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4-Thio derivatives of sydnone imines

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3-*n*-Butyl-N_6-benzoylsydnone imine

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3-*n*-Butyl-N_6-trifluoroacetylsydnone imine

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3-*n*-Butyl-N_6-pivaloylsydnone imine

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3-Dimethylamino-N_6-acetylsydnone imine

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3-Dimethylamino-N_6-benzoylsydnone imine

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3-Isopropyl-N_6-acetylsydnone imine

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3-Isopropyl-N_6-benzoylsydnone imine

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3-Isopropyl-4-mercapto-N_6-benzoylsydnone imine 5. To a stirred mixture of 0.5 g (2.16 mmol) of 3-isopropyl-N_6-benzoylsydnone imine in 25 ml THF at –90˚C, 0.95 ml (2.38 mmol) of 2.5 M *n*-BuLi solution in hexane was added dropwise, mixture was stirred for 30 min at –85˚C,

0.076 g (2.38 mmol) of powdered S_8 was added, and the mixture was stirred for 10 min at the same temperature. Cooling bath was removed and the mixture was stirred for 30 min at room temperature, then 1 ml of H_2O was added. The mixture was dried by Na_2SO_4 and passed through the layer of Al_2O_3 (2x3 cm), the solvent was removed in a vacuum, the residue was purified by chromatography on SiO_2 (30x2 cm, $CHCl_3$/ethyl acetate, 5:1) and crystallization from Pr^iOH–hexane. Yield of **5,** 0.45 g (80%), mp 93–94^{0}C. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.05 [d, 6H, ($\underline{CH_3}$)$_2$CH)], 1.6 (s, 1H, SH), 4.36–4.41 [m, 1H, (CH$_3$)$_2\underline{CH}$)], 7.42–7.49 (m, 3H) and 8.31 (m, 2H, C_6H_5). Found (%): C, 54.54; H, 4.90; N, 15.62. Calc. for $C_{12}H_{13}N_3O_2S$ (%): C, 54.74; H, 4.98; N, 15.96.

3-*n*-Butyl-4-methylthio-N$_6$-benzoylsydnone imine 6a

To a stirred mixture of 0.5 g (2.04 mmol) of 3-*n*-butyl-N$_6$-benzoylsydnone imine in 25 ml THF at –90˚C, 0.90 ml (2.24 mmol) of 2.5 M *n*-BuLi solution in hexane was added dropwise, the mixture was stirred for 30 min at –85˚C, 0.076 g (2.38 mmol) of powdered S_8 was added, and the mixture was stirred for 10 min at the same temperature. Cooling bath was removed and the mixture was stirred for 30 min at room temperature, 0.15 ml (2.35 mmol) of MeI was added and the mixture was stirred overnight. Then 1 ml of H_2O was added, the mixture was dried by Na_2SO_4 and passed through the layer of Al_2O_3 (2x3 cm), the solvent was removed in a vacuum, the residue was purified by chromatography on SiO_2 (30x2 cm, $CHCl_3$–ethyl acetate, 5:1) and crystallization from Pr^iOH–hexane. Yield of **6a** 0.40 g (68%), mp 78–79^{0}C. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.00 (t, 3H, CH_2-$CH_2CH_2C\underline{H_3}$), 1.39-1.49 (m, 2H, $CH_2CH_2C\underline{H_2}CH_3$), 1.93–2.00 (m, 2H, $CH_2C\underline{H_2}CH_2CH_3$), 2.54 (s, 3H, SCH_3), 4.51 (t, 2H, $C\underline{H_2}CH_2CH_2CH_3$), 7.40–7.49 (m, 3H) and 8.29 (m, 2H, C_6H_5). Found (%): C, 57.53; H, 6.00; N, 14.77. Calc. for $C_{14}H_{17}N_3O_2S$ (%): C, 57.71; H, 5.88; N, 14.42.

