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4*H*-Thiopyrans bearing mesoionic ring

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3-Methylsydnone

B. Walker, *J. Chem. Soc.,* 1957, 4409.

3-Phenylsydnone

Y. Ogata, A. Kawasaki and H. Kojoh. *J. Org. Chem.*, 1974, **39**, 3676.

3-Phenyl-4-formylsydnone

C.J. Thoman, D.J. Voaden and I.M. Hunsberger, *J. Org. Chem.*, 1964, **29**, 2044.

1-Methoxy-*N*,*N*-dimethylmethanaminium methylsulphate

R. Knorr, P. Loew, P. Hassel and H. Bronberger, *J. Org. Chem.*, 1984, **49**, 1288.

3-Methyl-4-formylsydnone

To a stirred mixture of 1.0 g (9.8 mmol) 3-methylsydnone in 50 ml THF at –90 °C 4.32 ml (10.8 mmol) 2.5 M solution *n*-BuLi in hexane was added dropwise, mixture stirred 30 min at –85˚C and 3.38 g (11.8 mmol) 1-methoxy-*N*,*N*-dimethylmethanaminium methyl sulfate. Cooling bath was removed and mixture was stirred 30 min at room temperature, 1 ml sat. $NaHCO_3$ was added. Mixture was dried by Na_2SO_4 and passed through layer of Al_2O_3 (2x3 cm), the solvent removed in vacuum, residue purified by chromatography on SiO_2 30x2 cm $CHCl_3$/ethyl acetate 5/1 and crystallization from *i*-PrOH/hexane. Yield of 3-methyl-4-formylsydnone 1.0 g (80%), mp 104-106 °C (lit.[8] mp 104-106 °C).

3-Isopropyl-N_6-benzoylsydnone imine

V.G. Yashunskii and V.G. Ermolaeva, *Zh. Obshch. Khim,* 1962, **32**, 182 (in Russian).

3-Isopropyl-4-formyl-N_6-benzoylsydnone imine 4. To a stirred mixture of 0.5 g (2.16 mmol) 3-isopropyl-N_6-benzoylsydnone imine in 25 ml THF at –90˚C 0.95 ml (2.38 mmol)

2.5 M solution n-BuLi in hexane was added dropwise, mixture stirred 30 min at –85 °C and 0.53 g (2.60 mmol) 1-methoxy-*N*,*N*-dimethylmethanaminium methyl sulfate. Cooling bath was removed and mixture was stirred 30 min at room temperature, 1 ml sat. $NaHCO_3$ was added. Mixture was dried by Na_2SO_4 and passed through the layer of Al_2O_3 (2x3 cm), the solvent removed in vacuum, residue purified by chromatography on SiO_2 30x2 cm $CHCl_3$/ethyl acetate 5/1 and crystallization from i-PrOH/hexane. Yield **4** 1.0 g (91%), mp 112-113 °C. ^{1}H NMR ($CDCl_3$, δ, ppm, *J*/Hz): 1.61 (d, 6H, $CH(\underline{CH}_3)_2$, *J* = 6.8); 5.63 (m, 1H, $C\underline{H}(CH_3)_2$); 7.34-7.49 (m, 3H) and 8.16-8.20 (m, 2H, C_6H_5); 10.01 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, δ, ppm): 21.29, 60.12, 110.94, 128.12, 129.79, 132.26, 136.11, 167.22, 173.14, 177.58. Found (%): C, 60.33; H, 4.94; N, 16.34. Calc. for $C_{13}H_{13}N_3O_3$ (%): C, 60.23; H, 5.05; N, 16.21.

2,6-Diamino-4-(3-methyl-1,2,3-oxadiazolium-5-olate-4-yl)-4*H*-thiopyran-3,5-dicarbonitrile 2a

To the mixture of 0.13 g, (10.0 mmol) 3-methyl-4-formylsydnone {0,19g for 3-Ph-sydnone}, 0,10 g, (10.0 mmol) 2-cyanothioacetamide and (0,06g, 10mmol) malononitrile in boiling ethanol (25-30ml) 0,1-0,2ml of triethylamine added and keep boiling within 2-3 hours. Upon cooling to room temperature the orange solid precipitated, which filtered and washed with ethanol and hexane. Recrystallization from ethanol gives of 4*H*-thiopyran **2a**. Yield 0.18g (65%). Mp 182-184 °C (decomp.). ^{1}H NMR (DMSO-d_6, δ, ppm): 4.11 (s, 3H, CH_3); 4.81 (s, 1 H, CH); 7.07 (s, 4H, $2NH_2$). ^{13}C NMR (DMSO-d_6, δ, ppm): 32.26, 38.66, 66.47, 107.68, 118.69, 153.36, 166.55. Found (%): C, 43.20; H, 2.99; N, 31.00. Calc. for $C_{10}H_8N_6O_2S$ (%): C, 43.48; H, 2.92; N, 30.42.

