

[4,5]-Bicyclic sydnone imines

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Experimental

3-Isopropylsydnone imine hydrochloride

See V. G. Yashunskii, V. G. Ermolaeva, *Z. Org. Khim.*, 1960, **32**, 186 (in Russian).

3-Isopropyl-N₆-chloroacetylsydnone imine 4a.

Solution of triethylamine 19.7 ml (142 mmol) in 20 ml of dichloromethane was added dropwise to a stirred suspension of 3-isopropylsydnone imine hydrochloride 10.0 g (61.5 mmol) and chloroacetyl chloride 6.15 ml (73.8 mmol) in 150 ml of dichloromethane. The mixture was stirred for 1 h at -30 °C and warmed up to room temperature. Water (100 ml) was added, organic phase was separated, dried over Na₂SO₄, filtered through the pad of Al₂O₃ and evaporated *in vacuo*. Product was crystallized from isopropyl alcohol–hexane mixture. Yield 11.9 g (80%) **4a** as white crystals, mp 60–62 °C. ¹H NMR (CDCl₃, δ, ppm): 1.72 (d., J_{AB}=6.68 Hz, 6H, (CH₃)₂CH), 4.21 (s., 2H CH₂Cl), 5.12 (sp., J_{AB}=6.68 Hz, 1H, (CH₃)₂CH), 8.25 (s., 1H, 4-H). ¹³C NMR (CDCl₃, δ, ppm): 21.93, 46.88, 58.82, 104.92, 173.97, 174.71. Found (%): C 41.34, H 4.90, N 20.32. Calc. for C₇H₁₀ClN₃O₂ (%): C 41.29, H 4.95, N 20.64.

3-Isopropyl-N₆-α-bromopropionylsydnone imine 4b.

The title compound was prepared in the same way as compound **4a** starting from 19.7 ml (142 mmol) of triethylamine, 10.0 g (61.5 mmol) of 3-isopropylsydnone imine hydrochloride and 7.36 ml (73.8 mmol) of α-bromopropionyl chloride. Yield 13.2 g (82%) **4a** as white crystals, mp 73–74 °C. ¹H NMR (CDCl₃, δ, ppm): 1.71 (d., J_{AB}=6.76 Hz, 6H, (CH₃)₂CH), 1.84 (d., J_{AB}=6.86 Hz, 3H, CH₃CHBr); 4.59 (q., J_{AB}=6.86 Hz, 1H, CHBr), 4.98 (sp., J_{AB}=6.76 Hz, 1H, (CH₃)₂CH), 8.14 (s., 1H, 4-H). ¹³C NMR (CDCl₃, δ, ppm): 21.95, 21.96, 22.37, 46.01, 48.38, 58.61, 104.49, 174.59, 178.39. Found (%): C 36.50, H 4.95, N 15.88. Calc. for C₈H₁₂BrN₃O₂ (%): C 36.66, H 4.61, N 16.03.

3-Isopropyl-4-[(4-trifluoromethyl-phenyl)-hydroximethyl]-N₆-chloroacetylsydnone imine **6a.**

To a stirred mixture of 0.3 g (1.47 mmol) of 3-isopropyl-N₆-chloroacetylsydnone imine in 25 ml of THF at -90 °C, 1.08 ml (1.62 mmol) of 1.5 M n-BuLi solution in hexane was added dropwise, mixture was stirred for 30 min at -85 °C and 0,22 ml (1.62 mmol) of 4-(trifluoromethyl)benzaldehyde was added and the mixture was additionally 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 H₂O was added. Mixture was dried with Na₂SO₄ and passed through the layer of Al₂O₃ (2x3 cm), the solvent was removed *in vacuo*, the residue was purified by chromatography on SiO₂ (30x2 cm, CHCl₃ : ethyl acetate, 5:1) and crystallization from PrⁱOH/hexane. Yield of **6a** 0.42 g (76%), mp 190–192 °C. ¹H NMR (DMSO-d₆, δ, ppm): 1.18 (d., J_{AB}=6.67 Hz, 3H) and 1.60 (d., J_{AB}=6.67 Hz, 3H, (CH₃)₂CH), 4.19 (s., 2H, CH₂Cl), 5.09 (sp., J_{AB}=6.68 Hz, 1H, (CH₃)₂CH), 6.25 (d., J_{AB}=4.35 Hz, 1H, OH), 7.06 (d., J_{AB}=4.35 Hz, 1H, CH-OH), 7.65-7.70 (m., 2H) and 7.74-7.77 (m., 2H, C₆H₄). ¹³C NMR (DMSO-d₆, δ, ppm): 21.67, 22.10, 47.20, 57.93, 63.29, 117.98, 124.62 (q., J_{CF}=272 Hz), 125.84 (q., J³_{CF}=3 Hz), 128.55 (q., J²_{CF}=32 Hz), 144.89, 167.43, 172.19. ¹⁹F NMR (DMSO-d₆, δ, ppm): 17.34. Found (%): C 47.80, H 4.30, N 12.12. Calc. for C₁₅H₁₅ClF₃N₃O₃ (%): C 47.69, H 4.00, N 11.12.

