Preparation, X-ray structure and propylaminolysis of 7,7-dichloro-5,7-dihydro-thieno[3,4-*b*]pyridin-5-one

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Refluxing 2-methylpyridine-3-carboxylic acid with thionyl chloride for 6–7 h gave (~50%) title compound dichlorothienolactone **2** as was confirmed by a X-ray structure analysis. The propylaminolysis of 2 provides a new and convenient access to highly functionalised pyrrolo[3,4-*b*]pyridine derivatives.

Keywords: 7,7-dichloro-5,7-dihydrothieno[3,4-*b*]pyridin-5-one, X-ray structure, 3,3-dichloro-4-ethylthieno[3,4-*b*]quinoline-1, 9-dione, derivatives, reaction mechanisms

The alkylaminolysis of 3,3,9-trichlorothieno[3,4-*b*]quinolin-1-one **1** is a convenient new methodology for accessing highly functionalised pyrrolo[3,4-*b*]quinoline derivatives.[1] Here we describe the preparation and structure of a hitherto undocumented pyridine analogue of **1**, namely, title compound **2**, and the outcomes stemming from its propylaminolysis which offers an alternate and convenient access to a variety of functionalised pyrrolo[3,4-*b*]pyridine derivatives. Of the 10 isomeric methylpyridinecarboxylic aãds, six cannot be converted by thionyl chloride to a corresponding dichlorothiolactone derivative owing to structural considerations. To date, only 4-methylpyridine-3-carboxylic aãd has provided such a compound, namely **3**,[2] while from 2,6-dimethyl-4-(3-thieny)pyridine-3,5-dicarboxylicaãd was obtained the dichlorothiolactone product **5**.[3] The product(s) generally isolated from the various methylpyridinecarboxylic aãds has/(have) been either the appropriate methylpyridinecarboxylic aãd chloride[4] and/or other chlorinated material.[5,6] There is, however, a dearth of relevant follow-up research in this area.

Here, we show that refluxing (79°C) 2-methylpyridine-3-carboxylic aãd with (excess of) $SOCl_2$ affords title dichlorothiolactone derivative **2**, the yield increasing to ~56% after 6 h, *via* initial production of 2-methylpyridine-3-carboxylic aãd chloride **4** which transforms during heating with the reagent to end-product **2**. It is noteworthy that little if any change is effected on **4** at 50°C for 5 h[4] or at 60°C for 3.5 h. Structure **2** was unambiguously established from X-ray crystallographic analysis (Fig.1).

Compound **2** when treated with propylamine (as representative amine) provided different products, the nature and yields of which were determined by the reaction conditions: Thus: (i) stirring 2 with $PrNH_2$ (in slight molar excess) in dioxan solution at 0°C for a relatively short time (~20 min), gave (67%) *N*-propyl-2-[(propylamino)thioxomethyl]pyridine-3-carboxamide **6** (Scheme 1), while (ii) stirring 2 with neat propylamine (in large molar excess) at room temperature for 12 h provided (68%) 6-propyl-6,7-dihydro-7-(propylimino)pyrrolo[3,4-*b*]pyridin-5-one **7** as end-product. In subsequent transformations: (i) aãd-catalysed cyclisation of **6** gave 6-propyl-6,7-dihydro-7-thioxopyrrolo[3,4-*b*]pyridin-5-one **8**, (ii) propylamine converted compounds **6** and **8** each to end-product **7**, and (iii) aãd hydrolysis of **7** gave (85%) 6-propyl-6,7-dihydropyrrolo[3,4-*b*]pyridine-5,7-dione **9**. Possible reaction transformations and sequences giving rise to the aforementioned transformations are outlined in Scheme 2. The known[7] thieno[3,4-*b*]pyridine-5,7-dione **10** was isolated from the mother liquor of crystallisation of title compound **2**.

