Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Imido Transfer of Sulfonylimino-λ^3-Bromane Makes Possible the Synthesis of Sulfonylimino-λ^3-Iodanes

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General Information. IR spectra were recorded on JASCO FT/IR-420 spectrometers. ^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL JNM-AL300 or JNM-AL400 spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) downfield from internal Me_4Si. Mass spectra (MS) were obtained on a Waters LCT Premier spectrometer. Melting points were determined with a Yanaco micro melting points apparatus and are uncorrected. Dichloromethane was dried over CaH_2 and distilled.

General Procedure for Transimidation of Imino-λ^3-Bromane 1 Yielding Sulfonylimino-λ^3-Iodanes 2. A Typical Example (Table 1, Entry 1): [*N*-(Trifluoromethanesulfonyl)imino]-phenyl-λ^3-iodane (2a). To a stirred solution of [*N*-(trifluoromethanesulfonyl)imino](*p*-trifluoromethylphenyl)-λ^3-bromane (**1**)[1] (27.8 mg, 0.075 mmol) in dichloromethane (1 mL) was added iodobenzene (18.4 mg, 0.09 mmol) at room temperature under argon and the mixture was stirred for 1 h. After evaporation under an aspirator vacuum, repeated decantation of the crude reaction mixture with dichloromethane gave (trifluoromethanesulfonyl)imino-λ^3-iodane **2a** (25.3 mg, 97%).[2] White powder; mp 214-217 °C; IR (KBr) 1631, 1284, 1176, 1132, 976, 648, 602 cm^{-1}; ^{1}H NMR (400 MHz, CD_3CN) δ 8.11 (d, *J* = 7.2 Hz, 2H), 7.71 (t, *J* = 7.2 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 2H); HRMS (ESI, positive) calcd for $C_9H_8F_3IN_2NaO_2S$ [(M+MeCN+Na)$^+$] 414.9201, found 414.9226. Anal. Calcd for $C_7H_5F_3INO_2S$: C, 23.95; H, 1.44; N, 3.99. Found: C, 23.81; H, 1.62; N, 4.31.

[*N*-(Trifluoromethanesulfonyl)imino](2-methylphenyl)-λ^3-iodane (2b): white powder; mp 119-121 °C; IR (KBr) 1635, 1284, 1182, 1132, 976, 652, 598 cm^{-1}; ^{1}H NMR (400 MHz, CD_3CN) δ 8.16 (d, *J* = 7.2 Hz, 1H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 2.69 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 142.7, 138.5, 134.8, 132.2, 129.9, 123.8, 121.8 (q, $^1J_{CF}$ = 324.5 Hz), 25.2; HRMS (ESI, positive) calcd for $C_{10}H_{10}F_3IN_2NaO_2S$ [(M+MeCN+Na)$^+$] 428.9358, found 428.9319. Anal. Calcd for $C_8H_7F_3INO_2S$: C, 26.32; H, 1.93; N, 3.84. Found: C, 26.43; H, 2.14; N, 3.74.

[*N*-(Trifluoromethanesulfonyl)imino](4-methylphenyl)-λ^3-iodane (2c): white powder; mp 181-184 °C; IR (KBr) 1631, 1282, 1173, 1130, 970, 648, 596 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.34 (d, *J* = 7.4 Hz, 2H), 2.40 (s, 3H); HRMS (ESI, positive) calcd for $C_{10}H_{10}F_3IN_2NaO_2S$ [(M+MeCN+Na)$^+$] 428.9358, found 428.9339. Anal. Calcd for $C_8H_7F_3INO_2S$: C, 26.32; H, 1.93; N, 3.84. Found: C, 26.39; H, 2.10; N, 3.71.

