Electronic Supplementary Information (ESI)

Catalytic version of hypervalent aryl-λ^3-iodane-induced Hofmann rearrangement of primary carboxamides: iodobenzene as an organocatalyst and *m*-chloroperbenzoic acid as a terminal oxidant

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General Information. IR spectra were recorded on Perkin Elmer 1720 FT-IR spectrometers. ^{1}H NMR spectra were obtained on either a JEOL JNM-AL300, JNM-AL400, or Bruker AV400 spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) downfield from external Me_4Si. Mass spectra (MS) were obtained on Waters LCT Premier spectrometer. Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel (MERCK, silica gel F-254). Kieselgel 60 (Merck, 230-400 mesh) was used for column chromatography. Melting points were determined with a Yanaco micro melting points apparatus and are uncorrected.

General Procedure for Catalytic Phenyl-λ^3-iodane-induced Hofmann Rearrangement. A Typical Example (Table 1, Entry 10). *m*-Chloroperbenzoic acid (72% purity, 58 mg, 0.24 mmol) was dried under vacuum for 15 min at room temperature prior to use. To a stirred solution of *m*-CPBA in dichloromethane (0.94 mL) and water (49 μL) was added a 48% aqueous solution of tetrafluoroboric acid (31 μL, 0.24 mmol), a 0.89 M dichloromethane solution of iodobenzene (11 μL, 0.01 mmol) and then α-phenylacetamide (27 mg, 0.20 mmol) at 25 ºC under argon and the mixture was stirred for 39 h. A 10% aqueous HCl solution (2 mL) was added and the reaction mixture was extracted with dichloromethane four times to remove *m*-chlorobenzoic acid and iodobenzene. Combined organic phase was extracted with a 10% aqueous HCl solution two times. Combined aqueous phase was concentrated under reduced pressure to determine the ^{1}H NMR yield (100%, acetonitrile was used as an internal standard) of benzylammonium chloride (**3a**).[S1] Evaporation under vacuum gave **3a** (24 mg, 87%) as a white solid: colorless needles (recrystallized from acetonitrile); mp >170 ºC (sublimation); IR (KBr) 3320-2420, 1593, 1477, 1383, 1215, 1113, 1059, 970, 920, 877, 748, 696 cm^{-1}; ^{1}H NMR (400 MHz, D_2O) δ 7.56-7.44 (m, 5H), 4.23 (s, 2H).

Propylammonium Chloride (3b):[S2] a white powder (recrystallized from ethyl acetate-hexane); mp 160-164 ºC; IR (KBr) 3310-2690, 2684, 1570, 1504, 1394, 1302, 1240-930 cm^{-1}; ^{1}H NMR (400 MHz, D_2O) δ 2.96 (t, J = 7.3 Hz, 2H), 1.68 (sext, J = 7.3 Hz, 2H), 0.97 (t, J = 7.3 Hz, 3H).

Pentylammonium Chloride (3c):[S3] a white powder (recrystallized from ethyl acetate-hexane); mp 216-217 ºC; IR (KBr) 3670-2570, 1591, 1498, 1296, 1220-950 cm^{-1}; ^{1}H NMR (400 MHz, D_2O) δ 3.01 (t,

J = 7.6 Hz, 2H), 1.68 (quint, *J* = 7.6 Hz, 2H), 1.40-1.31 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H).

Heptylammonium Chloride (3d):[S4] colorless prisms (recrystallized from acetonitrile); mp 228-230 ºC; IR (KBr) 3680-2260, 2150-1800, 1603, 1508, 1469, 1398, 1379, 1149, 1095, 904, 771, 725 cm^{-1}; ^1H NMR (400 MHz, D_2O) δ 3.01 (t, *J* = 7.5 Hz, 2H), 1.75-1.62 (m, 2H), 1.46-1.24 (m, 8H), 0.89 (t, *J* = 6.6 Hz, 3H); ESIMS (positive) *m/z* 116 [$(M-Cl)^+$].

Nonylammonium Chloride (3e):[S3] a white powder (recrystallized from ethyl acetate-hexane); mp >190 ºC (sublimation); IR (KBr) 3310-2200, 1581, 1520, 1469, 1151, 1109, 943, 930, 722 cm^{-1}; ^1H NMR (400 MHz, D_2O) δ 3.0 (t, *J* = 7.3 Hz, 2H), 1.67 (quint, *J* = 7.3 Hz, 2H), 1.44-1.23 (m, 12H), 0.88 (t, *J* = 7.2 Hz, 3H); ESIMS (positive) *m/z* 144 [$(M-Cl)^+$].

