

Synthesis of 2*H*-Thiopyrans by Rhodium(II) Acetate-Catalyzed Reaction of 4-Amino-2,5-dihydro-3-thiophenecarbonitriles with α -Diazocarbonyl Compounds. Part 1

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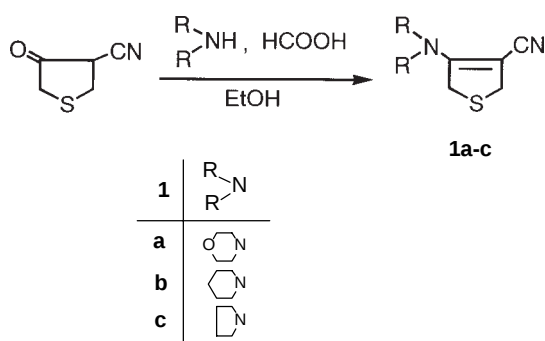
Abstract. 4-Amino-2,5-dihydro-3-thiophenecarbonitriles **1** reacted with dimethyl diazomalonate in the presence of rhodium(II) acetate to give regioselectively 4-cyano-2*H*-thiopyrans **2** (C_2 -S insertion), and 5-cyano-2*H*-thiopyrans (C_5 -S insertion) were not isolated. Similar insertion was also ob-

served in the reaction of **1** with methyl diazoacetoacetate and ethyl diazobenzoylacetate. The starting compounds **1** were synthesized by the reaction of tetrahydro-4-oxo-3-thiophenecarbonitrile with morpholine, piperidine, and pyrrolidine in the presence of formic acid in ethanol.

The transition-metal-catalyzed reactions of diazo compounds with various types of compounds containing sulfur atom have been extensively studied [1–3]. These reactions have been proposed to proceed through ylide formation by reactions of carbenoids derived from diazo compounds [4–8].

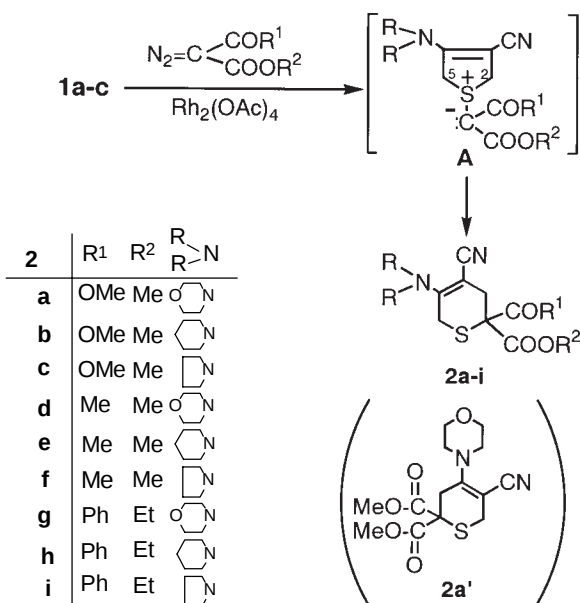
We have already reported that 4,5-dihydro-3-thiophenecarbonitriles react with diethyl diazomalonate in the presence of copper powder to form stable 4,5-dihydrothiophenium-1-bis(ethoxycarbonyl)methylides [9]. In recent study, we showed that 4,5-dihydro-3-thiophenecarbonitriles react with ethyl diazoacetoacetate in the presence of rhodium(II) acetate to yield 1,4-oxathiocines [10]. The formation of the 1,4-oxathiocines involves initial generation of unstable sulfonium ylides which subsequently undergo a thermal rearrangement to give the observed products. In continuation of these studies we investigated the reactions of 2,5-dihydro-3-thiophenecarbonitriles **1** with α -diazocarbonyl compounds in the presence of rhodium(II) acetate in order to prove whether or not stable sulfonium ylides are formed. α -Diazocarbonyl compounds used in this study include dimethyl diazomalonate [11], methyl diazoacetoacetate [12], and ethyl diazobenzoylacetate [13].