[*N*-(Trifluoromethanesulfonyl)imino](4-methoxyphenyl)-λ^3-iodane (2d): white powder; mp 115-117 °C; IR (KBr) 1587, 1487, 1456, 1275, 1167, 1124, 987, 658, 598 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.14 (d, *J* = 7.2 Hz, 2H), 7.12 (d, *J* = 7.2 Hz, 2H), 3.93 (s, 3H); HRMS (ESI, positive) calcd for $C_{10}H_{10}F_3IN_2NaO_3S$ [(M+MeCN+Na)$^+$] 444.9307, found 444.9269. Anal. Calcd for $C_8H_7F_3INO_3S$: C, 25.21; H, 1.85; N, 3.68. Found: C, 25.09; H, 1.99; N, 3.63.

[*N*-(Trifluoromethanesulfonyl)imino](4-fluorophenyl)-λ^3-iodane (2e):[2] white powder; mp 229-231 °C; IR (KBr) 1630, 1275, 1161, 1124, 987, 650, 604 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6)

δ 8.20-8.10 (m, 2H), 7.46-7.36 (m, 2H); HRMS (ESI, positive) calcd for $C_9H_7F_4IN_2NaO_2S$ [(M+MeCN+Na)$^+$] 432.9107, found 432.9099. Anal. Calcd for $C_7H_4F_4INO_2S$: C, 22.78; H, 1.09; N, 3.80. Found: C, 22.54; H, 1.23; N, 4.17.

[*N*-(Trifluoromethanesulfonyl)imino](4-chlorophenyl)-λ^3-iodane (2f): pale yellow powder; mp 224-226 °C; IR (KBr) 1624, 1468, 1275, 1213, 1165, 1124, 987, 806, 658, 606 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.22 (d, J = 8.7 Hz, 2H), 7.66 (d, J = 8.7 Hz, 2H); HRMS (ESI, positive) calcd for $C_9H_7ClF_3IN_2NaO_2S$ [(M+MeCN+Na)$^+$] 448.8811, found 448.8831.

[*N*-(Trifluoromethanesulfonyl)imino](4-bromophenyl)-λ^3-iodane (2g): white powder; mp 224-226 °C; IR (KBr) 1620, 1469, 1275, 1163, 1126, 987, 804, 656, 606 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.14 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H); HRMS (ESI, positive) calcd for $C_9H_7{}^{79}BrF_3IN_2NaO_2S$ [(M+MeCN+Na)$^+$] 492.8306, found 492.8296. Anal. Calcd for $C_7H_4BrF_3INO_2S$: C, 19.55; H, 0.94; N, 3.26. Found: C, 19.72; H, 1.18; N, 3.18.

[*N*-(Trifluoromethanesulfonyl)imino][4-(trifluoromethyl)phenyl]-λ^3-iodane (2h): white powder; mp 204-206 °C; IR (KBr) 1626, 1282, 1180, 1132, 970, 650, 600 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.42 (d, J = 8.0 Hz, 2H), 7.98 (d, J = 8.0 Hz, 2H); HRMS (ESI, positive) calcd for $C_8H_4F_6INNaO_2S$ [(M+Na)$^+$] 441.8809, found 441.8832; calcd for $C_9H_8F_6INNaO_3S$ [(M+MeOH+Na)$^+$] 473.9072, found 473.9057. Anal. Calcd for $C_8H_4F_6INO_2S$: C, 22.93; H, 0.96; N, 3.34. Found: C, 23.14; H, 1.23; N, 3.51.

[*N*-(Trifluoromethanesulfonyl)imino](4-cyanophenyl)-λ^3-iodane (2i): white powder; mp 166-168 °C; IR (KBr) 2227, 1624, 1579, 1475, 1392, 1282, 1176, 976, 818, 648, 594 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.39 (d, J = 8.1 Hz, 2H), 8.04 (d, J = 8.1 Hz, 2H); HRMS (ESI, positive) calcd for $C_{10}H_7F_3IN_3NaO_2S$ [(M+MeCN+Na)$^+$] 439.9154, found 439.9146. Anal. Calcd for $C_8H_4F_3IN_2O_2S$: C, 25.55; H, 1.07; N, 7.45. Found: C, 25.83; H, 1.28; N, 7.47.