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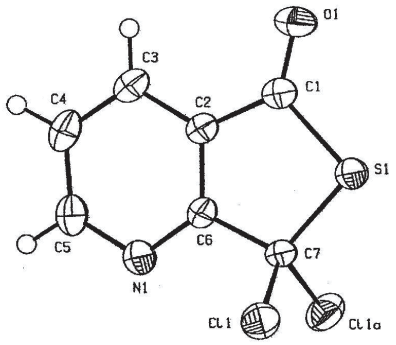


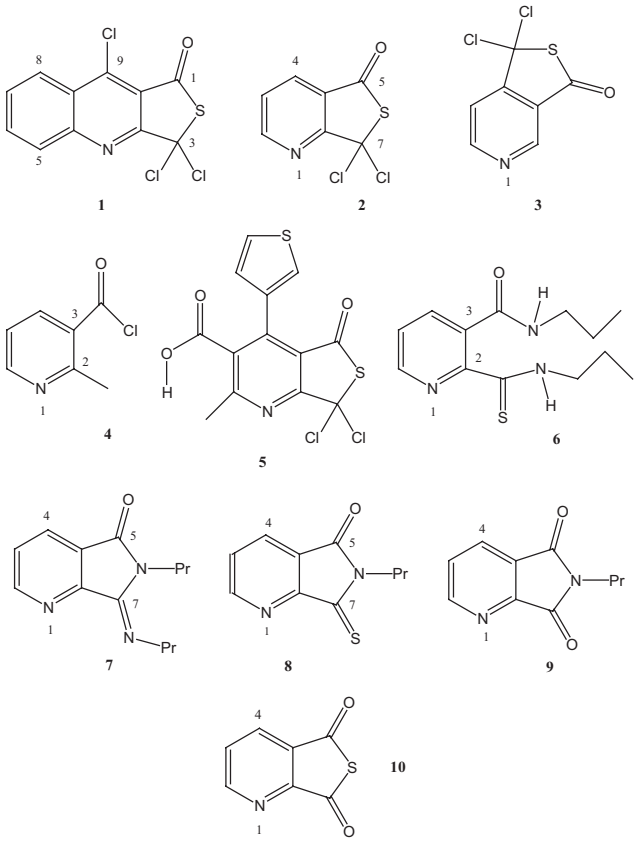
Fig.1 Ortep diagram (50% ellipsoids) for **2**, showing the labelling of the non-hydrogen atoms.

Mechanistic considerations

We currently assume that dichlorothiolactone **2** forms *via* mechanistic events similar to those proposed[2] for dichlorothiolactone **3** and likewise involve the production and intramolecular cyclisation of an appropriate thioacyl chloride intermediate **11** (from 2-methylpyridine-3-carbonyl chloride **4**, Scheme 3A). An additional and cruãal factor in the reactions of both the 2- and 4-methylpyridine-3-carboxylic aãds with $SOCl_2$ in forming **2** and **3**, respectively, may be considered, *viz*., a tautomerism in the initially formed aãd chloride, corresponding to the enolisation[8] in 3-phenylpropanoyl chloride, thereby faãlitating the addition of $SOCl_2$ to a methylene double bond[8] and the production of a thioacyl intermediate (Scheme 3A).

Although the Wenkert[2] mechanism shows no role for the pyridine *N*, an imine-enamine tautomerism also may be envisaged to complement/replace the aforementioned one (Scheme 3B). However, this possibility is unlikely in the instance of 1-ethyl-2-methyl-4-oxoquinoline-3-carboxylic aãd **12** which with $SOCl_2$ yields the 3,3-dichlorothieno[3,4-*b*] quinoline derivative **17** (Scheme 3B) at room temp.[9] It is noteworthy that **17** forms more readily than does **2,** on account perhaps of more tautomeric possibilities being available in carboxylic aãd chloride **13**.

Consideration of the above suggested the following possibilities: (i) were 2-methyl-3-nitrobenzoyl chloride to exhibit the requisite tautomerism(s), its reaction with $SOCl_2$ might result in the novel dichlorothiolactone derivative **19** (Scheme 3C). (ii) Imidoyl chloride **20** bears a close structural and chemical reactivity relationship to aãd chloride **13**, and in reaction with $SOCl_2$ might provide the unusual 3,3-dichloro-1-phenylimino-thieno[3,4-*b*]quinoline derivative **18** (Scheme 3B).

