Double Elimination Protocol for Convenient Synthesis of Dihalo Diphenylacetylens: Versatile Building Blocks for Tailor-Made Phenylene-Ethynylenes

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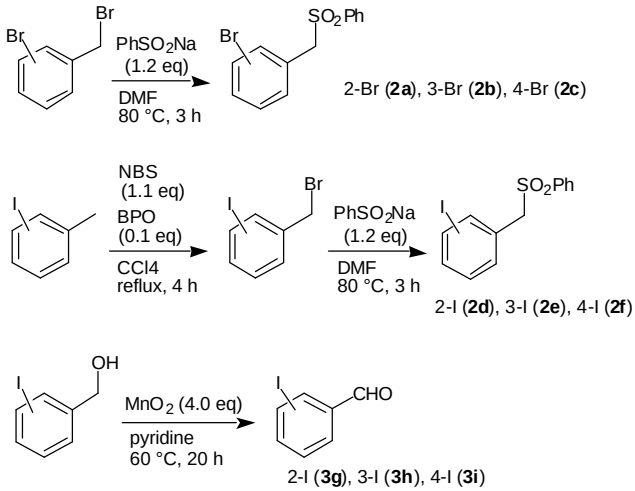
Supporting Information

Phenyl sulfones **2a-f** and iodobenzaldehyde **3g-i** were prepared from the corresponding benzyl bromides and benzyl alcohols, respectively.



Preparation of 2-bromobenzyl phenyl sulfone (2a) (representative). A DMF solution (50 mL) of 2-bromobenzyl bromide (5.0 g, 20.0 mmol) and $PhSO_2Na$ (dihydrate, 4.80 g, 24.0 mmol) was heated at 80 °C for 12 h. After usual workup with CH_2Cl_2/water, the combined CH_2Cl_2 layer was washed with water (three times) and NaClaq, dried over $MgSO_4$, filtered and evaporated. The crude mixture was dissolved in a small amount of CH_2Cl_2 by heating, and, after addition of hexane, the solution was kept in the refrigerator. 2-Bromobenzyl phenyl sulfone (**2a**) was obtained as colorless

crystals in 88 %. Bromo derivatives **2b** and **2c** were prepared in the same procedure.
2-Bromobenzyl phenyl sulfone (2a):[1] 88%:^{1}H NMR (300 MHz, $CDCl_3$) δ 4.59 (s, 2H), 7.19 (t, *J* = 8.5 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.42-7.52 (m, 4H), 7.63 (t, *J* = 8.9 Hz, 3H).

3-Bromobenzyl phenyl sulfone (2b):[2] 93%: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.26 (s, 2H), 7.05 (d, *J* = 7.7 Hz, 1H), 7.15 (t, *J* = 7.9 Hz, 1H), 7.19 (s,1H), 7.43-7.54 (m, 3H), 7.65 (t, *J* = 7.6 Hz, 3H).

4-Bromobenzyl phenyl sulfone (2c):[2] 94%: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.26 (s, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.48 (t, *J* = 7.9 Hz, 2H), 7.60-7.68 (m, 3H).

Preparation of 2-iodobenzyl phenyl sulfone (2d) (representative). To a CCl_4 solution (100 mL) of 2-iodotoluene (4.36 g, 20.0 mmol) and NBS (3.92 g, 22.0 mmol) was added benzoyl peroxide (484.5 mg, 2.0 mmol), and the mixture was heated at reflux for 12 h. After filtration of the mixture, the solid obtained was washed with CH_2Cl_2, and the filtrate was washed with $NaHCO_3$. The combined aqueous layer was extracted with AcOEt, and the CH_2Cl_2 and AcOEt layers were combined, dried over $MgSO_4$ and evaporated. The crude products were dissolved in AcOEt by heating, and, after addition of hexane, the solution was kept at r.t. 2-Iodobenzyl bromide was obtained as colorless crystals. A DMF solution (80 mL) of 2-iodobenzyl bromide obtained and $PhSO_2Na$ (dihydrate, 4.80 g, 24.0 mmol) was heated at 80 °C for 12 h. After usual workup with CH_2Cl_2/water, the combined CH_2Cl_2 layer was washed with water (three times) and NaClaq, dried over $MgSO_4$, filtered and evaporated. The crude mixture was dissolved in a small amount of CH_2Cl_2 by heating, and, after addition of hexane, the solution was kept in the refrigerator. 2-Iodobenzyl phenyl sulfone (**2d**) was obtained as colorless crystals in 73 %. Iodo derivatives **2e** and **2f** were prepared in the same procedure.

2-Iodobenzyl phenyl sulfone (2d):[3] 73%:^{1}H NMR (300 MHz, $CDCl_3$) δ 4.59 (s, 2H), 7.02 (t, *J* = 7.7 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.43-7.53 (m, 3H), 7.61-7.67 (m, 3H), 7.74 (d, *J* = 8.0 Hz, 1H).