[*N*-(Trifluoromethanesulfonyl)imino][4-(ethoxycarbonyl)phenyl]-λ^3-iodane (2j): white powder; mp 220-221 °C; IR (KBr) 2985, 1714, 1635, 1587, 1394, 1369, 1286, 1207, 1174, 1133, 1009, 978, 847, 754, 646, 596 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.32 (d, J = 7.6 Hz, 2H), 8.17 (d, J = 7.6 Hz, 2H), 4.41 (q, J = 7.2 Hz, 2H), 1.40 (t, J = 7.2 Hz, 3H); HRMS (ESI, positive) calcd for $C_{11}H_{13}F_3INNaO_5S$ [(M+MeOH+Na)$^+$] 477.9409, found 477.9453. Anal. Calcd for $C_{10}H_9F_3INO_4S$: C, 28.38; H, 2.14; N, 3.31. Found: C, 28.37; H, 2.28; N, 3.24.

[*N*-(Trifluoromethanesulfonyl)imino][2-(acetyl)phenyl]-λ^3-iodane (2k): colorless prisms (recrystallized from dichloromethane–hexane); mp 101-102 °C; IR (nujol) 1631, 1576, 1309, 1292, 1173, 1119, 953, 781, 642, 602 cm^{-1}; ^{1}H NMR (400 MHz, CD_3CN) δ 8.49 (d, J = 8.1 Hz, 1H), 8.37 (d, J = 8.1 Hz, 1H), 8.15 (m, 1H), 7.92 (m, 1H), 2.88 (s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 202.6, 138.2, 134.2, 131.9, 131.7, 127.3, 121.5 (q, $^1J_{CF}$ = 324.5 Hz), 117.6, 25.7. Anal. Calcd for $C_9H_7F_3INO_3S\cdot 1/2H_2O$: C, 26.88; H, 2.01; N, 3.48. Found: C, 26.95; H, 1.96; N, 3.69.

[*N*-(Trifluoromethanesulfonyl)imino](2,2,2-trifluoroethyl)-λ^3-iodane (3): white powder;

mp 161 °C; IR (KBr) 1626, 1282, 1182, 1132, 974, 756, 650, 600 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ 5.06 (q, $^3J_{HF}$ = 10.9 Hz, 2H); HRMS (ESI, positive) calcd for $C_5H_5F_6IN_2NaO_2S$ [(M+MeCN+Na)$^+$] 420.8918, found 420.8926.

1-(Trifluoromethanesulfonamido)-1,2-benziodoxol-3(1*H*)-one (6): white powder; mp 194 °C; IR (KBr) 3095, 1666, 1630, 1568, 1371, 1292, 1232, 1200, 1124, 926, 831, 746 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 8.16 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.08-7.99 (m, 2H), 7.82 (ddd, *J* = 9.1, 6.6, 1.5 Hz, 1H); HRMS (ESI, positive) calcd for $C_{10}H_8F_3IN_2NaO_4S$ [(M+MeCN+Na)$^+$] 458.9099, found 458.9091. Anal. Calcd for $C_8H_5F_3INO_4S$: C, 24.32; H, 1.28; N, 3.55. Found: C, 24.32; H, 1.50; N, 3.88.

[*N*-(Trifluoromethanesulfonyl)imino](2-carbamoylphenyl)-λ^3-iodane (8a): colorless prisms (recrystallized from methanol–water); mp 87-93 °C; IR (KBr) 3384, 3228, 2744, 1664, 1587, 1545, 1441, 1319, 1300, 1211, 1151, 1130, 966, 741, 607 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ 8.43 (d, *J* = 7.2 Hz, 1H), 8.34 (d, *J* = 7.2 Hz, 1H), 8.10 (br t, *J* = 7.2 Hz, 1H), 7.87 (br t, *J* = 7.2 Hz, 1H); HRMS (ESI, positive) calcd for $C_{10}H_9F_3IN_3NaO_3S$ [(M+MeCN+Na)$^+$] 457.9259, found 457.9278. Anal. Calcd for $C_8H_6F_3IN_2O_3S$: C, 24.38; H, 1.53; N, 7.11. Found: C, 24.24; H, 1.70; N, 7.40.

