Oxyhalogenation of thiols and disulfides into sulfonyl chlorides/bromides in water using oxone-KX(X= Cl or Br)

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General Information: Oxone®(2KHSO5·KHSO4·K2SO4), N-chlorosuccinimide, KBr, were purchased from Sigma-Aldrich India Ltd., aq. HCl, aq. HBr, NaCl, KCl, KI and other solvents used in this study were procured from SD Fine Chem. Ltd., India. Melting points of the compounds were recorded on Veego programmable melting point apparatus in open capillaries and are uncorrected. IR spectra were recorded on a PerkinElmer FT-IR 240-C spectrophotometer using KBr & neat optics. 1H NMR spectra were recorded on Bruker AV 300 MHz in CDCl3 using TMS as the internal standard. All the reactions were monitored by thin layer chromatography (TLC) on precoated silica gel 60 F254 (mesh); spots were visualized...
with UV light or by charring with anisaldehyde solution. Merck silica gel (60-120 mesh) was used for column chromatography.

**General procedure for the preparation of sulfonyl chlorides with oxone-KX:** A mixture of thiol (3.4 mmol), oxone (8.6 mmol) and KCl (3.4 mmol), water (10 mL) was taken into a round bottomed flask and stirred at room temperature. This reaction is slightly exothermic and temperature of the mixture rose to 45°C. After completion of the reaction (TLC), the reaction mixture was extracted with ethyl acetate (4x5 mL). The combined organic layers was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product obtained was purified by normal column chromatography (silica gel 60-120 mesh, n-hexane) to obtain corresponding sulfonyl chloride. A similar procedure was used for preparation of sulfonyl bromides with oxone-KBr.

**General procedure for the preparation of sulfonyl chlorides from disulfides:** A mixture of disulfide (1.7 mmol), oxone (3.5 mmol) and KCl (3.5 mmol), water (10 mL) was taken into a round bottomed flask and stirred at room temperature. After completion of the reaction (TLC), the reaction mixture was extracted with ethyl acetate (4x5 mL) and the combined organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product obtained was purified by normal column chromatography (silica gel 60-120 mesh, n-hexane) to obtain corresponding sulfonyl chloride.

**Characterization data:**

![Benzenesulfonyl chloride (2a).](image)

Benzenesulfonyl chloride (2a). Colorless oil, (0.31 g, 98%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.05-8.04 (m, 2H), 7.76 (t, $J$ = 7.3 Hz, 1H), 7.62 (t, $J$ = 7.7 Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ =136.4, 133.6, 131.3, 129.3, 128.7, 127.4; IR (neat): $\nu$ 3065,
2926, 2855, 1444, 1077, 750, 593 cm\(^{-1}\). EI-MS 176, 159, 112, 95, 75, 57; EI-HRMS: Exact mass observed for C\(_6\)H\(_5\)ClO\(_2\)S: 175.9695 (calculated: 175.9698).

**4-chlorobenzene-1-sulfonyl chloride (2b).** White solid, m.p. 51-52°C (lit\(^1\) 52-54) (0.28 g, 97%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.98\) (d, \(J = 8.6\) Hz, 2H) 7.60 (d, \(J = 8.6\) Hz, 2H), \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 142.4, 140.4, 137.6\); IR (neat): \(\nu = 3109, 3052, 1573, 1474, 1184, 1088, 825, 755, 559\) cm\(^{-1}\). EI-MS 212, 201, 177, 175, 111, 75, 69; EI-HRMS: Exact mass observed for C\(_6\)H\(_4\)ClO\(_2\)S: 209.9319 (calculated: 209.9309).

**3-Fluorobenzene-1-sulfonyl chloride (2c).** Pale yellow solid m.p. 96-98°C, (0.28 g, 95%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.98\) (d, \(J = 8.1\) Hz, 2H), 7.30 (d, \(J = 8.1\) Hz, 2H), 6.69 (s, 1H), 2.44 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 185.5, 145.6, 129.7, 129.5, 128.0, 39.9, 21.7\); IR (neat): \(\nu = 3108, 3056, 2927, 2757, 1593, 1474, 1368, 1228, 1163, 884, 595\) cm\(^{-1}\). EI-HRMS: Exact mass observed for C\(_6\)H\(_4\)ClFO\(_2\)S: 193.9602 (calculated: 193.9604).

