Supplementary Material (ESI) for Chemical Communications

Supplementary Information for

Ketoximes to *N*-substituted thioamides *via* $PSCl_3$ mediated Beckmann Rearrangement

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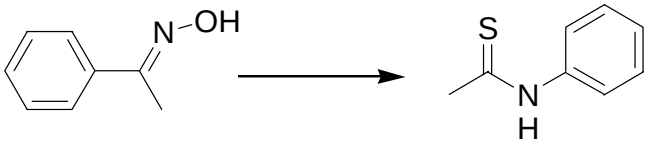
General Information: Reagents were obtained from commercial supplier, and used without further purification. Ketoximes for entry 3, 5, 6, 7, 8, 9, 10, 12, 13, were prepared from corresponding ketones by reported procedure[1]. Solvents were purified by the usual method and stored over molecular sieves. Freshly distilled thiophosphoryl chloride was used. The reaction was monitored by GC using 30m x 0.32 mm with 0.25µ phase film BP-5 column. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on 400 MHz spectrometer, with chemical shift value being

reported in ppm. All coupling consatants (*J*) are reported in Hertz (Hz). Mass spectra were obtained using gas chromatography (GC) methodology on a GC-MS instrument.

Table1. Optimization of Reaction Condition

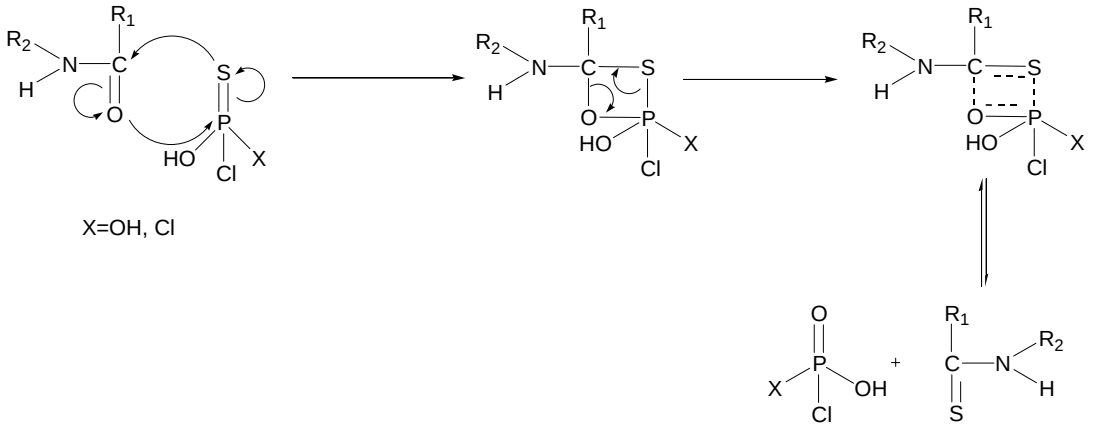


1a **1 b**

S No.	Solvent	Reaction condition	Conversion (%)	Thioamide Selectivity[a] (%)
1.	Benzene	1equiv of $PSCl_3$, H_2O and 1a, 0-5 ^oC, 3 h	85	10
2.	Benzene	1equiv of $PSCl_3$ and 1a, 0-5 ^oC, 3 h	95	25
3.	Benzene	1 equiv of $PSCl_3$ added to 1a at rt, 3 h	98	35
4.	Benzene	1 equiv of $PSCl_3$ added to 1a at rt, reflux 1h	98	45
5.	Benzene	2 equiv of $PSCl_3$ added to 1a at rt, reflux 3h	98	45
6.	Ethylacetate	1 equiv of $PSCl_3$ added to 1a at rt, 3 h	98	30
7.	Ethylacetate	1 equiv of $PSCl_3$ added to 1a at rt, reflux 1 h	98	40
8.	Chloroform	1 equiv of $PSCl_3$ added to 1a at rt, reflux 1 h	98	45
9.	Acetonitrile	1 equiv of $PSCl_3$ added to 1a at rt, reflux 1 h	98	60
10.	Acetonitrile	1 equiv of $PSCl_3$ added to 1a at rt, then add 1 equiv of H_2O and 1.5 equiv of Et_3N, Heat at 80 ^oC	98	70
11.	Nitromethane	1.5 equiv of $PSCl_3$ added to 1a at rt, then add 1 equiv of H_2O and 1.5 equiv of Et_3N, Heat at 80 ^oC	99	70
12.	Nitromethane	1.5 equiv of $PSCl_3$ added to 1a dropwise at 0-5 ^oC, reflux 1h	99	93*
13.	-	1 equiv each of $PSCl_3$, 1a at 0 ^oC	70	20
14.	-	1 equiv each of $PSCl_3$, 1a at rt, violent reaction	95	50
15.	-	To 1 equiv of $PSCl_3$ and H_2O each, add 1.5 equiv of Et_3N slowly at 0-5 ^oC, add 1a and heat at 70-80 ^oC for 0.5 h	99	91