[*N*-(Trifluoromethanesulfonyl)imino](2-carbamoyl-4-methylphenyl)-λ^3-iodane (8b): pale yellow powder; mp 135-139 °C; IR (KBr) 3352, 3205, 1660, 1558, 1452, 1387, 1294, 1180, 1122, 958, 652, 606 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ 8.25 (s, 1H), 8.17 (d, *J* = 9.1 Hz, 1H), 7.92 (d, *J* = 9.1 Hz, 1H), 2.56 (s, 3H); HRMS (ESI, positive) calcd for $C_9H_8F_3IN_2NaO_3S$ [(M+Na)$^+$] 430.9150, found 430.9159.

References

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2 L. M. Yagupolskii, V. I. Popov, N. V. Pavlenko, I. I. Maletina, A. A. Mironova, R. Yu. Gavrilova and V. V. Orda, *Zh. Org. Khim. USSR,* 1986, **22**, 2169.

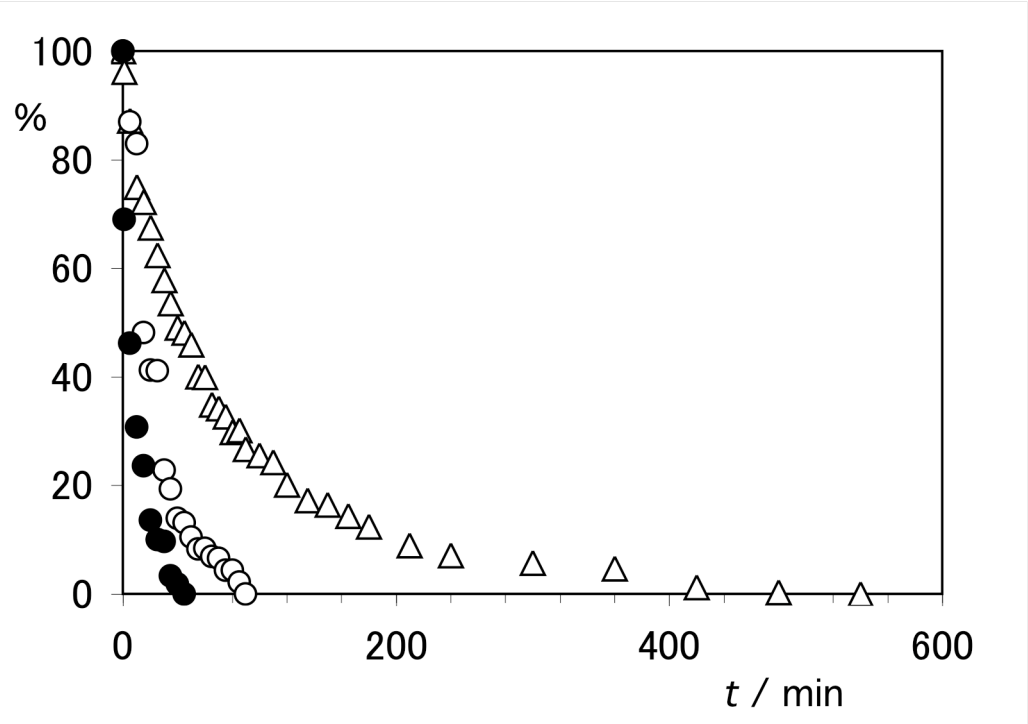

Fig. Time-course for transimidation to PhI with the λ^3-bromane **1** (0.05 M) in MeCN-d_3 at 23 °C under argon: decrease (%) of **1** was evaluated by ^{1}H NMR. Concentration of PhI: (Δ) 0.05 M, (○) 0.125 M, (●) 0.25 M.

