

Electronic Supplementary Information (ESI) for

Phosphovanadomolybdic acids catalyzed desulfurization–oxygenation of secondary and tertiary thioamides into amides using molecular oxygen as the terminal oxidant

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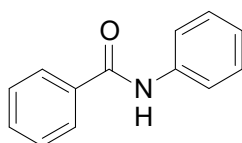
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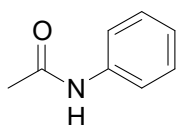
Isolation of elemental sulfur and gas-phase analysis

The 2.5 mmol-scale reaction of **1a** was carried out using $H_6PV_3Mo_9O_{40}$ under the standard reaction conditions. After **1a** was quantitatively converted into **2a**, acetonitrile was completely removed by evaporation. Then, the residue (containing elemental sulfur, **2a**, and HPA) was washed with a mixture of ethanol and water (10/1 v/v) to remove **2a** and HPA, giving 59 mg of elemental sulfur (74 % based on **1a**). In addition, the 0.25 mmol-scale reaction of **1a** was carried out using $H_6PV_3Mo_9O_{40}$ under the standard reaction conditions, and the gas-phase was analyzed by MS spectrometry during the reaction. We confirmed by the MS analysis that SO_2 was not formed during the reaction. Therefore, the by-product of the present transformation is elemental sulfur, and sulfur is not oxidized to SO_2 under the present conditions.

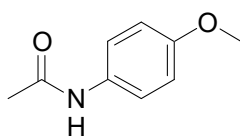
Compound data



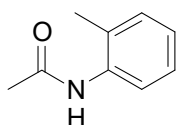
N-Phenylbenzamide (2a) [CAS No. 93-98-1]: 99% isolated yield (white solid). MS (EI) m/z (%): 50 (9), 51 (35), 65 (17), 77 (85), 78 (6), 105 (100), 106 (8), 197 (26) [M^+]. 1H NMR (500.16 MHz, $DMSO-d_6$, TMS): δ = 10.25 (s, 1H), 7.95 (d, J = 7.5 Hz, 2H), 7.77 (d, J = 7.5 Hz, 2H), 7.61–7.57 (m, 1H), 7.53 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.10 (t, J = 7.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (125.77 MHz, $DMSO-d_6$, TMS): δ = 165.68, 139.20, 135.03, 131.65, 128.69, 128.48, 127.71, 123.78, 120.47.



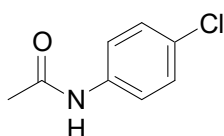
N-Phenylacetamide (2b) [CAS No. 103-84-4]: 99% isolated yield (white solid). MS (EI) m/z (%): 51 (7), 65 (17), 66 (25), 92 (5), 93 (100), 94 (7), 135 (20) [M^+]. ^1H NMR (500.16 MHz, DMSO- d_6 , TMS): δ = 9.93 (s, 1H), 7.56 (d, J = 7.0 Hz, 2H), 7.28 (dd, J = 7.5, 7.0 Hz, 2H), 7.01 (d, J = 7.0 Hz, 1H), 2.03 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, DMSO- d_6 , TMS): δ = 168.45, 139.36, 128.75, 123.10, 119.07, 24.06.



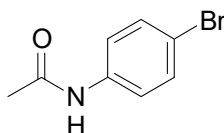
N-(4-Methoxyphenyl)acetamide (2c) [CAS No. 51-11-1]: 77% isolated yield (pale white solid). MS (EI) m/z (%): 51 (7), 52 (20), 53 (15), 65 (6), 80 (16), 108 (100), 109 (7), 122 (9), 123 (57), 124 (6), 165 (48) [M^+]. ^1H NMR (500.16 MHz, DMSO- d_6 , TMS): δ = 9.78 (s, 1H), 7.48–7.45 (m, 2H), 6.86–6.84 (m, 2H), 3.70 (s, 3H), 1.99 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, DMSO- d_6 , TMS): δ = 167.92, 155.11, 132.55, 120.66, 113.86, 55.21, 23.86.



N-(2-Methylphenyl)acetamide (2d) [CAS No. 120-66-1]: 72% HPLC yield. MS (EI) m/z (%): 77 (13), 78 (5), 79 (7), 106 (66), 107 (100), 108 (9), 149 (55) [M^+], 150 (6).

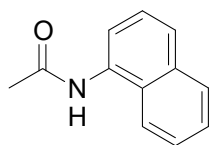


N-(4-Chlorophenyl)acetamide (2e) [CAS No. 539-03-7]: 76% HPLC yield. MS (EI) m/z (%): 63 (9), 64 (6), 65 (9), 73 (5), 92 (8), 99 (8), 100 (5), 127 (100), 128 (7), 129 (33), 169 (22) [M^+], 171 (8).