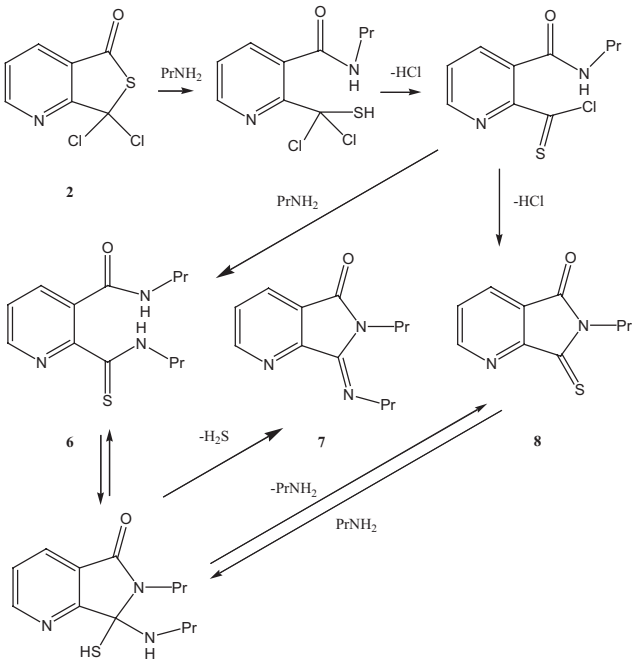


Scheme 1

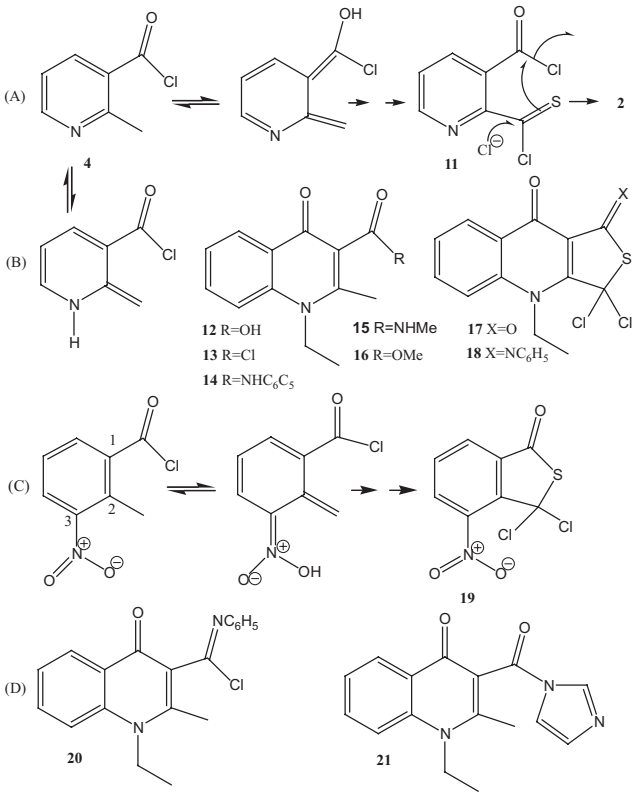
The experimental outcomes were as follows: (i) Refluxing (79°C) a mixture of 2-methyl-3-nitrobenzoic aãd, $SOCl_2$ and pyridine catalyst (the latter to promote[8] enolisation/ tautomerism in the antiãpated aãd chloride) for up to 65 h merely furnished (>90%) 2-methyl-3-nitrobenzoyl chloride, indicative perhaps of the absence of the requisite tautomerism(s) in this particular aãd chloride. (ii) 1-Ethyl-1,4-dihydro-2-methyl-4-oxo-*N*-phenylquinoline-3-carboxamide **14** was selected for *in situ* conversion in $SOCl_2$ to the representative imidoyl chloride **20** and was prepared as follows: Aãd **12** was reacted with 1,1[1]-carbonyldiimidazole[10] in DMF to form acylimidazole **21**. Heating (~120°C) the latter with aniline provided anilide **14** [in comparison to forming the *N*-methyl carboxamide **15** from **21** and (the more basic) methylamine at room temperature].

It was found that acylimidazole **21** itself reacted with $SOCl_2$ to give dichlorothiolactone **17** at room temperature, and trichlorothiolactone **1** at reflux temperature, the outcomes presumably stemming from initial production of aãd chloride **13** followed on by the Wenkert[2] events (Scheme 3). In support, aãd chloride **13** was formed when hydrogen chloride was bubbled into a dioxan solution of acylimidazole **21** at room temperature. A similar explanation accounts also for the production of trichlorothiolactone 1 on refluxing methyl ester **16** with $SOCl_2$.