**4-Methylbenzene-1-sulfonyl chloride (2d):** White solid m.p. 72-73 °C (lit\(^2\) 71-72) (0.29 g, 96%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.89\) (d, \(J = 8.4\) Hz, 2H), 7.43 (d, \(J = 8.4\) Hz, 2H), 2.59 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 146.8, 130.2, 126.9, 21.7\); IR (KBr):
Naphthalene-1-sulfonyl chloride (2e). White solid, m.p. 74-75 °C (lit1 73-74); (0.25 g, 92%). 1H NMR (300 MHz, CDCl3): $\delta = 8.61$ (s, 1H), 8.08-7.96 (m, 4H), 7.78-7.67 (m, 2H); 13C NMR (75 MHz, CDCl3): $\delta = 130.3, 130.2, 129.8, 128.9, 128.3, 128.1, 121.2$; IR (neat): $\nu$ 3108, 3073, 2928, 1589, 1492, 1380, 1182, 1081, 840 cm$^{-1}$. EI-MS: 226, 210, 208, 146, 127, 115, 77, 57; EI-MS: Exact mass observed for C$_{10}$H$_7$ClO$_2$S: 225.9854 (calculated: 225.9855).

Cyclohexanesulfonyl chloride (2f). Colorless oil (0.27 g, 89%). 1H NMR (300 MHz, CDCl3): $\delta = 3.56-3.46$ (m, 1H), 2.42-2.37 (m, 2H), 2.01-1.95 (m, 2H), 1.75-1.62 (m, 3H), 1.48-1.18 (m, 3H); 13C NMR (75 MHz, CDCl3): $\delta = 74.7, 27.0, 24.8, 24.5$; IR (neat): $\nu$ 2938, 2859, 1451, 1369, 1219, 1160, 751, 589 cm$^{-1}$; EI-MS: m/z. 182, 118, 99, 83, 67, 55; EI-MS: Exact mass observed for C$_6$H$_{11}$ClO$_2$S : 182.0164 (calculated:182.0168).

4-Fluorobenzene-1-sulfonyl chloride (2g). Colorless oil (0.28 g, 95). 1H NMR (300 MHz, CDCl3): $\delta = 8.10-8.07$ (m, 2H), 7.33-7.28 (m, 2H); 13C NMR (75 MHz, CDCl3): $\delta = 168.1, 130.1, 130.0, 117.2, 116.9$; IR (neat): $\nu$ 3108, 3073, 2928, 1589, 1492,
1380, 1182, 840, 569 cm\(^{-1}\). EI-HRMS: Exact mass observed for C\(_6\)H\(_4\)ClFO\(_2\)S: 193.9601 (calculated: 193.9604).

3-Chloro-4-fluorobenzene-1-sulfonyl chloride (2h). Colorless oil (0.25 g, 92). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 8.14 (~dd, J = 2.4 \text{ Hz}, 1H), 8.01-7.92 (m, 1H), 7.43-7.39 (m, 1H); ^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta =163.7, 130.1, 127.8, 127.6, 118.2, 117.8;\) IR (neat): \(\nu = 2927, 2757, 1593, 1474, 1228, 1163, 1101, 884 \text{ cm}^{-1}\). EI-MS: 227, 224, 195, 193, 129, 109, 94, 79; EI-HRMS: Exact mass observed for C\(_6\)H\(_3\)ClFO\(_2\)S: 227.9211 (calculated: 227.9214).