The starting compounds 2,5-dihydro-3-thiophenecarbonitriles **1a–c** were synthesized by reaction of tetrahydro-4-oxo-3-thiophenecarbonitrile with morpholine, piperidine, and pyrrolidine in the presence of formic acid in ethanol (Scheme 1).



Scheme 1 Preparation of 2,5-dihydro-3-thiophenecarbonitriles **1**

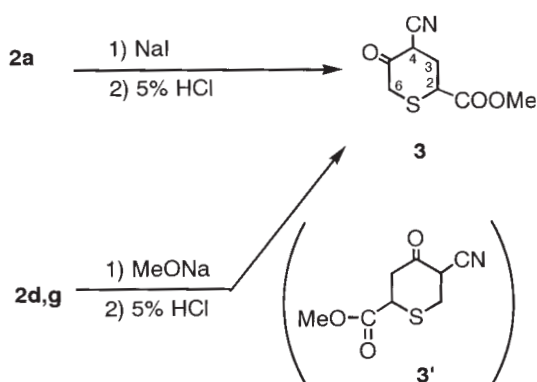
When a mixture of 2,5-dihydro-4-morpholino-3-thiophenecarbonitrile **1a**, dimethyl diazomalonate, and a catalytic amount of rhodium(II) acetate in toluene was refluxed for 2h, dimethyl 4-cyano-2*H*-thiopyran-2,2-dicarboxylate **2a** (C_2 -S insertion) was obtained in 63% yield, and the corresponding sulfonium ylide was not isolated (Scheme 2). Ando *et al.* have reported that the photolysis of dimethyl diazomalonate in 2,5-dihydrothiophene give dimethyl 3,6-dihydro-2*H*-thiopyran-2,2-dicarboxylate [14]. The mass spectrum and the results of elemental analysis of **2a** indicate that **2a** has the molecular composition $C_{14}H_{18}N_2O_5S$. The IR spectrum of **2a** displays a band due to the non-conjugated ester carbonyl groups at 1740 cm^{-1} . The reaction was regioselective, and only one of the two possible regioisomers **2a** and dimethyl 5-cyano-2*H*-thiopyran-2,2-dicarboxylate **2a'** (C_5 -S insertion) was isolated.



Scheme 2 Reaction of 2,5-dihydro-3-thiophenecarbonitriles **1** with α -diazocarbonyl compounds

In order to confirm the structure of **2a**, successive treatment of **2a** with sodium iodide and hydrochloric acid resulted in the formation of methyl 4-cyanotetrahydro-5-oxo-2*H*-thiopyran-2-carboxylate **3** (Scheme 3). The ^1H NMR spectrum of **3** indicates a pair of one-proton doublets at $\delta = 3.14$ and 3.77 ppm attributable to the two protons of the 6-H of the thiopyran ring and two one-proton double double doublets at $\delta = 2.84$ and 3.07 ppm assignable to the two protons of the 3-H, in addition to the signals due to two methine protons (2-H and 4-H) and a methyl ester protons. In the NOESY spectrum of **3**, the absence of a NOE effect between 2-H and 4-H suggests a *trans* relationship of both protons. These results are consistent with the 4-cyano-5-oxothiopyran **3** rather than the 5-cyano-4-oxothiopyran **3'**. The formation of **3** confirms structure **2a** for the isolated insertion product, since the reaction of regioisomer **2a'** should lead to the formation of **3'**. The formation of the C₂-S insertion product **2a** can be deduced by the mechanism as shown in Scheme 2. Dimethoxycarbonyl-carbenoid generated by the rhodium(II) acetate-catalyzed decomposition of dimethyl diazomalonate attacks the sulfur atom of **1a** to form the unstable sulfonium ylide **A**, which undergoes a Stevens rearrangement to form **2a**.