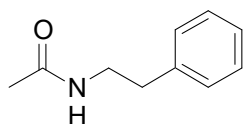


N-(4-Bromophenyl)acetamide (2f) [CAS No. 103-88-8]: 99% isolated yield (white solid). MS (EI) m/z (%): 50 (11), 51 (6), 52 (9), 61 (5), 62 (12), 63 (42), 64 (26), 65 (61), 66 (6), 75 (6), 76 (5), 90 (11), 91 (28), 92 (95), 93(9), 143(5), 171 (100), 172 (9), 173 (95), 174 (7), 213

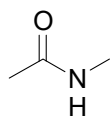
(31), 214 (3) [M^+], 215 (29). ^1H NMR (500.16 MHz, $\text{DMSO-}d_6$, TMS): δ = 10.07 (s, 1H), 7.55–7.53 (m, 2H), 7.46–7.44 (m, 2H), 2.03 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, $\text{DMSO-}d_6$, TMS): δ = 168.65, 138.72, 131.57, 121.00, 114.62, 24.09.



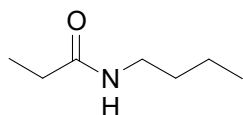
***N*-1-Naphthalenylacetamide (2g)** [CAS No. 575-36-0]: 80% HPLC yield. MS (EI) m/z (%): 89 (5), 115 (32), 116 (11), 143 (100), 144 (13), 185 (31) [M^+].



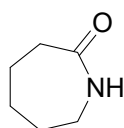
***N*-(2-Phenylethyl)acetamide (2h)** [CAS No. 877-95-2]: 85% HPLC yield. MS (EI) m/z (%): 65 (9), 72 (19), 91 (15), 104 (100), 105 (10), 163 (22) [M^+].



***N*-Methylacetamide (2i)** [CAS No. 79-16-3]: 54% GC yield. MS (EI) m/z (%): 58 (53), 73 (100) [M^+], 74(4).

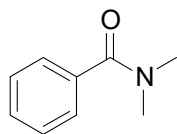


***N*-Butylpropanamide (2j)** [CAS No. 2955-67-1]: 84% isolated yield (colorless liquid). MS (EI) m/z (%): 55 (6), 56 (9), 57 (100), 58 (18), 72 (5), 74 (14), 86 (36), 87 (43), 100 (41), 114 (5), 129 (8) [M^+]. ^1H NMR (500.16 MHz, $\text{DMSO-}d_6$, TMS): δ = 7.71 (s, 1H), 3.01 (q, J = 6.5 Hz, 2H), 2.04 (d, J = 7.5 Hz, 2H), 1.38–1.32 (m, 2H), 1.29–1.21 (m, 2H), 0.97 (t, J = 7.5 Hz, 3H), 0.85 (t, J = 7.5 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, $\text{DMSO-}d_6$, TMS): δ = 172.88, 38.18, 31.38, 30.48, 28.62, 19.67, 13.74, 10.11.

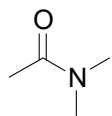


ϵ -Caprolactam (2k) [CAS No. 105-60-2]: 52% isolated yield (white solid). MS (EI) m/z (%):

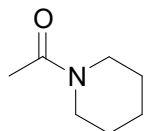
53 (5), 55 (100), 56 (97), 57 (12), 67 (14), 68 (7), 83 (9), 84 (50), 85 (74), 113 (87) [M^+], 114 (6). ^1H NMR (500.16 MHz, $\text{DMSO-}d_6$, TMS): δ = 7.40 (s, 1H), 3.05–3.02 (m, 2H), 2.29–2.27 (m, 2H), 1.67–1.63 (m, 2H), 1.53–1.46 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, $\text{DMSO-}d_6$, TMS): δ = 177.21, 41.52, 36.44, 30.05, 29.84, 23.03.



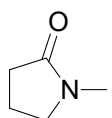
***N,N*-Dimethylbenzamide (2l)** [CAS No. 611-74-5]: 99% isolated yield (white solid). MS (EI) m/z (%): 50 (5), 51 (18), 77 (61), 105 (100), 106 (8), 148 (78), 149 (24) [M^+]. ^1H NMR (500.16 MHz, $\text{DMSO-}d_6$, TMS): δ = 7.44–7.36 (m, 5H), 2.97 (s, 3H), 2.88 (s, 3H); ^1H NMR (500.16 MHz, $\text{DMSO-}d_6$, TMS): δ = 7.43–7.31 (m, 5H), 3.04 (s, 3H), 2.90 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, $\text{DMSO-}d_6$, TMS): δ = 170.24, 136.55, 129.41, 128.36, 126.96, 34.78 (one methyl signal was overlapped with the DMSO signals); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, $\text{chloroform-}d_1$, TMS): δ = 171.64, 136.38, 129.53, 128.37, 127.06, 39.61, 35.35.



***N,N*-Dimethylacetamide (2m)** [CAS No. 127-19-5]: 53% GC yield. MS (EI) m/z (%): 56 (5), 72 (34), 87 (100) [M^+].



1-Acetylpiperidine (2n) [CAS No. 618-42-8]: 93% HPLC yield. MS (EI) m/z (%): 55 (9), 56 (53), 57 (42), 60 (7), 69 (8), 70 (51), 84 (98), 85 (17), 98 (7), 99 (11), 112 (21), 126 (11), 127 (100) [M^+], 128 (9).



1-Methyl-2-pyrrolidone (2o) [CAS No. 872-50-4]: >99% HPLC yield. MS (EI) m/z (%): 56 (5), 70 (8), 71 (9), 98 (61), 99 (100) [M^+], 100 (6).