3-*n*-Butyl-4-methylthio-N$_6$-trifluoroacetylsydnone imine 6b

The title compound was prepared in the same way as compound **6a,** starting from 0.7 g (2.95 mmol) of 3-*n*-butyl-N$_6$-trifluoroacethylsydnone imine, 1.3 ml (3.25 mmol) of 2.5M solution of *n*-BuLi in hexane, 0.11 g (3.37 mmol) of S_8 and 0.22 ml (3.54 mmol) of MeI. Yield of **6b,** 0.48 g (58%), mp 50–51^{o}C. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.01 (t, 3H, $CH_2CH_2CH_2C\underline{H_3}$), 1.48–1.50 (m, 2H, $CH_2CH_2C\underline{H_2}CH_3$), 1.96–2.03 (m, 2H, $CH_2C\underline{H_2}CH_2CH_3$), 2.55 (s, 3H, SCH_3), 4.57 (t, 2H, $C\underline{H_2}CH_2CH_2CH_3$). Found (%): C, 37.99; H, 4.53; N, 14.58. Calc. for $C_9H_{12}F_3N_3O_2S$ (%): C, 38.16; H, 4.27; N, 14.83.

3-*n*-Butyl-4-methylthio-N_6-pivaloylsydnone imine 6c

The title compound was prepared in the same way as compound **6a,** starting from 0.66 g (2.93 mmol) of 3-*n*-butyl-N_6-pivaloylsydnone imine, 1.29 ml (3.23 mmol) of 2.5 M solution of *n*-BuLi in hexane, 0.11 g (3.37 mmol) of S_8 and 0.22 ml (3.54 mmol) of MeI. Yield of **6c,** 0.56 g (70%), mp 48–49°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.98 (t, 3H, $CH_2CH_2CH_2C\underline{H}_3$), 1.25 [s, 9H, $C(CH_3)_3$], 1.39–1.49 (m, 2H, $CH_2CH_2C\underline{H}_2CH_3$), 1.93–2.00 (m, 2H, $CH_2C\underline{H}_2CH_2CH_3$), 2.47 (s, 3H, SCH_3), 4.45 (t, 2H, $C\underline{H}_2CH_2CH_2CH_3$). Found (%): C, 53.55; H, 4.13; N, 14.89. Calc. for $C_{12}H_{21}N_3O_2S$ (%): C, 53.11; H, 7.80; N, 15.48.

3-Dimethylamino-4-methylthio-N_6-acetylsydnone imine 6d

The title compound was prepared in the same way as compound **6a,** starting from 0.5 g, (2.94 mmol) of 3-dimethylamino-4-methylthio-N_6-acetylsydnone imine, 1.30 ml (3.25 mmol) of 2.5 M solution of *n*-BuLi in hexane, 0.11 g (3.38 mmol) of S_8 and 0.22 ml (3.54 mmol) of MeI. Yield of **6d,** 0.53 g (83%), mp 75–76°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 2.23 (s, 3H, $COCH_3$), 2.44 (s, 3H, SCH_3), 3.16 [s, 6H, $N(CH_3)_2$]. Found (%): C, 38.23; H, 6.15; N, 25.77. Calc. for $C_7H_{12}N_4O_2S$ (%): C, 38.83; H, 6.75; N, 25.49.

3-Dimethylamino-4-methylthio-N_6-benzoylsydnone imine 6e

The title compound was prepared in the same way as compound **6a,** starting from 0.5 g (2.15 mmol) of 3-dimethylamino-N_6-benzoylsydnone imine, 0.95 ml (2.36 mmol) of 2.5 M solution of *n*-BuLi in hexane, 0.079 g (2.47 mmol) of S_8 and 0.16 ml (2.58 mmol) of MeI. Yield of **6e,** 0.41 g (68%), mp 78–80°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 2.55 (s, 3H, SCH_3), 3.17 [s, 6H, $N(CH_3)_2$], 7.38–7.48 (m, 3H) and 8.25 (m, 2H, C_6H_5). Found (%): C, 51.63; H, 5.59; N, 19.98. Calc. for $C_{12}H_{14}N_4O_2S$ (%): C, 51.78; H, 5.07; N, 20.13.