Subsequently, the rhodium(II) acetate-catalyzed reaction of **1a** with methyl diazoacetate and ethyl diazobenzoylacetate in fluorobenzene afforded methyl 2-acetyl-4-cyano-2*H*-thiopyran-2-carboxylate **2d** and ethyl 2-benzoyl-4-cyano-2*H*-thiopyran-2-carboxylate **2g** in 69 and 70% yield, respectively. Successive treatment of **2d** with sodium methoxide and hydrochloric acid furnished **3**. Under the same conditions, compound **2g** was also converted into **3**. These findings indicate that both **2d** and **2g** have 4-cyano-5-morpholino-2*H*-thiopyran structure.



Scheme 3 Formation of 4-cyano-5-oxothiopyran **3**

Reactions of 2,5-dihydro-4-piperidino-(and -4-pyrrolidino)-3-thiophenecarbonitriles **1b,c** with α -diazocarbonyl compounds described above gave the corresponding 5-amino-4-cyano-2*H*-thiopyrans **2b,c,e,f,h,i** in 54–73% yields. The structural assignments of **2b,c,e,f,h,i** were based on the similarity of the ^1H NMR signals of 2*H*-thiopyran ring protons with those of **2a,d,g**.

Experimental

All melting points are uncorrected. IR spectra (KBr) were recorded with a Jasco A-302 instrument. ^1H NMR spectra were measured on a Jeol JNM-GX-400 (400 MHz) and Jeol JNM-A500 (500 MHz) in CDCl_3 with TMS as internal standard, δ scale; coupling constants in Hz. Mass spectra were recorded with a Jeol JMS-D300, 70eV.

Tetrahydro-4-oxo-3-thiophenecarbonitrile was obtained from commercial source (Tokyo Chemical Industry Co., Ltd.) and used without further purification.

Preparation of 4-Amino-2,5-dihydro-3-thiophenecarbonitriles **1** (General Procedure)

To an ice-cooled and stirred solution of tetrahydro-4-oxo-3-thiophenecarbonitrile (7.62 g, 60 mmol) and formic acid (8.28 g, 180 mmol) in EtOH (150 ml) morpholine (15.66 g, 180 mmol) [piperidine (15.30 g, 180 mmol) or pyrrolidine (12.78 g, 180 mmol)] was added. The mixture was refluxed for 3h. The solvent was removed and H_2O (150 ml) was added to the residue. The mixture was extracted with CH_2Cl_2 . The extract was washed with 5% NaOH (50 ml), and then H_2O , dried with Na_2SO_4 , and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with CH_2Cl_2 as eluent. Yields: **1a** (10.76 g, 91%), **1b** (8.31 g, 71%), and **1c** (10.11 g, 94%).

2,5-Dihydro-4-morpholino-3-thiophenecarbonitrile (**1a**)

Colorless needles; *m.p.* 88–89 °C (acetone/petroleum ether). – IR: $\nu/\text{cm}^{-1} = 2190$ ($\text{C}\equiv\text{N}$). – ^1H NMR (400 MHz): $\delta/\text{ppm} = 3.51\text{--}3.56$ [m, 4H, 2CH_2 (morpholine)], 3.71–3.75 [m, 4H, 2CH_2 (morpholine)], 3.79–3.83 (m, 4H, 2-H, 5-H). – MS (FAB) m/z (%): 197 (100) [$\text{M}^+ + \text{H}$].

$\text{C}_9\text{H}_{12}\text{N}_2\text{OS}$ Calcd.: C 55.08 H 6.16 N 14.27 (196.3) Found: C 55.18 H 6.19 N 14.27.

2,5-Dihydro-4-piperidino-3-thiophenecarbonitrile (**1b**)

Colorless columns; *m.p.* 70–71 °C (Et_2O). – IR: $\nu/\text{cm}^{-1} = 2170$ ($\text{C}\equiv\text{N}$). – ^1H NMR (400 MHz): $\delta/\text{ppm} = 1.60\text{--}1.70$ [m, 6H, 3CH_2 (piperidine)], 3.45–3.55 [m, 4H, 2CH_2 (piperidine)], 3.75–3.85 (m, 4H, 2-H, 5-H). – MS (FAB) m/z (%): 195 (86) [$\text{M}^+ + \text{H}$].