3-Iodobenzyl phenyl sulfone (2e): 74%: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.23 (s, 2H), 7.02 (t, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 7.35 (s, 1H), 7.47-7.52 (m, 2H), 7.62-7.67 (m, 4H).

4-Iodobenzyl phenyl sulfone (2f): 75%: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.24 (s, 2H), 6.96 (d, *J* = 8.3 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.58-7.67 (m, 5H).

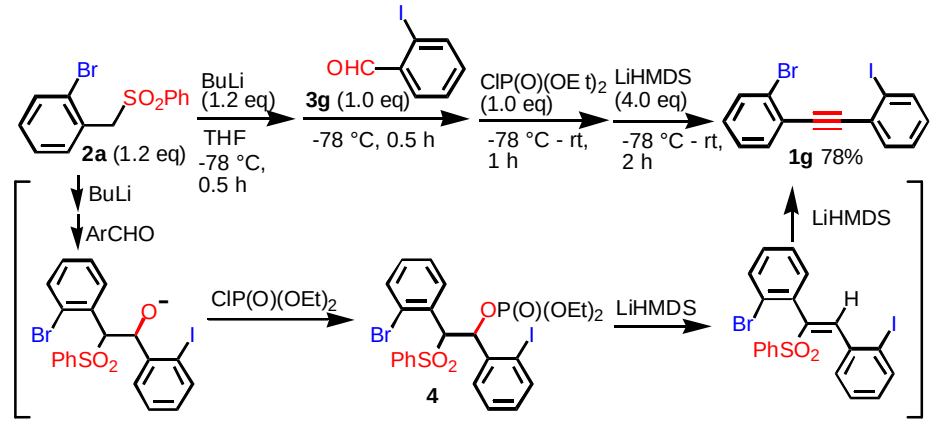
Preparation of 2-iodobenzaldehyde (3g) (representative). A suspension of 2-iodobenzyl alcohol (4.68 g, 20.0 mmol) and manganese oxide (6.96 g, 80.0 mmol) in pyridine (30 mL) was heated at 60 °C for 20 h. After filtration through a celite pad, the solid obtained was washed with water, and the aqueous layer was extracted with AcOEt. The combined organic layer was washed with NaClaq, dried over $MgSO_4$, filtered and evaporated. The crude mixture was subjected to column chromatography on silica gel (5% AcOEt/hexane) to furnish **3g** in pure form (4.27 g, 92%). Iodo derivatives **3h** and **3i** were prepared in the same procedure.

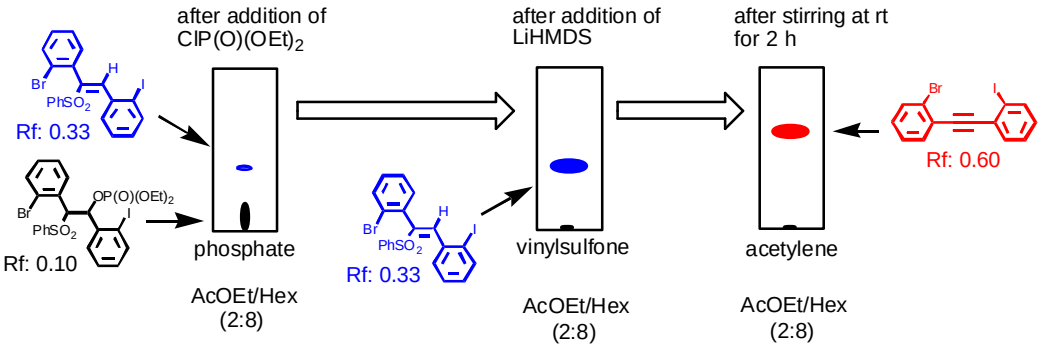
2-Iodobenzaldehyde (3g):[4] 92%:^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 10.08 (s, 1H).

3-Iodobenzaldehyde (3h): 96%: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.7 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 8.21 (s, 1H), 9.93 (s, 1H).

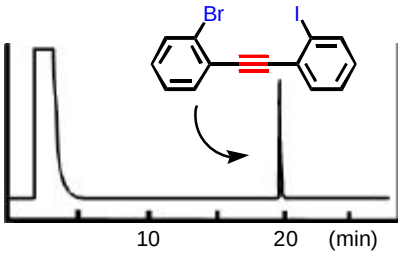
4-Iodobenzaldehyde (3i):[5] 96%: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.92 (d, *J* = 8.2 Hz, 2H), 9.96 (s, 1H).

One-pot process for dihalo-substituted diphenylacetylene derivatives

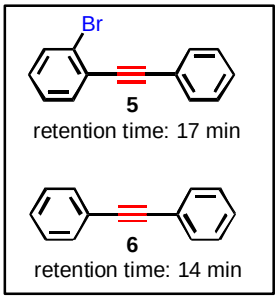




GLC analysis of crude products



CBP5-M25
Injection temp: 270 °C
Column temp: 60-260 °C (10 °C/min)



not detected

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