Bulky Diarylammonium Arenesulfonates as Selective Esterification Catalysts

Kazuaki Ishihara,* Shoko Nakagawa, and Akira Sakakura

Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan.

Dimesitylamine.[1,2] Sodium *tert*-butoxide (5.8 g, 60 mmol), bis(dibenzylideneacetone) palladium (288 mg, 0.5 mmol) and BINAP (467 mg, 0.75 mmol) were placed into a flask and dissolved into distilled toluene (25 mL). To this solution was added mesityl bromide (7.7 mL, 50 mmol) and 2,4,6-trimethylaniline (0.7 mL, 5 mmol) dropwise with stirring at room temperature and the mixture was refluxed at 120°C for 48 h. After the mixture was cooled, 1 M HCl was added and extracted with ether. The combined organic layer was washed with $NaHCO_3$ and dried by $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2, *n*-hexane : EtOAc = 1 : 0 → 100 : 1) and recrystallization by hexane give product as a colorless solid. IR (KBr) 3414, 2958, 2911, 2851, 2730, 1477, 1439, 1314, 1257, 1009, 858 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$) δ 6.79 (s, 4H), 4.61 (s, 1H), 2.24 (s, 6H), 1.97 (s, 12H); ^{13}C NMR (75MHz, $CDCl_3$) δ 139.4 (s, 2C), 130.7 (s, 4C), 129.4 (s, 2C), 129.3 (s, 4C), 20.5 (s, 2C), 19.0 (s, 4C).

***N*-(2,6-Diisopropylphenyl)-*N*-(2,4,6-mesityl)amine:** This amine was prepared according to the similar manner with that of dimesitylamine using 2,6-diisopropylaniline instead of 2,4,6-trimethylaniline; IR (KBr) 3430, 2961, 2925, 2863, 1484, 1466, 1442, 1340, 1270, 857, 740 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.10 (s, 3H), 6.76 (s, 2H), 4.68 (br, 1H), 3.12 (septet, *J*=6.9 Hz, 2H), 2.22 (s, 3H), 1.95 (s, 6H), 1.11 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3 (s, 1C), 140.4 (s, 1C), 139.1 (s, 1C), 130.0 (s, 2C), 129.0 (s, 1C), 126.3 (s, 2C), 124.2 (s, 2C), 123.2 (s, 2C), 27.9 (s, 2C), 23.4 (s, 4C), 20.4 (s, 1C), 19.3 (s, 2C); HRMS (FAB) calcd for $C_{21}H_{29}N$ ($M+H^+$) 295.2300, found 295.2308.

Dimesitylammonium Pentafluorobenzenesulfonate (1b). A mixture of dimesitylamine (279 mg, 1.1 mmol) and pentafluorobenzenesulfonic acid (248 mg, 1.0 mmol) in toluene (3 mL) was stirred for 1 h at room temperature. The mixture was centrifuged, and then toluene layer was decanted from solid phase. This solid was washed with hexane (3 mL x 3) by stirring and dried over *in vacuo* (1 Torr, 60°C). IR (KBr) 3414, 2971, 2926, 1490, 1247, 1227, 1188, 1103, 1045, 984, 634 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.75 (s, 4H), 2.22 (d, *J* = 6.0 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6 (d, *J* = 259 Hz, 2C), 141.8 (d, *J* = 255 Hz, 1C), 139.3 (s, 2C), 137.0 (d, *J* = 252 Hz, 2C), 132.6 (s, 4C), 131.3 (s, 2C), 130.7 (s, 4C), 118.4 (t, *J* = 17 Hz, 1C), 20.4 (s, 2C), 18.5 (s, 4C); ^{19}F NMR (282

MHz, $CDCl_3$) δ –138.2 (dd, *J* = 6.1, 21.3 Hz, 2F), –153.6 (t, *J* = 21.4 Hz, 1F), –162.7 (dt, *J* = 5.4, 21.4 Hz, 2F)