$\text{C}_{10}\text{H}_{14}\text{N}_2\text{S}$ Calcd.: C 61.82 H 7.26 N 14.42 (194.3) Found: C 62.04 H 7.31 N 14.57.

2,5-Dihydro-4-pyrrolidino-3-thiophenecarbonitrile (**1c**)

Colorless needles; *m.p.* 91–92 °C (acetone/petroleum ether). – IR: $\nu/\text{cm}^{-1} = 2190$ ($\text{C}\equiv\text{N}$). – ^1H NMR (400 MHz): $\delta/\text{ppm} = 1.90\text{--}2.00$ [m, 4H, 2CH_2 (pyrrolidine)], 3.55–3.65 [m, 4H, 2CH_2 (pyrrolidine)], 3.82 (s, 4H, 2-H, 5-H). – MS (FAB) m/z (%): 181 (90) [$\text{M}^+ + \text{H}$].

$\text{C}_9\text{H}_{12}\text{N}_2\text{S}$ Calcd.: C 59.96 H 6.71 N 15.54 (180.3) Found: C 60.13 H 6.73 N 15.57.

Reactions of **1** with α -Diazocarbonyl Compounds (General Procedure)

Procedure A: A mixture of **1** (5 mmol), dimethyl diazomalonate [11] (0.87 g, 5.5 mmol), and $\text{Rh}_2(\text{OAc})_4$ (0.02 g) in toluene (10 ml) was refluxed for 2h. The solvent was removed and the residue was purified by column chromatography on

silica gel with CH_2Cl_2 as eluent. Yields: **2a** (1.02 g, 63%), **2b** (0.98 g, 60%), and **2c** (0.99 g, 64%).

Procedure B: A mixture of **1** (5 mmol), methyl diazoacetate [12] (0.78 g, 5.5 mmol), and $\text{Rh}_2(\text{OAc})_4$ (0.02 g) in $\text{C}_6\text{H}_5\text{F}$ (10 ml) was refluxed for 2 h. The solvent was removed and the residue was purified by column chromatography on silica gel with CH_2Cl_2 as eluent. Yields: **2d** (1.07 g, 69%), **2e** (1.07 g, 66%), and **2f** (0.79 g, 54%).

Procedure C: From **1** (5 mmol) and ethyl diazobenzoylacetate [13] (1.20 g, 5.5 mmol) as described for **Procedure B**. Yields: **2g** (1.36 g, 70%), **2h** (1.40 g, 73%), and **2i** (1.30 g, 70%).

Dimethyl 4-Cyano-3,6-dihydro-5-morpholino-2H-thiopyran-2,2-dicarboxylate (2a)

From **1a** (0.98 g, 5 mmol). Colorless prisms; *m.p.* 84–85 °C (acetone/petroleum ether). – IR: ν/cm^{-1} = 2180 ($\text{C}\equiv\text{N}$), 1740 ($\text{C}=\text{O}$). – ^1H NMR (500 MHz): δ/ppm = 3.00 (s, 2H, 3-H), 3.24 (s, 2H, 6-H), 3.42–3.60 [m, 4H, 2CH_2 (morpholine)], 3.72–3.76 [m, 4H, 2CH_2 (morpholine)], 3.81 (s, 6H, 2OCH_3). – MS (FAB) *m/z* (%): 327 (100) [$\text{M}^+ + \text{H}$].

$\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_5\text{S}$ Calcd.: C 51.52 H 5.56 N 8.58 (326.4) Found: C 51.59 H 5.47 N 8.59.