2-Propylammonium Chloride (3f):[S2] a white powder (hygroscopic); IR (KBr) 3710-2300, 2160-1770, 1579, 1502, 1396, 1300, 1280-920 cm^{-1}; ^1H NMR (400 MHz, D_2O) δ 3.51 (sept, *J* = 7.0 Hz, 1H), 1.31 (d, *J* = 7.0 Hz, 6H).

1,1-Dimethylethylammonium Chloride (3g):[S5] colorless needles (recrystallized from acetonitrile); mp >170 ºC (sublimation); IR (KBr) 3330-2100, 2079, 1508, 1400, 1375, 1302, 1219, 995, 885 cm^{-1}; ^1H NMR (400 MHz, D_2O) δ 1.39 (s, 9H).

Cyclopentylammonium Chloride (3h):[S6] a white powder (recrystallized from ethyl acetate-hexane); mp 182-184 ºC; IR (KBr) 3450-2300, 2023, 1601, 1496, 1452, 1394, 1296, 1200-900 cm^{-1}; ^1H NMR (400 MHz, D_2O) δ 3.67 (tt, *J* = 7.4, 5.5 Hz, 1H), 2.13-2.01 (m, 2H), 1.82-1.56 (m, 6H).

Cyclohexylammonium Chloride (3i):[S7] a white powder (recrystallized from ethyl acetate-hexane); mp 180-182 ºC; IR (KBr) 3500-2500, 2000-1700, 1612, 1508, 1446, 1387, 1230-900 cm^{-1}; ^1H NMR (400 MHz, D_2O) δ 3.23-3.12 (m, 1H), 2.05-1.94 (m, 2H), 1.87-1.76 (m, 2H), 1.71-1.63 (m, 1H), 1,43-1.12 (m, 5H); ESIMS (positive) *m/z* 100 [$(M-Cl)^+$].

Cycloheptylammonium Chloride (3j):[S8] a white powder (recrystallized from ethyl acetate-hexane); mp 168-170 ºC; IR (KBr) 3500-2500, 2100-1940, 1603, 1498, 1464, 1385, 1298, 1220-900 cm^{-1}; ^1H NMR (400 MHz, D_2O) δ 3.42-3.34 (m, 1H), 2.06-1.97 (m, 2H), 1.78-1.41 (m, 10H); ESIMS (positive) *m/z* 114 [$(M-Cl)^+$].

1-Adamantylammonium Chloride (**3k**):[S7] a white powder (recrystallized from methanol); mp >300 ºC; IR (KBr) 3700-2500, 2100-1900, 1599, 1520, 1493, 1454, 1377, 1365, 1315, 1270-900, 764, 704, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.37 (br s, 3H), 2.22-2.16 (m, 3H), 1.93 (br s, 6H), 1.75-1.64 (m, 6H); ESIMS (positive) *m/z* 152 [$(M-Cl)^+$].

5-Bromopentylammonium Chloride (3l):[S9] a white powder (recrystallized from ethyl acetate-hexane); mp 175-178 ºC; IR (KBr) 3700-2500, 2030-1790, 1572, 1489, 1468, 1331, 1298, 1271, 1240-950, 910, 812, 731, 652 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 3.47 (t, *J* = 6.6 Hz, 2H), 2.94 (t, *J* =

7.5 Hz, 2H), 1.95-1.86 (m, 2H), 1.73-1.63 (m, 2H), 1.59-1.49 (m, 2H); ESIMS (positive) *m/z* 166 [(M-Cl)$^+$].

5-Nitropentylammonium Chloride (**3m**):[S10] IR (neat) 3608, 3263, 2941, 1614, 1550, 1508, 1435, 1387, 1280-890 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD) δ 4.49 (t, *J* = 6.8 Hz, 2H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.08-1.97 (m, 2H), 1.76-1.64 (m, 2H), 1.52-1.42 (m, 2H); ESIMS (positive) *m/z* 133 [(M-Cl)$^+$].