2,6-Diamino-4-(3-phenyl-1,2,3-oxadiazolium-5-olate-4-yl)-4*H*-thiopyran-3,5-dicarbonitrile 2b

To the mixture of 0,19 g, (10.0 mmol) 3-phenyl-4-formylsydnone, 0,10 g, (10.0 mmol) 2-cyanothioacetamide and (0,06g, 10mmol) malononitrile in boiling ethanol (25-30ml) 0,1-0,2ml of triethylamine added and keep boiling within 2-3 hours. Upon cooling to room temperature the orange solid precipitated, which filtered and washed with ethanol and hexane. Recrystallization from ethanol gives of 4*H*-thiopyran **2b**, as solvate with ethanol. Yield 0.27g (78%). ^{1}H NMR (DMSO-d_6, δ, ppm): 1.01 (t, 3H, $C\underline{H}_3$-CH_2-OH); 4.29 (s, 1H, CH); 4.33 (m, 2H, CH_3-$C\underline{H}_2$-OH), 7.04 (s, 4H, $2NH_2$); 7.55-7.80 (m, 5H C_6H_5). ^{13}C NMR (DMSO-d_6, δ, ppm): 18.95, 33.36, 56.54, 65.86, 109.66, 118.65, 126.04, 130.75, 133.01, 133.11, 153.17 166.17.

(3-Isopropyl-6-phenylcarbonyl-1,2,3-oxadiazolium-5-amidine-4-yl)methylenemalononitrile 6

A solution of 1.0 g (3.86 mmol) 3-isopropyl-4-formyl-N_6-benzoylsydnone imine **4**, 0.27 g (4.1 mmol) malononitrile, 0.024 g (0.2 mmpl) DMAP and 0.11 ml AcOH in 8 ml of isopropanol reflux with stirring 30 min, precipitate filtered off and dried in vacuum. Yield **6** 1.17 g (95%), mp 160 °C (decomp.). ^{1}H NMR (DMSO-d_6, δ, ppm): 1.68 (d, 6H, C<u>H</u>$_3$-CH-C<u>H</u>$_3$); 5.13 (m, 1H, CH_3-C<u>H</u>-CH_3); 7.45-7.60 (м, 3H) and 8.16-8.20 (m, 2H, C_6H_5); 8.60 (s. 1H, CH=C$(CN)_2$). Found (%): C, 62.71; H, 4.42; N, 22.55. Calc. for $C_{16}H_{13}N_5O_2$ (%): C 62.53; H 4.26; N 22.79.

A. 2,6-Diamino-4-(3-isopropyl-N6-benzoyl-1,2,3-oxadiazolium-5-amidine-4-yl)-4*H*-thiopyran-3,5-dicarbonitrile 5

A solution of 0.2 g (0.77 mmol) 3-isopropyl-4-formyl-N_6-benzoylsydnone imine, 0.051 g (0.77 mmol) malononitrile and 0.077 g (0.77 mmol) 2-cyanothioacetamide, 4.86 μl (3.8 μmol) Et_3N in 5 ml isopropanol reflux with stirring 30 min, precipitate filtered off and dried in vacuum. Yield of **5** 0.14 g (40%) as solvate with isopropanol. ^{1}H-NMR (DMSO, δ, ppm): 1.01 (d, 6H, C<u>H</u>$_3$-CH(OH)-C<u>H</u>$_3$); 1.64 (d, 6H, C<u>H</u>$_3$-CH-C<u>H</u>$_3$); 3.75 (m, 1H, CH_3-C<u>H</u>(OH)-CH_3); 5.26 (s, 1H, CH); 5.35 (m, 1H, CH_3-C<u>H</u>-CH_3); 7.19 (s, 4H, $2NH_2$); 7.30-7.50 (m, 3H) and 8.10-8.13 (m, 2H, C_6H_5). ^{13}C (DMSO-d_6, δ, ppm): 22.58, 25.90 (*i*-PrOH), 32.74, 56.40, 62.54 (*i*-PrOH), 65.15, 115.94, 118.90, 128.33, 129.86, 131.64

B. 2,6-Diamino-4-(3-isopropyl-N6-benzoyl-1,2,3-oxadiazolium-5-amidine-4-yl)-4*H*-thiopyran-3,5-dicarbonitrile 5

A solution of 0.1 g (0.33 mmol) (1,2,3-oxadiazolium-5-amidine-4-yl)methylenemalononitrile and 0.032 g (0.33 mmol) 2-cyanothioacetamide, 4.86 μl (3.8 μmol) Et_3N in 5 ml isopropanol reflux with stirring 30 min, precipitate filtered off and dried in vacuum. Yield of **5** 0.14 g (90%) as solvate with isopropanol.