Ionic Introduction of an N_1 Unit to C_{60} and Unique Rearrangement of Aziridinofullerene

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Experimental Procedures

General Methods.

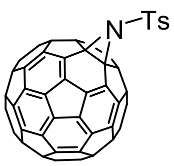
IR spectra were obtained on a Jasco FT/IR-410 infrared spectrophotometer. UV/Vis spectra were performed on a Shimadzu UV-265 spectrophotometer. ^{1}H and ^{13}C-NMR spectra were recorded on a JEOL FT-NMR JNM EX 270 spectrometer (^{1}H-NMR, 270 MHz; ^{13}C-NMR, 68 MHz) using tetramethylsilane as an internal standard. FAB-Mass spectra were measured with a JEOL TMS-700 spectrometer. Column chromatography was performed using silica gel 60 (0.063-0.200 mm, Merck). Analytical thin layer chromatography was performed using EM reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light.

General procedure for preparation of ion-exchanged chloramines.

A suspension of chloramine (chloramines-T or chloramines-B) (1.1 mmol) and Aliquat®336 (1 mmol) was stirred in CH_2Cl_2 (10 mL) for 5 min, quenched with water (10 mL), extracted with CH_2Cl_2 (10 mL x 3), dried over Na_2SO_4, and concentrated under reduced pressure. Ion-exchanged chloramin (**1a** or **1b**) was obtained as yellow oil in good yield (85-90%).

N-(4-Methylbenzenesulfonyl)aziridinofullerene (2a)

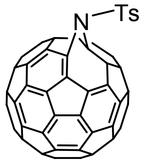
A solution of C_{60} (72 mg, 0.1 mmol) and chloramine **1a** (76 mg, 0.1 mmol) was heated in toluene (50 mL) for 10 min under reflux and vigorous stirring. The solution was passed through a short column of silica gel and the solvent then was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: toluene/hexane = 6/4) to give 59 mg (81%) of unconverted C_{60} (1st fraction) and 15 mg (17%) of the corresponding aziridinofullerene **2a** (2nd fraction).



black crystalline solid; FT-IR (KBr) cm^{-1} 3425, 2919 1641, 1352, 1169, 1090, 818, 527; ^1H NMR (270 MHz, $CDCl_3$): δ 2.55 (s, 3H, Ar-C*H*$_3$), 7.53 (d, 2H, *J* = 8.1 Hz, Ar*H*), 8.25 (d, 2H, *J* = 8.1 Hz, Ar*H*); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.99, 79.88, 128.46, 130.19, 135.36, 140.85, 141.37, 141.81, 142.10, 142.73, 143.05, 143.09, 143.16, 143.84, 144.13, 144.48, 145.01, 145.11, 145.27, 145.76; UV-Vis (CH_2Cl_2) λ_{max} nm 321, 254, 229; FAB-MS *m/z* 889 ($[M]^+$+1), 720 (C_{60}); HR-MS: calcd for ($C_{67}H_7NO_2S$): 889.0198, found: 889.0203 R_f= 0.37 (TLC, SiO_2, hexane : toluene = 1 : 1)

N-(4-Methylbenzenesulfonyl)azafulleroid[1] (3a)

A solution of C_{60} (72 mg, 0.1 mmol) and chloramine **1a** (76 mg, 0.1 mmol) was heated in toluene (50 mL) for 10 min under reflux and vigorous stirring in the presence of 400 mg of MS4A. The solution was passed through a short column of silica gel and the solvent was then evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: toluene/hexane = 6/4) to give 50 mg (70%) of unconverted C_{60} (1st fraction), 9 mg (10%) of **2a** (2nd fraction), and 15 mg (17%) of corresponding azafulleroid **3a**. Spectroscopic data were in agreement with those for previously reported material.[1]



black crystalline solid; ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.47 (s, 3H, Ar-C*H*$_3$), 7.37 (d, 2H, *J* = 8.2 Hz, Ar*H*), 8.06 (d, 2H, *J* = 8.2 Hz, Ar*H*); FAB-MS *m/z* 889 ($[M]^+$+1), 720 (C_{60}); HR-MS: calcd for ($C_{67}H_7NO_2S$): 889.0198, found: 889.0206. R_f= 0.30 (TLC, SiO_2, hexane : toluene = 1 : 1)

N-(Benzenesulfonyl)aziridinofullerene **(2b)** and *N*-(*p*-Benzenesulfonyl)azafulleroid (**3b**) were synthesized using the procedure described above.

N-(Benzenesulfonyl)aziridinofullerene (2b)

black crystalline solid; FT-IR (KBr) cm^{-1} 3413, 2920, 2852, 1350, 1170, 1084, 812, 528; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.77 (m, Ar*H*) 8.31 (d, 2H, *J*=7.0 Hz, Ar*H*); ^{13}CNMR (68 MHz, $CDCl_3$) δ 79.70, 128.24, 129.45, 134.37, 138.31, 140.77, 141.22, 141.70, 142.00, 142.63, 142.86, 142.95, 143.73, 143.99, 144.36, 144.89, 144.94, 145.00, 145.17 UV-Vis (CH_2Cl_2) λ_{max} nm 325, 255, 227; FAB-MS *m/z* 875 ($[M]^+$+1), 720 (C_{60}); HR-MS: calcd for ($C_{66}H_5NO_2S$): 875.0041, found: 875.0047. R_f= 0.37 (TLC, SiO_2, hexane : toluene = 1 : 1)

N-(*p*-Benzenesulfonyl)azafulleroid (**3b**)

black crystalline solid; FT-IR (KBr) cm^{-1} 3423, 2923 1652, 1367, 1170, 1088; ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.59 (dd, 2H, *J*=7.0 Hz, 7.6 Hz, Ph-C*H*$_2$), 7.67 (d, 1H, *J*=7.6 Hz, Ar*H*), 8.19 (d, 2H, *J* =7.0 Hz, Ar*H*); ^{13}C NMR (68 MHz, $CDCl_3$) δ 78.02, 128.24, 128.85, 129.12, 133.08, 133.94, 134.67, 135.02, 137.78, 137.83, 138.17, 138.41, 138.98, 139.58, 139.92, 141.42, 141.51, 142.42, 142.49, 142.78, 142.84, 143.05, 143.28, 143.47, 143.51, 143.65, 143.80, 143.84, 143.97, 144.02, 144.19, 144.58, 147.09, 148.49; UV-Vis (CH_2Cl_2) λ_{max} nm 326, 259, 229; FAB-MS *m/z* 875 ($[M]^{+}$+1), 720 (C_{60}); HR-FAB-MS: calcd for ($C_{67}H_7NO_2S$): 875.0041, found: 875.0027. R_f= 0.29 (TLC, SiO_2, hexane : toluene = 1 : 1)

Reference

(1) Ulmer, L.; Mattay, J. *Eur. J. Org. Chem*. **2003**, 2933.