3,4-Dimethoxybenzene-1-sulfonyl chloride (2i). White solid, 63-65, (lit\(^3\)64-65), (0.24 g, 90%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.68 (~dd, J = 2.2 \text{ Hz}, 1H), 7.44 (~d, J = 2.2 \text{ Hz}, 1H), 7.68 (~d, J = 8.5 \text{ Hz}, 1H), 3.99 (s, 3H), 3.97 (s, 3H); ^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta =154.6, 149.2, 135.8, 121.6110.4, 108.956.4, 56.3;\) IR (neat): \(\nu = 2929, 2862, 1461, 1406, 1229, 1183, 1119, 1034, 819 \text{ cm}^{-1}\). EI-MS: 236, 201, 153, 137, 94, 79; EI-HRMS: Exact mass observed for C\(_8\)H\(_{10}\)ClO\(_4\)S: 235.9916 (calculated: 235.9910).
Pyridine-2-sulfonyl chloride (2j). Colorless oil (0.28 g, 88%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.64-8.55 (m, 1H), 7.98-7.85 (m, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$+DMSO-D$_6$): $\delta$ = 155.2, 146.0, 140, 126.1, 123.3; IR (neat): $\nu$ 3029, 1453, 1028, 638 cm$^{-1}$. EI-MS 177, 175, 159, 111, 69, 57; EI-HRMS: Exact mass observed for C$_5$H$_4$ClO$_2$S: 176.96526 (calculated: 176.96513).

4-(Trifluoromethyl)benzene-1-sulfonyl chloride (2k): Colourless oil (0.24 g, 90%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.20 (d, $J$ = 8.3 Hz, 2H), 7.92 (d, $J$ = 8.3 Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 147.0, 136.9136.4, 136.1, 127.6, 127.0, 126.9; IR (neat): $\nu$ 3026, 1454, 1242, 1145, 1014, 940, 780 cm$^{-1}$; EI-HRMS: Exact mass observed for C$_7$H$_4$ClF$_3$O$_2$S: 243.9569 (calculated: 243.9572).

4-Methoxybenzene-1-sulfonyl chloride (2l). Colorless oil (0.27 g, 93%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.97 (d, $J$ = 9.0 Hz, 2H), 7.04 (d, $J$ = 9.0 Hz, 2H), 3.92 (s, 3H) $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 159.8, 132.6, 128.3, 114.5, 55.3; IR (neat): $\nu$ 3052, 3007, 2926, 2854, 1574, 1463, 1367, 1281, 1171, 1088, 944 cm$^{-1}$. EI-MS 206, 190, 175, 142, 75, 55; EI-HRMS: Exact mass observed for C$_7$H$_4$ClO$_3$S: 205.9803 (calculated: 205.9804).
**1-Methyl-1H-tetrazole-5-sulfonyl chloride (2m).** Colorless oil (0.27 g, 88%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 40.18 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 143.08; IR (neat): $\nu$ 2928, 2858, 1633, 1343, 1056, 771 cm$^{-1}$. Mass: ESI-MS:181(M+H), 203 (M+Na).

**Hexane-1-sulfonyl chloride (2n).** Colorless oil (0.21 g, 68). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 3.38 (t, $J$ = 7.3, 7.4 Hz, 2H), 1.69-1.62 (m, 2H), 1.41-1.30 (m, 6H), 0.89 (t, J = 6.6, 6.7 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 62.5, 36.1, 31.0, 23.3, 22.3, 13.8; IR (neat): $\nu$ 2929, 2857, 1463, 1378, 1256, 988, 725 cm$^{-1}$. EI-MS 184, 141, 125, 109, 77, 69, 57; EI-HRMS: Exact mass observed for C$_6$H$_{13}$ClO$_2$S: 184.0322 (calculated: 184.0324).

**Benzenesulfonyl bromide (3a).** Colorless oil (0.38 g, 96%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.02-7.99 (m, 2H), 7.76 (t, $J$ = 7.3 Hz, 1H), 7.63 (t, $J$ = 7.7 Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ =136.4, 133.6, 131.3, 129.3, 128.7, 127.4; IR (neat): $\nu$ 3022, 2919, 1489, 1329, 1143, 806, 653 cm$^{-1}$. EI-MS 220, 171, 158, 137, 97, 69; EI-HRMS: Exact mass observed for C$_6$H$_5$ClO$_2$S: 219.91920 (calculated: 219.91936).