Contrary to expectations, anilide **14** on heating (79°C) with $SOCl_2$ for 2.5 h furnished 9-chloro-2-phenylpyrrolo[3,4-*b*] quinoline-1,3-dione **22** (53%) as major product. The MS of the **22** contained a minor peak at *m/z* 324 attributable to a proposed thioxo intermediate **23** (Scheme 4). With the knowledge that dichlorothienolactone **17** will form prior to trichlorothienolactone 1,[9] and that the MS of the (the slightly impure) **22** contained a minor peak at *m/z* 324 attributable to a (proposed) thioxo intermediate **23** a tentative sequence of



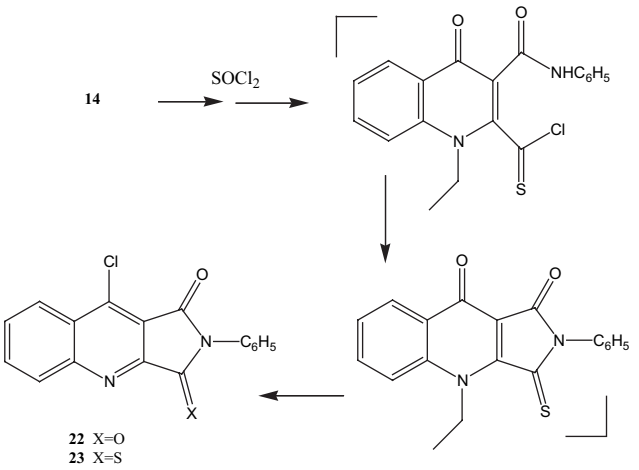
Scheme 2



Scheme 3

events leading to **22** is outlined in Scheme 4, but details of this reaction remain to be clarified.

In summary, the recently developed aminolysis methodology[1] with 2-methylquinoline-3-carboxylic aãds has been extended to a pyridine analogue *viz*., 2-methylpyridine-3-carboxylic aãd to now provide an alternative and convenient access to highly functionalised thieno- and pyrrolo[3,4-*b*] pyridine derivatives suitable for further synthetic procedures and biological testing.



Scheme 4

Experimental

General procedure

Melting points were recorded on a hot-stage microscope apparatus and are uncorrected. TLC was performed on aluminium-backed plates, precoated with 0.25 mm silica gel. Column chromatography was carried out on silica gel. HPLC solvent generally used to elute: hexane: isopropyl alcohol; 450 : 50. ^{1}H NMR spectra were determined in $CDCl_3$ using a Bruker DRX (399.900 MHz specrometer. *J* values are in Hz. High-resolution mass spectra were recorded on a VG 70 SEQ mass spectrometer. Extracts were dried over anhydrous sodium sulfate.

Several of the compounds formed in the propylaminolysis reaction(s) were very similar by TLC while analytical HPLC showed a number of compounds to have similar retention times. Therefore several of the compounds were difficult to separate cleanly by column (silica gel) chromatography. Moreover, several of the products such as thioamide **6** and thioxo derivative **8** reacted further with propylamine (and at different rates). Accordingly, in order to isolate a speãfic product, reaction conditions such as time, temperature and concentration, had to be manipulated to afford the desired compound in satisfactory yield. We have not attempted to optimise yields in every instance.

7,7-Dichloro-5,7-dihydrothieno[3,4-b]pyridin-5-one **2:** A mixture of 2-methylpyridine-3-carboxylic aãd (548 mg, 4.0 mmol) and thionyl chloride (5 ml) was refluxed (79°C) for various periods up to 24 h with TLC monitoring. The reaction mixture from 6.5 h estimated as containing an optimum yield of **2** was evaporated and the residue kept in a a vacuum dessicator (over solid KOH) to ensure the removal of all the $SOCl_2$. The crude material (~750 mg) was applied to a silica gel column using 15% acetone/benzene to obtain title compound **2** (412 mg, 1.87 mmol, 47%). Crystals (from EtOAc/hexane), m.p. 154–155°C. δ_H 7.60 (1H, m), 8.15 (1H, m), 9.06 (1H, m). Found: C,37.99; H, 1.50; N,6.17. $C_7H_3Cl_2NOS$ requires C, 38.20; H, 1.37; N, 6.36%. Also isolated from the column was 80 mg of thiolactone **10** (*vide infra*).

2-Methylpyridine-3-carbonyl chloride **4:** Keeping a mixture of 2-methylpyridine-3-carboxylic aãd (140 mg, 1.02 mmol) and $SOCl_2$ (5 ml) at 0°C, at room temperature up to 24 h, or even at 60°C for 5 h, followed by evaporation, gave in each instance, a residue of the known[4] title compound **4** as evidenced by treatment with methanol to form the methyl ester, identical (TLC) with authentic (commerãal) ester. Refluxing (79°C) **4** with $SOCl_2$ for an extended time provided dichlorothiolactone **2** (*vide supra*).