[a]Reaction was monitored by GC and GC-MS
*Conversion indicated by GC. But when the reaction was worked-up it was found to be contaminated with significant amount of corresponding amide.

Scheme1. Proposed mechanism for conversion of H to F (Scheme 2)



Characterizations Data

***N*-Phenyl-thioacetamide (1):** Mp 75-76 ^{o}C (Lit.[2] 76 ^{o}C), Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (br, s, 1H, NH), 8.87 (br, s, 1.3H, NH), 7.67-7.65 (m, 1.4H), 7.45-7.26 (m, 3H), 7.17-7.15 (m, 2H), 2.73 (s, 2.6H), 2.51 (s, 2H); EIMS: 151 [M^{+}], 150, 118, 110, 93, 77, 59. Anal. Calc for C_8H_9NS. C, 63.54; H, 6.00; N, 9.26; S, 21.20. Found C, 63.64; H, 5.83; N, 9.18; S, 21.33.

***N*-Phenyl-thiobenzamide (2):** Mp 100-101 ^{o}C (Lit.[2] 100 ^{o}C), Pale yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.09 (s, br, 1H, NH), 7.18-7.88 (m, 10 H); EIMS: 213 [M^{+}], 197, 180, 121, 110, 77, 51. Anal. Calcd for $C_{13}H_{11}NS$. C, 73.20; H, 5.20; N, 6.57; S, 15.03. Found: C, 73.36; H, 5.13; N, 6.62; S, 14.88.

Azepane-2-thione (4): Mp 106-107 ^{o}C (Lit.[2] 106 ^{o}C), Colorless solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, br, 1H, NH), 3.38 (dd, 2H, J_1=4 Hz, J_2=6 Hz), 3.00-2.97 (t, 2H, J=5.2 Hz), 1.79-1.63 (m, 6H); EIMS: 129 [M^+], 114, 100, 96, 71, 41. Anal. Calc for $C_6H_{11}NS$. C, 55.77; H, 8.58; N, 10.84; S, 24.81. Found C, 55.89; H, 8.74; N, 10.91; S, 24.45.

Azacyclotridecane-2-thione (5): Mp 107-108 ^{o}C (Lit.[3] 106.5 ^{o}C), White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (s, br, NH, 1H), 3.82-3.78 (m, 2H), 2.78-2.75 (m, 2H), 1.88-1.83 (m, 2H), 1.77-1.70 (m, 2H), 1.46-1.33 (m, 14H); EIMS: 213 [M^+], 180, 114, 89. Anal. Calc for $C_{12}H_{23}NS$. C, 67.54; H, 10.86; N, 6.56; S, 15.03. Found: C, 67.68, H, 10.74; N, 6.63; S, 14.93.

***N*-(4-Chloro-phenyl)-thioacetamide (6):** Mp 142-144 ^{o}C (Lit.[2] 144 ^{o}C), Beige solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.30 and 8.63 (each s, br, 1H, NH), 7.68 (dd, J_1=2 Hz, J_2=4.8 Hz), 7.40-7.47 (m), and 7.17 (d, J=8.4 Hz) for total 4H, 2.78 and 2.55 (each s, total 3H); EIMS: 185 [M^+], 151, 127, 111, 108, 75, 59. Anal. Calc for C_8H_8ClNS. C, 51.75; H, 4.34; N, 7.54; S, 17.27. Found: C, 51.85; H, 4.48; N, 7.45; S, 17.10.