3-Isopropyl-4-[(4-trifluoromethyl-phenyl)-hydroximethyl]-N₆--α-bromopropionylsydnone imine **6b.**

The title compound was prepared in the same way as compound **6a** starting from 0.3 g (1.15 mmol) of 3-isopropyl-N₆--α-bromopropionylsydnone imine, 0.84 ml (1.26 mmol) of 1.5 M solution of n-BuLi in hexane and 0.173 ml (1.26 mmol) of 4-(trifluoromethyl)benzaldehyde. Yield of **6b** 0.40 g (81%), as a mixture of diastereomers 0.66:1. ¹H NMR (CDCl₃, δ, ppm): 1.20-1.23 (m., 3H) and 1.73-1.70 (m., 4.22H, (CH₃)₂CH and CHBr-CH₃), 1.81 (d., J_{AB}=6.5 Hz, 1.7H, CHBr-CH₃), 4.40-4.60 (m., 1H, CHBr-CH₃), 5.05-5.15 (m., 1H, (CH₃)₂CH), 6.33 (s., 1H, CH-OH), 6.57 (br.s., 1H, OH), 7.50-7.60 (m., 2H) and 7.60-7.70 (m., 2H, C₆H₄). ¹³C NMR (CDCl₃, δ, ppm): 21.67, 22.04, 22.07, 22.27, 22.47, 25.29, 48.03, 48.27, 57.96, 63.52, 119.26, 119.37, 123.91 (q., J_{CF}=270 Hz), 125.85 (q., J³_{CF}=3 Hz), 130.30 (q., J²_{CF}=30 Hz), 143.12, 169.79, 169.82, 177.16, 177.30. ¹⁹F NMR (CDCl₃, δ, ppm): 15.09, 15.11 0.66:1.00. Found (%): C 44.25, H 4.00, N 9.55. Calc. for C₁₆H₁₇BrF₃N₃O₃ (%): C 44.05, H 3.93, N 9.63.

3-Isopropyl-7-oxo-9-thia-[4,6-propano]sydnone imine **7a**

To a stirred mixture of 0.3 g (1.47 mmol) of 3-isopropyl-N₆-chloroacetylsydnone imine in 25 ml of THF at -90 °C, 1.08 ml (1.62 mmol) of 1.5 M solution of n-BuLi in hexane was added

dropwise, the mixture was stirred for 30 min at $-85\text{ }^{\circ}\text{C}$ and 0.047g (1.47 mmol) of S_8 was added. The mixture was stirred for 30 min at $-85\text{ }^{\circ}\text{C}$ and warmed up on a bath, after stirring for 4 h at room temperature 1 ml H_2O was added. The mixture was dried with Na_2SO_4 and passed through the layer of Al_2O_3 (2x3 cm), the solvent was removed *in vacuo*, 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 **7a** 0.23 g (78%), mp 125–127 $^{\circ}\text{C}$. ^1H NMR (CDCl_3 , δ , ppm): 1.59 (d., $J_{\text{AB}}=6.84$ Hz, 6H, $(\text{CH}_3)_2\text{CH}$), 3.35 (s., 2H CH_2), 4.72 (sp., $J_{\text{AB}}=6.84$ Hz, 1H, $(\text{CH}_3)_2\text{CH}$). ^{13}C NMR (CDCl_3 , δ , ppm): 20.41, 27.14, 57.84, 102.47, 168.70, 172.77. Found (%): C 42.50, H 4.61, N 20.88. Calc. for $\text{C}_7\text{H}_9\text{N}_3\text{O}_2\text{S}$ (%): C 42.20, H 4.55, N 21.09.

3-Isopropyl-8-methyl-7-oxo-9-thia-[4,6-propano]sydnone imine 7b

The title compound was prepared in the same way as compound **7a** starting from 0.3 g (1.15 mmol) of 3-isopropyl- N_6 - α -bromopropionylsydnone imine, 0.84 ml (1.26 mmol) of 1.5 M solution of $n\text{-BuLi}$ in hexane and 0.040g (1.26 mmol) of S_8 . Yield of **7b** 0.13 g (53%). ^1H NMR (CDCl_3 , δ , ppm): 1.44 (d., $J_{\text{AB}}=6.83$ Hz, 3H, CH-CH_3), 1.64 (d., $J_{\text{AB}}=6.54$ Hz, 6H, $(\text{CH}_3)_2\text{CH}$), 3.56 (q., $J_{\text{AB}}=6.83$ Hz, 1H CH-CH_3), 4.75 (sp., $J_{\text{AB}}=6.54$ Hz, 1H, $(\text{CH}_3)_2\text{CH}$). ^{13}C NMR (CDCl_3 , δ , ppm): 18.06, 20.47, 20.52, 36.59, 57.75, 102.56, 171.44, 172.10. Found (%): C 45.10, H 5.19, N 20.00. Calc. for $\text{C}_8\text{H}_{11}\text{N}_3\text{O}_2\text{S}$ (%): C 45.06, H 5.20, N 19.70.