***N*-(2,6-Diisopropylphenyl)-*N*-(2,4,6-mesityl)ammonium pentafluorobenzenesulfonate (2b).** **2b** was prepared according to the same manner with that of **1b**. IR (KBr) 3430, 2962, 1489, 1247, 1227, 1115, 983, 657 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36 (t, *J*=7.8 Hz, 1H), 7.19 (d, *J*=8.1 Hz, 2H), 6.73 (s, 2H), 3.11 (septet, *J* = 6.8 Hz, 2H), 2.20 (s, 3H), 2.15 (s, 6H), 1.07 (d, *J*=6.6 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7 (t, *J* = 7.8 Hz, 2C), 143.3 (s, 1C), 142.0 (d, *J* = 255 Hz, 1C), 137.7 (s, 1C), 137.2 (d, *J* = 252 Hz, 2C), 134.1 (s, 1C), 132.3 (s, 1C). 131.4 (s, 2C), 130.9 (s, 2C), 129.2 (s, 2C), 125.0 (s, 2C), 118.7 (s, 1C), 28.6 (s, 2C), 23.5 (s, 4C), 20.3 (s, 1C), 19.1 (s, 2C); ^{19}F NMR (282 MHz, $CDCl_3$) δ –138.3 (dd, *J* = 6.2, 21.2 Hz, 2F), –153.0 (t, *J* = 21.2 Hz, 1F), –162.4 (dt, *J* = 6.2, 21.2 Hz, 2F).

4-(*N*-Mesitylamino)polystyrene resin (12). 4-Bromopolystyrene resin (**11**, 2% DVB, 2.71 mmol/g) (**5**, 369 mg, 1 mmol), sodium *tert*-butoxide (3.46 g, 36 mmol), bis(dibenzylideneacetone) palladium (115 mg, 0.2 mmol) and BINAP (280 mg, 0.45 mmol) were placed into a round-bottomed flask and decompressed. To this mixture was added degassed toluene (20 mL) and 2,4,6-mesitylaniline (0.84 mL, 6 mmol) dropwise under N_2. This mixture was refluxed at 120°C for 72 h. After the mixture was cooled, the resin was filtered and washed with THF. This resin was stirred for 0.5 h with thiocyanuric acid (532 mg, 3 mmol) in THF(10 mL) and then contrifuged. The organic layer was decanted from the resin and THF (10 mL) was added. After 0.5 h stirring, contrifuged, THF layer was removed, and Et_3N (5 mL)–THF (5 mL) was added. After 0.5 h stirring, contrifuged, organic layer was removed and 4 M HCl (5 mL)–1,4-dioxane (5 mL) was added. After 0.5 h stirring, centrifuged, organic layer was removed, washed with DMF and Et_3N (5 mL)–THF (5 mL) was added. After 0.5 h stirring, centrifuged, organic layer was removed and H_2O (5 mL)–THF (5 mL) was added. After 0.5 h stirring, centrifuged, liquid phase was removed and DMF (5 mL)–THF (5 mL) was added. After 0.5 h stirring, centrifuged, organic layer was removed and THF (10 mL) was added. After 0.5 h stirring, centrifuged, organic layer was removed and Et_2O (10 mL) was added. After 0.5h stirring, the resin was filtered and dried over *in vacuo* to give product **12** (1.76 mmol/g) as a brown solid. IR (KBr) 3407, 3021, 2918, 2852, 1510, 1484, 1452, 698, 542 cm^{-1}.

6-Bound pentafluorobenzenesulfonic acid (3b). To the mixture of **12** (1.76 mmol/g) in toluene (10 mL) was added pentafluorobenzenesulfonic asid (909 mg, 3 mmol) and stirred at rt for 6 h. This resin was filtered and washed with toluene, hexane, a little ether and dried over *in vacuo* to give product as a dark brown solid **3b** (1.12 mmol/g); IR (KBr) 3408, 3026, 2925, 1488, 1226, 1115, 982, 657, 545 cm^{-1}.

Experimental procedure for recovering and reusing 3b (See Figure 3): The reaction mixture, 4-phenylbutyric acid (181 mg, 1.1 mmol), 1-octanol (157 μL, 1.0 mmol), **3b** (1.12 mmol NH_2^+/g; 45 mg, 0.05 mmol), and heptane (2 mL), was stirred for 1 h at 80°C. Chloroform (1 mL) was added to the resultant mixture, which was further stirred at room temperature for 0.5 h to swell **3b**. Then the mixture was centrifuged and the solution phase was decanted to separate **3b**, which was washed twice with heptane. Recovered **3b** was reused for next reaction.

References

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