X-ray Data for 2k

A. Crystal Data: Empirical Formula ($C_9H_7F_3INO_3S$), Formula Weight (393.12)

Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.30 X 0.30 X 0.20 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Indexing Images	3 oscillations @ 90.0 seconds
Detector Position	127.40 mm
Pixel Size	0.100 mm
Lattice Parameters	a = 10.1845(3) Å, b = 19.9169(5) Å, c = 5.9157(2) Å V = 1199.96(6) Å^3
Space Group	$Pna2_1$ (No. 33)
Z value	4
D_{calc}	2.176 g/cm^3
F_{000}	752.00
μ(MoKα)	28.814 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID
Radiation	MoKα (λ = 0.71075 Å), graphite monochromated
Detector Aperture	280 mm x 256 mm
Data Images	41 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	130.0 - 190.0°
Exposure Rate	180.0 sec./°
ω oscillation Range (χ=45.0, ϕ=180.0)	0.0 - 160.0°
Exposure Rate	180.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	54.8°
No. of Reflections Measured	Total: 10881, Unique: 10360 (R_{int} = 0.023)
Corrections	Lorentz-polarization, Absorption (transmission factors: 0.8930 - 0.9459)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F
Function Minimized	Σ w (IFoI - IFcI)^2
Least Squares Weights	1
$2\theta_{max}$ cutoff	54.8°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	2720
No. Variables	165
Reflection/Parameter Ratio	16.48
Residuals: R (All reflections)	0.0157
Residuals: R1 (I>2.00σ(I))	0.0154
Residuals: wR2 (All reflections)	0.0379
Goodness of Fit Indicator	1.080
Max Shift/Error in Final Cycle	0.002
Maximum peak in Final Diff. Map	0.63 e$^-$/Å^3
Minimum peak in Final Diff. Map	0 e$^-$/Å^3

X-ray Data for 8a

A. Crystal Data: Empirical Formula ($C_8H_6F_3IN_2O_3S$), Formula Weight (394.11)

Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.20 X 0.20 X 0.20 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Indexing Images	3 oscillations @ 180.0 seconds
Detector Position	127.40 mm
Pixel Size	0.100 mm
Lattice Parameters	a = 11.1853(4) Å, b = 14.2294(4) Å, c = 14.5837(4) Å V = 2321.14(12) Å^3
Space Group	$P2_12_12_1$ (No. 19)
Z value	8
D_{calc}	2.255 g/cm^3
F_{000}	1504.00
μ(MoKα)	29.818 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID
Radiation	MoKα (λ = 0.71075 Å), graphite monochromated
Detector Aperture	280 mm x 256 mm
Data Images	44 exposures
ω oscillation Range (χ=45.0, ϕ=130.0)	130.0 - 190.0°
Exposure Rate	150.0 sec./°
ω oscillation Range (χ=45.0, ϕ=310.0)	0.0 - 160.0°
Exposure Rate	150.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	54.9°
No. of Reflections Measured	Total: 22608, Unique: 22562 (R_{int} = 0.030)
Corrections	Lorentz-polarization, Absorption (transmission factors: 0.536 - 0.551)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F
Function Minimized	Σ w (IFoI - IFcI)^2
Least Squares Weights	1
$2\theta_{max}$ cutoff	54.9°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	5281
No. Variables	326
Reflection/Parameter Ratio	16.20
Residuals: R (All reflections)	0.0223
Residuals: R1 (I>2.00σ(I))	0.0215
Residuals: wR2 (All reflections)	0.0520
Goodness of Fit Indicator	1.087
Max Shift/Error in Final Cycle	0.002
Maximum peak in Final Diff. Map	1.96 e$^-$/Å^3
Minimum peak in Final Diff. Map	0 e$^-$/Å^3