**4-Chlorobenzene-1-sulfonyl bromide (3b).** White solid, m.p. 74-75 $^\circ$C (lit$^4$ 73-74); (0.35 g, 95%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.98 (d, $J$ = 8.6 Hz, 2H) 7.60
(d, J = 8.6 Hz, 2H), $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 142.4, 140.4, 130.0; IR (neat): $\nu$ 3109, 3052, 1573, 1474, 1184, 1088, 825, 755, 559 cm$^{-1}$. EI-MS 256, 254, 177, 175, 113, 111, 75, 76; EI-HRMS: Exact mass observed for C$_6$H$_4$Cl$_2$O$_2$S: 253.87998 (calculated: 253.88039).

**3-Fluorobenzene-1-sulfonoyl bromide (3c).** Colorless oil (0.34 g, 92%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.84-7.80 (m, 2H), 7.72-7.60 (m, 2H), 7.49-7.43 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 163.5, 131.4, 122.7, 122.4, 114.1, 113.7; IR (neat): $\nu$ 3073, 2938, 1564, 1485, 1378, 1192, 846 cm$^{-1}$. EI-HRMS: Exact mass observed for C$_6$H$_4$BrFO$_2$S: 237.9096 (calculated: 237.9099).

**4-Methylbenzene-1-sulfonoyl chloride (3d).** White solid m.p. 74-75 °C (lit$^5$ 73-74); (0.33 g, 89%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.87 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 142.20, 136.81, 130.06, 126.40, 21.80; IR (KBr): $\nu$ 3010, 2923, 1584, 1457, 1027, 696 cm$^{-1}$. EI-MS 234, 202, 186, 171, 139, 123, 107, 92, 77; EI-HRMS: Exact mass observed for C$_7$H$_7$BrO$_2$S: 233.9348 (calculated: 233.9350).

**Naphthalene-2-sulfonoyl bromide (3e).** Pale yellow solid m.p. 74-75 °C (lit$^5$ 73-74); (0.30 g, 90%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.62 (s, 1H), 8.10-7.99 (m, 4H),
7.80-7.70 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 135.6, 132.1, 130.3, 130.1, 129.9, 128.3, 128.1, 121.0; IR (neat): $\nu$ 3063, 2946, 1589, 1455, 1237, 1025, 840 cm$^{-1}$. EI-MS: 270, 185, 149, 139, 123, 69, 57; EI-HRMS: Exact mass observed for C$_{10}$H$_7$ClO$_2$S: 269.93500 (calculated: 269.93501).

Cyclohexanesulfonyl bromide (3f). Colorless oil (0.37 g, 95%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 3.54-3.44 (m, 1H), 2.40-2.36 (m, 2H), 1.97-1.94 (m, 2H), 1.73-1.60 (m, 3H), 1.45-1.12 (m, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 74.7, 27.0, 24.8, 24.5; IR (neat): $\nu$ 2938, 2859, 1451, 1369, 1219, 1160, 751, 589 cm$^{-1}$; EI-MS: m/z. 227, 225, 191, 163, 148, 111, 97, 83, 69, 55; EI-HRMS: Exact mass observed for C$_6$H$_{11}$BrO$_2$S: 225.9661 (calculated:225.9663).

References:

SO₂Cl

$2f$

CDCl₃ $^1$H NMR 300 MHz

SO₂Cl

$2f$

CDCl₃ $^{13}$C NMR 75 MHz
$^2\text{a}$

CDCl$_3^1$H NMR 300 MHz

$^2\text{a}$

CDCl$_3^{13}$C NMR 75 MHz
$^1$H NMR CDCl$_3$, 300 MHz

$^13$C NMR CDCl$_3$, 75 MHz

$\text{F-} \text{SO}_2\text{Br}$

$3e$