***N*-(4-Methoxy-phenyl)-thioacetamide (8):** Mp 115-117 ^{o}C (Lit.[2] 116 ^{o}C), Off-white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 and 9.08 (each, s, br, 1H, NH), 7.53 (dd, J_1=2 Hz, J_2=4.8 Hz), 7.10 (dd, J_1=2 Hz, J_2=4.8 Hz), and 6.93-6.90 (m)

for total 4H, 3.84-3.81 (m, 3H), 2.72 and 2.45 (each s, total 3H); EIMS: 181 [M^+], 165, 140, 108, 77, 59. Anal. Calc for $C_9H_{11}NOS$. C, 59.64; H, 6.12; N, 7.73; S, 17.69. Found: C, 59.78; H, 5.98, N, 7.81; S, 17.59.

***N*-(4-Nitro-phenyl)-hioacetamide (9):** Mp 172-174 ^oC (Lit.[4] 173.5-175 ^oC), Yellow solid, ^1H NMR (400 MHz, $CDCl_3$): δ 8.86 (s, br, NH, 1H), 8.27 (d, 2H, J=6 Hz), 8.07 (d, 2H, J=12.4 Hz), 2.77 (s, 3H); EIMS: 196 [M^+], 163, 138, 117, 92, 76, 59. Anal. Calc for $C_8H_8N_2O_2S$. C, 48.97; H, 4.11; N, 14.28; S, 16.34. Found: C, 49.09; H, 3.98; N, 14.35; S, 16.27.

***N*-(3-Nitro-phenyl)-thioacetamide (10):** Mp 98-100 ^oC (Lit.[2] 98 ^oC), Yellow solid, ^1H NMR (400 MHz, $CDCl_3$): δ 8.3 (s, 1H), 7.96 (dd, 2H, J_1=2 Hz, J_2=6.4 Hz), 7.61 (s, br, 1H, NH), 7.49 (t, 1H, J=8.4 Hz), 2.23 (s, 3H); EIMS: 196 [M^+], 149, 117, 92, 59. Anal. Calc for $C_8H_8N_2O_2S$. C, 48.97; H, 4.11; N, 14.28; S, 16.34. Found: C, 49.05; H, 4.21; N, 14.21; S, 16.21.

***N*-Ethyl-thioacetamide (11):** Light yellow oil (Lit.[5]), ^1H NMR (400 MHz, DMSO-d_6): δ 9.92 (s, br, 1H, NH), 3.47 (dd, 2H, J_1=1.6 Hz, J_2=5.6 Hz), 2.36 (s, 3H), 1.12 (t, 3H, J=7.2 Hz); EIMS: 103 [M^+], 88, 74, 59. Anal. Calc for C_4H_9NS. C, 46.56; H, 8.79; N, 13.57; S, 31.08. Found: C, 46.67; H, 8.62; N, 13.48; S, 31.21.

***N*-Benzyl-thioacetamide (12):** Mp 65-66 ^{o}C (Lit.[6] 65.1-65.3 ^{o}C), White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.32 (m, 6H), 4.81 (d, 2H, *J*=5.2 Hz), 2.59 (s, 3H); EIMS: 165 [M^+], 132, 106, 91, 79, 65, 51. Anal. Calc for $C_9H_{11}NS$. C, 65.41; H, 6.71; N, 8.48; S, 19.40. Found: C, 65.53; H, 6.87; N, 8.41; S, 19.17.

***N*-Benzyl-2-phenyl-thioacetamide (13):** Mp 78-79 ^{o}C (Lit.[7] 80-81 ^{o}C), Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.15 (m, 11H), 4.81 (d, 2H, *J*=5.2 Hz), 4.17 (s, 2H); EIMS: 241 [M^+], 208, 167, 91, 65. Anal. Calc for $C_{15}H_{15}NS$. C, 74.65; H, 6.26; N, 5.80; S, 13.29. Found: C, 74.79; H, 6.18; N, 5.87; S, 13.14.

***N*-Methyl-thioacetamide (15):** Mp 56-58 ^{o}C (Lit.[8] 56-57 ^{o}C), White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, br, 1H, NH), 3.10 (d, 3H, *J*=4.8 Hz), 2.50 (s, 3H); EIMS: 89 [M^+], 74, 56. Anal. Calc for C_3H_7NS. C, 40.41; H, 7.91; N, 15.71; S, 35.96. Found C, 40.55; H, 8.05; N, 15.61; S, 35.77.

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