Dimethyl 4-Cyano-3,6-dihydro-5-piperidino-2H-thiopyran-2,2-dicarboxylate (2b)

From **1b** (0.97 g, 5 mmol). Colorless prisms; *m.p.* 74–75 °C (Et_2O /petroleum ether). – IR: ν/cm^{-1} = 2180 ($\text{C}\equiv\text{N}$), 1740 ($\text{C}=\text{O}$). – ^1H NMR (400 MHz): δ/ppm = 1.60–1.67 [m, 6H, 3CH_2 (piperidine)], 2.99 (s, 2H, 3-H), 3.24 (s, 2H, 6-H), 3.37–3.43 [m, 4H, 2CH_2 (piperidine)], 3.80 (s, 6H, 2OCH_3). – MS (FAB) *m/z* (%): 325 (100) [$\text{M}^+ + \text{H}$].

$\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_4\text{S}$ Calcd.: C 55.54 H 6.21 N 8.64 (324.4) Found: C 55.56 H 6.29 N 8.56.

Dimethyl 4-Cyano-3,6-dihydro-5-pyrrolidino-2H-thiopyran-2,2-dicarboxylate (2c)

From **1c** (0.90 g, 5 mmol). Colorless columns; *m.p.* 134–135 °C (acetone/petroleum ether). – IR: ν/cm^{-1} = 2180 ($\text{C}\equiv\text{N}$), 1740 ($\text{C}=\text{O}$). – ^1H NMR (400 MHz): δ/ppm = 1.90–1.96 [m, 4H, 2CH_2 (pyrrolidine)], 2.99 (s, 2H, 3-H), 3.30 (s, 2H, 6-H), 3.58–3.64 [m, 4H, 2CH_2 (pyrrolidine)], 3.81 (s, 6H, 2OCH_3). – MS (FAB) *m/z* (%): 311 (100) [$\text{M}^+ + \text{H}$].

$\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$ Calcd.: C 54.18 H 5.85 N 9.03 (310.4) Found: C 54.25 H 5.88 N 9.04.

Methyl 2-Acetyl-4-cyano-3,6-dihydro-5-morpholino-2H-thiopyran-2-carboxylate (2d)

From **1a** (0.98 g, 5 mmol). Colorless scales; *m.p.* 123–124 °C (acetone/petroleum ether). – IR: ν/cm^{-1} = 2200 ($\text{C}\equiv\text{N}$), 1730, 1705 ($\text{C}=\text{O}$). – ^1H NMR (400 MHz): δ/ppm = 2.30 (s, 3H, CH_3), 2.92 (AB quartet, J = 15.6, 2H, 3-H), 3.18 (AB quartet, J = 15.6, 2H, 6-H), 3.38–3.42 [m, 4H, 2CH_2 (morpholine)], 3.70–3.76 [m, 4H, 2CH_2 (morpholine)], 3.83 (s, 3H, OCH_3). – MS (FAB) *m/z* (%): 311 (100) [$\text{M}^+ + \text{H}$].

$\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$ Calcd.: C 54.18 H 5.85 N 9.03 (310.4) Found: C 54.35 H 5.66 N 9.07.

Methyl 2-Acetyl-4-cyano-3,6-dihydro-5-piperidino-2H-thiopyran-2-carboxylate (2e)

From **1b** (0.97 g, 5 mmol). Colorless needles; *m.p.* 66–68 °C

(Et_2O /petroleum ether). – IR: ν/cm^{-1} = 2200 ($\text{C}\equiv\text{N}$), 1740, 1710 ($\text{C}=\text{O}$). – ^1H NMR (400 MHz): δ/ppm = 1.60–1.65 [m, 6H, 3CH_2 (piperidine)], 2.30 (s, 3H, CH_3), 2.92 (AB quartet, J = 15.6, 2H, 3-H), 3.19 (AB quartet, J = 15.6, 2H, 6-H), 3.35–3.40 [m, 4H, 2CH_2 (piperidine)], 3.81 (s, 3H, OCH_3). – MS (FAB) *m/z* (%): 309 (100) [$\text{M}^+ + \text{H}$].

