 56%); ^1H NMR (C_6D_6 , 250 MHz): δ 0.82 (t, 2H, J = 7.1), 0.79-1.01 (superimposed m, 6 H), 1.25 (hex, 4H, J = 7.1), 1.38-1.52 (m, 4H), 1.91 (quint, 2H, J = 6.4), 3.45 (t, 2H, J = 6.4), 5.02 (s, 2H), 5.04 (m, 1H), 7.74 (t, 1H, J = 6.6), 7.80 (s, 2H), 7.89-7.99 (m, 5H), 8.39 (d, 1H, J = 9.3); ^{13}C NMR (C_6D_6 , 100.6 MHz): δ 5.1 (CH_2), 8.8 (CH_2), 14.0 (CH_3), 27.6 (CH_2), 28.4 (CH_2), 30.4 (CH_2), 71.9 (CH_2), 73.6 (CH_2), 124.2 (CH), 124.9 (CH), 125.6 (2CH), 126.3 (CH), 127.2 (CH), 127.8 (CH), 128.0 (2CH), 128.5 (CH), 129.3 (C), 129.9 (C), 131.6 (C), 131.8 (C), 132.0 (C), 132.7 (C). MS (FAB+, NBA matrix): 507 and 505 ($\text{C}_{28}\text{H}_{35}\text{O}^{120}\text{Sn}$, 2.8%, and $\text{C}_{28}\text{H}_{35}\text{O}^{118}\text{Sn}$, 2.3% respectively, isotopic pattern of tin ($[\text{M}-\text{H}]^+$), 215 (pyrene- CH_2^+ , 100%). Neither M^+ or MH^+ , nor $(\text{M}-\text{H})^+$ were detectable in HRMS.

Phenyl-acetic acid methyl ester (Table 1, entry 1). Spectral data were identical to those previously described in the literature (CAS Reg. No: 101-41-7; SDBS No: 3294).⁵

Dodecane (Table 1, entry 2). Spectral data were identical to those previously described in the literature (CAS Reg. No: 112-40-3; SDBS No: 2135).⁵

Butyl phenyl ether (Table 1, entry 3). Spectral data were identical to those previously described in the literature (CAS Reg. No: 1126-79-0; SDBS No: 2472).⁵

Ethyl (2-iodo-4,5-dimethoxy-phenyl)-acetate (Starting material, table 1, entry 4). To a 0°C solution of (2-iodo-4,5-dimethoxy-phenyl)-acetic acid⁶ (11.46g, 35.6 mmol) in ethanol (200 mL) was added thionyl chloride (6.77 mL, 56.9 mmol). The reaction mixture was allowed to warm up to room temperature and was stirred one night. The solvent was evaporated leading to the pure title compound (12.58g, 100% yield). ¹H NMR (CDCl₃, 200 MHz): δ 1.27 (t, 3H, *J* = 7.1), 3.72 (s, 2H), 3.83 (s, 6H), 4.17 (q, 2H, *J* = 7.1), 6.80 (s, 1H), 7.22 (s, 1H); ¹³C NMR (CDCl₃, 50 MHz): δ 14.3 (CH₃), 45.8 (CH₂), 55.9 (OCH₃), 56.1 (OCH₃), 61.1 (OCH₂), 88.9 (CI), 113.2 (CH), 121.6 (CH), 130.2 (C), 148.6 (C), 149.3 (C), 170.8 (CO).

(3,4-Dimethoxy-phenyl)-acetic acid ethyl ester (Table 1, entry 4). Spectral data were identical to those previously described in the literature (CAS Reg. No: 18066-68-7).⁷ ICP-MS analysis indicated that product contains 0.31 % (w/w) of elemental tin.

3-Methyl-2,3-dihydro-benzofuran (Table 1, entry 5). Spectral data were identical to those previously described in the literature (CAS Reg. No: 13524-73-7).⁸

1-Iodo-4,5-dimethyl-2-prenyloxy-benzene (Starting material, table 1, entry 6). 2-Iodo-4,5-dimethylphenol⁹ (0.9g, 3.63 mmol) was dissolved in THF (5 mL) and was added to a suspension of NaH (0.38 g, 9.43 mmol) in the same solvent (5 mL). After 0.5h at room temperature, the reaction mixture was cooled down to -40°C and prenyl bromide (0.63 mL, 5.44 mmol) was added in one portion. The reaction was allowed to stand overnight at room temperature, aqueous NH₄Cl was added (caution) and the reaction mixture was diluted with AcOEt (50 mL). The organic phase was washed with saturated NH₄Cl (20 mL) and brine (20 mL), and was then dried, filtered and evaporated. Column chromatography (pentane/AcOEt (99/1)) allowed to isolate the desired product (0.747 g, 65%). ¹H NMR (CDCl₃, 300 MHz): δ 1.75 (s, 3H), 1.82 (s, 3H), 2.18 (s, 3H), 2.22 (s, 3H), 4.54 (d, 2H, *J* = 6.5),

5.52 (bt, 1H, $J = 6.5$), 6.63 (s, 1H), 7.52 (s, 1H).); ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 19.1 (CH_3), 19.1 (CH_3), 20.7 (CH_3), 26.5 (CH_3), 67.3 (CH_2), 83.7 (C), 115.4 (CH), 120.5 (CH), 131.6 (C), 138.4 (C), 138.5 (C), 140.5 (C), 156.4 (C).