3-Isopropyl-4-methylthio-N_6-acetylsydnone imine 6f

The title compound was prepared in the same way as compound **6a,** starting from 1.0 g (5.92 mmol) of 3-isopropyl-N_6-acetylsydnone imine, 2.60 ml (6.51 mmol) of 2.5 M solution of *n*-BuLi in hexane, 0.20 g (6.51 mmol) of S_8 and 0.39 ml (7.10 mmol) of MeI. Yield of **6f,** 0.69 g (54%), mp 108–109°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.64 [d, 6H, $(C\underline{H}_3)_2CH$], 2.22 (s, 3H, $COCH_3$), 2.40 (s, 3H, SCH_3), 5.10–5.17 [m, 1H, $(CH_3)_2C\underline{H}$]. ^{13}C NMR ($CDCl_3$, δ, ppm): 17.35, 21.67, 27.56,

56.68, 107.73, 166.79, 179.55. Found (%): C, 44.20; H, 6.15; N, 19.62. Calc. for $C_8H_{13}N_3O_2S$ (%): C, 44.64; H, 6.09; N, 19.52.

3-Isopropyl-4-methylthio-N_6-benzoylsydnone imine 6g

The title compound was prepared in the same way as compound **6a** starting from 1.0 g, (4.33 mmol) of 3-isopropyl-N_6-benzoylsydnone imine, 1.90 ml (4.76 mmol) of 2.5 M solution of *n*-BuLi in hexane, 0.15 g (4.76 mmol) of S_8 and 0.34 ml (5.20 mmol) of MeI. Yield of **6g,** 0.94 g (83%), mp 73–74°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.66 [d, 6H, $(C\underline{H}_3)_2CH$], 2.50 (s, 3H, SCH_3), 5.11–5.18 [m, 1H, $(CH_3)_2C\underline{H}$], 7.36–7.46 (m, 3H) and 8.25 (m, 2H, C_6H_5). ^{13}C NMR ($CDCl_3$, δ, ppm): 16.96, 21.63, 56.77, 108.83, 127.91, 129.64, 131.43, 137.34, 167.92, 172.78. Found (%): C, 56.54; H, 5.15; N, 15.58. Calc. for $C_{13}H_{15}N_3O_2S$ (%): C, 56.30; H, 5.45; N, 15.15.

3-Isopropyl-4-benzylthio-N_6-benzoylsydnone imine 6h

The title compound was prepared in the same way as compound **6a,** starting from 1.0 g (4.33 mmol) of 3-isopropyl-N_6-benzoylsydnone imine, 1.90 ml (4.76 mmol) of 2.5M solution of *n*-BuLi in hexane, 0.15 g (4.76 mmol) of S_8 and 0.62 ml (5.20 mmol) of benzyl chloride. Yield of **6h,** 1.15 g (75%), mp 81–82°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.22 [d, 6H, $(C\underline{H}_3)_2CH$], 4.16 (s, 2H, SCH_2), 4.50–4.59 [m, 1H, $(CH_3)_2C\underline{H}$], 7.11–7.13 (m, 2H) and 7.21–7.33 (m, 3H, $CH_2C_6\underline{H}_5$), 7.41–7.48 (m, 3H) and 8.33–8.36 (m, 2H, COC_6H_5). ^{13}C NMR ($CDCl_3$, δ, ppm): 21.20, 37.45, 56.44, 106.56, 127.94, 127.98, 129.00, 129.74, 131.52, 137.02, 137.37, 168.16, 172.82. Found (%): C, 65.01; H, 5.85; N, 12.08. Calc. for $C_{19}H_{19}N_3O_2S$ (%): C, 64.57; H, 5.42; N, 11.89.