$\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$ Calcd.: C 58.42 H 6.54 N 9.08 (308.4) Found: C 58.44 H 6.40 N 9.16.

Methyl 2-Acetyl-4-cyano-3,6-dihydro-5-pyrrolidino-2H-thiopyran-2-carboxylate (2f)

From **1c** (0.90 g, 5 mmol). Colorless prisms; *m.p.* 96–97 °C (acetone/petroleum ether). – IR: ν/cm^{-1} = 2180 ($\text{C}\equiv\text{N}$), 1735, 1700 ($\text{C}=\text{O}$). – ^1H NMR (400 MHz): δ/ppm = 1.90–1.96 [m, 4H, 2CH_2 (pyrrolidine)], 2.30 (s, 3H, CH_3), 2.92 (AB quartet, J = 15.6, 2H, 3-H), 3.27 (AB quartet, J = 15.6, 2H, 6-H), 3.56–3.65 [m, 4H, 2CH_2 (pyrrolidine)], 3.82 (s, 3H, OCH_3). – MS (FAB) *m/z* (%): 295 (100) [$\text{M}^+ + \text{H}$].

$\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$ Calcd.: C 57.12 H 6.16 N 9.52 (294.4) Found: C 57.17 H 6.30 N 9.49.

Ethyl 2-Benzoyl-4-cyano-3,6-dihydro-5-morpholino-2H-thiopyran-2-carboxylate (2g)

From **1a** (0.98 g, 5 mmol). Pale yellow prisms; *m.p.* 115–116 °C (acetone/petroleum ether). – IR: ν/cm^{-1} = 2200 ($\text{C}\equiv\text{N}$), 1740, 1680 ($\text{C}=\text{O}$). – ^1H NMR (400 MHz): δ/ppm = 1.09 (t, J = 7.3, 3H, OCH_2CH_3), 3.07 (AB quartet, J = 15.6, 2H, 3-H), 3.25 (AB quartet, J = 15.6, 2H, 6-H), 3.40–3.46 [m, 4H, 2CH_2 (morpholine)], 3.72–3.77 [m, 4H, 2CH_2 (morpholine)], 4.10–4.22 (m, 2H, OCH_2CH_3), 7.40–7.45 (m, 2H, aryl), 7.52–7.57 (m, 1H, aryl), 7.85–7.88 (m, 2H, aryl). – MS (FAB) *m/z* (%): 387 (37) [$\text{M}^+ + \text{H}$].

$\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_4\text{S}$ Calcd.: C 62.16 H 5.74 N 7.25 (386.5) Found: C 62.13 H 5.62 N 7.26.

Ethyl 2-Benzoyl-4-cyano-3,6-dihydro-5-piperidino-2H-thiopyran-2-carboxylate (2h)

From **1b** (0.97 g, 5 mmol). Colorless columns; *m.p.* 92–93 °C (Et_2O /petroleum ether). – IR: ν/cm^{-1} = 2180 ($\text{C}\equiv\text{N}$), 1745, 1680 ($\text{C}=\text{O}$). – ^1H NMR (400 MHz): δ/ppm = 1.09 (t, J = 7.3, 3H, OCH_2CH_3), 1.60–1.66 [m, 6H, 3CH_2 (piperidine)], 3.08 (AB quartet, J = 15.6, 2H, 3-H), 3.27 (AB quartet, J = 15.6, 2H, 6-H), 3.35–3.45 [m, 4H, 2CH_2 (piperidine)], 4.10–4.25 (m, 2H, OCH_2CH_3), 7.40–7.44 (m, 2H, aryl), 7.52–7.56 (m, 1H, aryl), 7.84–7.87 (m, 2H, aryl). – MS (FAB) *m/z* (%): 385 (68) [$\text{M}^+ + \text{H}$].