3-Isopropyl-5,6-dimethyl-2,3-dihydro-benzofuran (Table 1, entry 6). ^1H NMR (CDCl_3 , 300 MHz): δ 0.87 (d, 3H, $J = 6.8$), 0.93 (d, 3H, $J = 6.8$), 1.93 (m, 1H), 2.19 (s, 3H), 2.21 (s, 3H), 3.25 (dt, 1H, $J = 9.1$ and 5.2), 4.33 (dd, 1H, $J = 9.1$ and 5.2), 3.25 (pseudo t, 1H, $J = 9.1$), 6.61 (s, 1H), 6.96 (s, 1H); ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 19.0 (CH_3), 19.8 (CH_3), 20.3 (CH_3), 20.5 (CH_3), 32.1 (CH), 48.6 (CH), 74.4 (CH_2), 110.8 (CH), 126.4 (CH), 127.0 (C), 128.1 (C), 136.7 (C), 159.1 (C).

2-Phenyl-pent-4-enoic acid methyl ester (Table 2, entry 1). Spectral data were identical to those previously described in the literature (CAS Reg. No: 14815-73-7).¹⁰ ICP-MS analysis indicated that product contains 0.37 % (w/w) of elemental tin.

3-Allyl-3-methyl-dihydrofuran-2-one (Table 2, entry 2). Spectral data were identical to those previously described in the literature (CAS Reg. No: 115094-65-0).¹¹ ICP-MS analysis indicated that product contains 0.77 % (w/w) of elemental tin.

4-(1-Hydroxy-but-3-enyl)-benzonitrile (Table 2, entry 3). Spectral data were identical to those previously described in the literature (CAS Reg. No: 71787-53-6).¹² ICP-MS analysis indicated that product contains 0.20 % (w/w) of elemental tin.

4-Methoxy-biphenyl (Table 2, entry 4). Spectral data were identical to those previously described in the literature (CAS Reg. No: 613-37-6; SDBS No: 18836).⁵

Biphenyl-3-ol (Table 2, entry 5). Spectral data were identical to those previously described in the literature (CAS Reg. No: 92-69-3; SDBS No: 3219).⁵

2-Nitro-biphenyl (Table 2, entry 6). Spectral data were identical to those previously described in the literature (CAS Reg. No: 86-00-0; SDBS No: 7034).⁵

¹ Hay, A. M.; Hobbs-Dewitt, S.; MacDonald, A. A.; Ramage, R. *Synthesis* **1999**, 1979-1985.

-
- ² Nieman, J.A.; Ennis, M.D. *J. Org. Chem.* **2001**, *66*, 2175-2177.
- ³ Pritts, W.A.; Peters, D.G. *J. Electroanal. Chem.* **1995**, *380*, 147-160.
- ⁴ Busch, B. B.; Staiger, C. L.; Stoddard, J. M.; Shea, K. J. *Macromolecules* **2002**, *35*, 8330-8337.
- ⁵ <http://www.aist.go.jp/RIODB/SDBS/> (access date: December 1, 2003)
- ⁶ Qandil, A. M.; Miller, D. W. D.; Nichols, E. *Synthesis* **1999**, 2033-2035.
- ⁷ Brenna, E.; Caraccia, N.; Fogliato, G.; Fronza, G.; Fuganti, C. *Tetrahedron* **1997**, *53*, 10555-10564.
- ⁸ Chen, D.-W.; Ochiai, M. *J. Org. Chem.* **1999**, *64*, 6804-6814.
- ⁹ Kajigaeshi, S.; Kakinami, T.; Yamasaki, H.; Fujisaki, S.; Kondo, M.; Okamota, T. *Chem. Lett.* **1987**, 2109-2112.
- ¹⁰ Beckwith, A. L. J.; Gerba, S. *Aust. J. Chem.* **1992**, *45*, 289-308.
- ¹¹ Toru, T.; Yamada, Y.; Ueno, T.; Maekawa, E.; Ueno, Y. *J. Am. Chem. Soc.* **1988**, *110*, 4815-4817.
- ¹² Fuerstner, A.; Voigtlaender, D. *Synthesis* **2000**, 959-969.

HERTZ

HERTZ

Dibutyl-[3-(pyren-1-ylmethoxy)-propyl]-stannane (6)

- 134.7707
- 131.7961
- 131.2215
- 130.5815
- 129.0614
- 128.0723
- 127.8614
- 127.7087
- 127.3305
- 126.3777
- 125.5340
- 125.3449
- 125.3158
- 123.3158

Methanesulfonic acid 3-pyren-1-yl-propyl ester (9b).

— 69.7355

— 37.7852

— 31.3122
— 29.5740

128.0723
127.8614
127.7087
127.3305
126.3777
125.5340
125.3449
125.3158
123.3158

Methanesulfonic acid 3-pyren-1-yl-propyl ester (9b).

69.7355

37.7852

31.3122
29.5667

Ethyl (2-iodo-4,5-dimethoxy-phenyl)-acetate
(Starting material, table 1, entry 4)

Ethyl (2-iodo-4,5-dimethoxy-phenyl)-acetate (Starting material, table 1, entry 4)

1663.39
1662.07
1660.75
1656.97
1655.65
1654.33
1650.36
1649.04
1647.72

1365.58
1359.16

1-iodo-4,5-dimethyl-2-prenyloxybenzene (Starting material, table 1, entry 6)

3-Isopropyl-5,6-dimethyl-2,3-dihydro-benzofuran
(Table 1, entry 6).

3-Isopropyl-5,6-dimethyl-2,3-dihydro-benzofuran
(Table 1, entry 6).