3-Isopropyl-4-cyclopropylmethylthio-N_6-benzoylsydnone imine 6i

The title compound was prepared in the same way as compound **6a,** starting from 1.0 g (4.33 mmol) of 3-isopropyl-N_6-benzoylsydnone imine, 1.90 ml (4.76 mmol) of 2.5M solution of *n*-BuLi in hexane, 0.15 g (4.76 mmol) of S_8 and 0.51 ml (5.20 mmol) of cyclopropylmethyl bromide. Yield of **6i,** 1.22 g (89%), as oil. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.17–0.21 (m, 2H) and 0.50–0.55 (m, 2H, CH_2CH_2), 0.90–1.00 (m, 1H, CH), 1.66 [d, 6H, $(C\underline{H}_3)_2CH$], 2.94 (d, 2H, SCH_2), 5.19–5.27 [m, 1H, $(CH_3)_2C\underline{H}$], 7.35–7.46 (m, 3H) and 8.24–8.30 (m, 2H, C_6H_5). ^{13}C NMR ($CDCl_3$, δ, ppm): 5.67, 11.50, 21.64, 39.61, 56.59, 108.23, 127.89, 129.62, 131.39, 137.42, 137.37, 168.03, 172.97. Found (%): C, 60.60; H, 6.16; N, 13.00. Calc. for $C_{16}H_{19}N_3O_2S$ (%): C, 60.55; H, 6.03; N, 13.24.

3-Isopropyl-4-(4-chloro-5-formyl-1,3-thiazol-2-yl)thio-N_6-benzoylsydnone imine 6j

To a stirred mixture of 0.5 g (2.04 mmol) of 3-*n*-butyl-N_6-benzoylsydnone imine in 25 ml of THF at –90˚C, 0.90 ml (2.24 mmol) of 2.5 M solution of *n*-BuLi in hexane was added dropwise, the mixture was stirred for 30 min at –85˚C, 0.076 g (2.38 mmol) of powdered S_8 was added, and the mixture was stirred for 10 min at the same temperature. Cooling bath was removed and the mixture was stirred for 30 min at room temperature. The resulting mixture replaced into dropped funnel and added dropwise to a solution of 0.41 g (2.27 mmol) of 2,4-dichloro-5-formylthiazole in 20 ml of THF and the mixture was stirred overnight. Then 1 ml of H_2O was added, the mixture was dried by Na_2SO_4 and passed through the layer of Al_2O_3 (2x3 cm), the solvent was removed in a vacuum, the residue was purified by chromatography on SiO_2 (30x2 cm, $CHCl_3$–ethyl acetate, 5:1) and crystallization from Pr^iOH–hexane. Yield of **6j,** 0.77 g (83%), mp 135–136°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.71 [d, 6H, $(C\underline{H}_3)_2CH$], 5.10–5.18 [m, 1H, $(CH_3)_2C\underline{H}$], 7.24–7.46 (m, 3H) and 8.13–8.16 (m, 2H, C_6H_5), 9.84 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, δ, ppm): 21.87, 58.53, 99.69, 128.01, 129.79, 131.97, 132.24, 136.33, 146.38, 166.57, 169.66, 173.00, 180.48. Found (%): C, 46.89; H, 3.01; N, 14.00. Calc. for $C_{16}H_{13}ClN_4O_3S_2$ (%): C, 47.00; H, 3.20; N, 13.70.

3-Isopropyl-4-(2-formyl-4-nitrophenyl-1)thio-N_6-benzoylsydnone imine 6k

The title compound was prepared in the same way as compound **6a,** starting from 0.5 g (2.17 mmol) of 3-isopropyl-N_6-benzoylsydnone imine, 0.95 ml (3.38 mmol) of 2.5 M solution of *n*-BuLi in hexane, 0.076 g (2.38 mmol) of S_8 and 0.44 g (2.38 mmol) of 2-chloro-5-nitrobenzaldehyde. Yield of **6k,** 0.89 g (76%), mp 179–180°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.66 [d, 6H, $(C\underline{H}_3)_2CH$], 5.07–5.16 [m, 1H, $(CH_3)_2C\underline{H}$], 7.23–7.39 (m, 3H) and 8.23–8.26 (m, 2H, C_6H_5), 7.26 (d, 1H) and 8.02 (d, 1H) and 8.70 (s, 1H, C_6H_3), 10.20 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, δ, ppm): 21.77, 58.04, 99.69, 101.75, 127.54, 127.91, 128.11, 129.66, 129.92, 131.85, 132.72, 136.40, 145.07, 146.11, 167.31, 172.99, 189.99. Found (%): C, 55.21; H, 4.11; N, 13.85. Calc. for $C_{19}H_{16}N_4O_5S$ (%): C, 55.33; H, 3.91; N, 13.58.