$\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_3\text{S}$ Calcd.: C 65.60 H 6.29 N 7.29 (384.5) Found: C 65.52 H 6.44 N 7.29.

Ethyl 2-Benzoyl-4-cyano-3,6-dihydro-5-pyrrolidino-2H-thiopyran-2-carboxylate (2i)

From **1c** (0.90 g, 5 mmol). Colorless plates; *m.p.* 146–148 °C (acetone/petroleum ether). – IR: ν/cm^{-1} = 2180 ($\text{C}\equiv\text{N}$), 1745, 1680 ($\text{C}=\text{O}$). – ^1H NMR (400 MHz): δ/ppm = 1.09 (t, J = 7.3, 3H, OCH_2CH_3), 1.92–1.96 [m, 4H, 2CH_2 (pyrrolidine)], 3.08 (AB quartet, J = 15.2, 2H, 3-H), 3.32 (AB quartet, J = 14.7, 2H, 6-H), 3.56–3.68 [m, 4H, 2CH_2 (pyrrolidine)], 4.10–4.23 (m, 2H, OCH_2CH_3), 7.40–7.44 (m, 2H, aryl), 7.51–7.56 (m, 1H, aryl), 7.84–7.87 (m, 2H, aryl). – MS (FAB) *m/z* (%): 371 (77) [$\text{M}^+ + \text{H}$].

$\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_3\text{S}$ Calcd.: C 64.84 H 5.99 N 7.56 (370.5) Found: C 64.78 H 5.75 N 7.62.

Methyl trans-4-Cyanotetrahydro-5-oxo-2H-thiopyran-2-carboxylate (3)

Procedure A: A mixture of **2a** (1.09 g, 3.3 mmol) and NaI (0.75 g, 5 mmol) in DMF (3 ml) was stirred at 130 °C for 1 h. The DMF was removed *in vacuo* and 5% HCl (10 ml) was added to the residue. The resulting mixture was stirred at room temp. for 5 min. The mixture was extracted with CH₂Cl₂. The extract was washed with H₂O and dried with Na₂SO₄, and concentrated. The residue was purified by column chromatography on silica gel with CH₂Cl₂ as eluent to give **3** (0.33 g, 50%).

Procedure B: A mixture of **2d** (1.03 g, 3.3 mmol) and sodium methoxide (0.27 g, 5 mmol) in MeOH (10 ml) was refluxed for 7 h. The solvent was removed under reduced pressure and 5% HCl (15 ml) was added to the residue. The resulting mixture was stirred for 5 min. The mixture was extracted with CH₂Cl₂. The extract was washed with H₂O and dried with Na₂SO₄, and concentrated. The residue was chromatographed on silica gel with CH₂Cl₂ as eluent to afford **3** (0.07 g, 11%).

Procedure C: From **2g** (1.29 g, 3.3 mmol) as described for **Procedure B**. Yield **3** (0.05 g, 8%).

Colorless prisms; *m.p.* 89–90 °C (Et₂O). – IR: ν/cm^{-1} = 2250 (C≡N), 1720, 1715 (C=O). – ¹H NMR (500 MHz): δ/ppm = 2.84 (ddd, *J* = 3.5/12.5/13.5, 1H, 3-H), 3.07 (ddd, *J* = 3.5/5.5/13.5, 1H, 3-H), 3.14 (d, *J* = 13.5, 1H, 6-H), 3.61 (t, *J* = 3.5, 1H, 2-H), 3.77 (d, *J* = 13.5, 1H, 6-H), 3.86 (s, 3H, OCH₃), 4.53 (dd, *J* = 5.5/12.5, 1H, 4-H). – MS (FAB) *m/z* (%): 200 (100) [M⁺ + H].

C ₈ H ₉ NO ₃ S	Calcd.: C 48.23	H 4.55	N 7.03
(199.2)	Found: C 48.31	H 4.45	N 7.12.

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