6-(*p*-Toluenesulfonamido)hexylammonium Chloride (**3n**):[S11] a pale yellow solid; IR (KBr) 3800-2400, 1597, 1550-1360, 1311, 1250-990 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 2.90 (t, *J* = 7.4 Hz, 2H), 2.82 (t, *J* = 6.9 Hz, 2H), 2.42 (s, 3H), 1.68-1.57 (m, 2H), 1.53-1.42 (m, 2H), 1.42-1.30 (m, 4H).

3-Aminopiperidine Dihydrochloride (**3o**):[S12] a white powder (recrystallized from ethyl acetate-hexane); mp 170-172 ºC; IR (KBr) 3700-2300, 1662, 1610, 1441, 1396, 1200-900, 899 cm^{-1}; ^{1}H NMR (400 MHz, D_2O) δ 3.40 (dd, *J* = 12.9, 3.7 Hz, 1H), 3.33-3.23 (m, 1H), 3.18 (dd, *J* = 12.9, 9.6 Hz, 1H), 3.12-3.02 (m, 1H), 2.90-2.80 (m, 1H), 2.14-1.87 (m, 2H), 1.87-1.71 (m, 2H).

4-Methoxybenzylammonium Chloride (**3p**):[S13] colorless needles (recrystallized from acetonitrile); mp >200 ºC (sublimation); IR (KBr) 3350-2200, 2067, 1610, 1518, 1375, 1255, 1186, 1124, 1024, 833, 741 cm^{-1}; ^{1}H NMR (400 MHz, D_2O) δ 7.45 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 4.17 (s, 2H), 3.89 (s, 3H); ESIMS (positive) *m/z* 138 [(M-Cl)$^+$].

4-Methylbenzylammonium Chloride (**3q**):[S14] a white powder (recrystallized from acetonitrile); mp >189 ºC (sublimation); IR (KBr) 3600-2300, 1620, 1595, 1516, 1383, 1207, 1111, 1074, 972, 814 cm^{-1}; ^{1}H NMR (400 MHz, D_2O) δ 7.38, 7.35 (each AB type, *J* = 8.8 Hz, each 2H), 4.18 (s, 2H), 2.39 (s, 3H).

4-Chlorobenzylammonium Chloride (**3r**):[S15] a white powder (recrystallized from acetonitrile); mp >197 ºC (sublimation); IR (KBr) 3600-2300, 1599, 1520, 1493, 1381, 1213, 1093, 1066, 1018, 974, 879, 829, 791 cm^{-1}; ^{1}H NMR (400 MHz, D_2O) δ 7.53 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 4.21 (s, 2H).

4-(Trifluoromethyl)benzylammonium Chloride (**3s**):[S16] white needles (recrystallized from acetonitrile); mp >167 ºC (sublimation); IR (KBr) 3400-2300, 1593, 1514, 1454, 1421, 1325, 1171, 1124, 1068, 833 cm^{-1}; ^{1}H NMR (400 MHz, D_2O) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 4.31 (s, 2H); ESIMS (positive) *m/z* 176 [(M-Cl)$^+$].

2-Phenylethylammonium Chloride (**3t**):[S17] a white powder (recrystallized from ethyl acetate-hexane); mp >210 ºC (sublimation); IR (KBr) 3500-2600, 1585, 1498, 1456, 1421, 1220-900, 742, 696 cm^{-1}; ^{1}H NMR (400 MHz, D_2O) δ 7.47-7.33 (m, 5H), 3.30 (t, *J* = 7.3 Hz, 2H), 3.02 (t, *J* = 7.3 Hz, 2H); ESIMS (positive) *m/z* 122 [(M-Cl)$^+$].

***endo*-2-Norbornylammonium Chloride** (**5**):[S18] a white powder (recrystallized from ethyl

acetate-hexane); mp 197-199 ºC; IR (KBr) 3800-2300, 2015, 1595, 1491, 1475, 1389, 1306, 1250-900, 800 cm^{-1}; ^1H NMR (400 MHz, D_2O) δ 3.58 (ddt, J = 11.0, 1.8, 5.3 Hz, 1H), 2.53-2.48 (m, 1H), 2.35-2.31 (m, 1H), 2.11-2.01 (m, 1H), 1.74-1.41 (m, 5H), 1.36-1.27 (m, 1H), 1.10-1.03 (m, 1H); ESIMS (positive) m/z 112 [$(M\text{-}Cl)^+$].

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