N-Propyl-2-[(propylamino)thioxomethyl]pyridine-3-carboxamide **6:** The reaction of **2** in neat propylamine is comparatively fast and results in mixtures of **6, 7** and **8** and, eventually in end-product, **7** (*vide infra*). To prepare title compound **6** the reaction rate was reduced by conducting the propylaminolysis in 10% w/w propylamine in dioxan, at 0°C: 1.20 g $PrNH_2$/dioxan solution (120 mg $PrNH_2$, 2.0 mmol) cooled in ice was slowly added with stirring to dichlorothiolactone **2** (100 mg, 0.45 mmol). The reaction progress was monitored by TLC (solvent), and after 20 min (when the yield of **6** was estimated as optimum) the reaction was extracted with $CHCl_3/H_2O$. Evaporation of the $CHCl_3$ under reduced pressure and temperature gave crude title compound **6** (120 mg.) which was stirred with hexane at room temperature. The comparatively pure title product was filtered off (80 mg, 67%) and crystallised from EtOAc/hexane; m.p. 69–70°C. δ_H 0.94 (3H, t *J* = 7.4), 1.05 (3H, t, *J* = 7.4), 1.65 (2H, m), 1.76 (2H, m), 3.35 (2H, m), 3.75 (2H,m), 7.53 (1H,m), 8.0–8.2 (~3H, m), 8.6 (1H, m). Found: C,58.43; H,7.12; N, 15.42; *m/z* 265 (M^+, 20%), 206 [M-59, 100%), corresponding (to loss of propylamine) to thioxo derivative **8**]. $C_{13}H_{19}N_3OS$ requires C, 58.84; H, 7.22; N, 15.84%; M, 265. Aãd-sensative **6** underwent cyclisation to thiolactone **8** in the course of chromatography on (aãdic) silica gel (*vide infra*).

6-Propyl-5,7-dihydro-7-(propylimino)pyrrolo[3,4-b]pyridin-5-one **7:** Dichloro compound **2** (313 mg, 1.42 mmol) was slowly added (over ~ 10 min) with stirring to neat propylamine (5 ml) cooled in ice. The solution was kept at room temperature overnight and treated with $CHCl_3/H_2O$. Evaporation of the $CHCl_3$ extract gave (crude) title compound **7** (320 mg), which were washed with hexane (cooled to –80°C) to provide crystals (100 mg) of **7**, m.p. 43–44°C; concentration of the mother liquor and chilling to ~80°C afforded a further 125 mg of product **7** (total yield, 225 mg, 69%). δ_H 0.94 (3H,t, *J* = 7.5), 1.01 (3H, t, *J* = 7.4), 1.71 (2H, m), 1.78 (2H, m), 3.81 (2H,t, *J* = 7.3), 4.43 (2H, t, *J* = 7.0), 7.46 (1H, m, 3-H), 8.14 (1H, m, 2-H), 8.85 (1H,m, 4-H). Found: C, 67.33; H, 7.35; N, 17.81; *m/z* 231, M^+, 100%; 216, M-15, 35%; 202, M-29, 40%, 174, M-57, 50%. $C_{13}H_{17}N_3O$ requires C, 67.51; H, 7.41; N, 18.17%; M, 231.

6-Propyl-5,7-dihydro-7-thioxopyrrolo[3,4-b]pyridin-5-one **8:** (a) A mixture of amide **6** (43 mg, 0.16 mmol) and 2 ml glaãal HOAc was warmed at 50°C for 30 min. The solution was diluted with ice-H_2O and the red (crude **8**) solid which had separated (30 mg, 90%) was collected by filtration and crystallised from EtOAc (m.p.103–104°C). δ_H 0.99 (3H, t, *J* = 7.4), 1.79 (2H, sextet), 4.09 (2H, t, *J* = 7.4), 7.62 (1H, m, 3-H), 8.13 (1H, m, 2-H), 8.96 (1H, m, 4-H). Found: C, 57.86; H,4.76; N, 13.21%; *m/z,* 206(M^+, 100%), 191 (M-15, 20%),178 (M-28, 35%). $C_{10}H_{10}N_2OS$ requires C,58.23; H, 4.89; N, 13.58%; M, 206.

(b) Dichlorolactone **2** (550 mg, 2.49 mmol) was added over 5 min in portions to ice-cold stirred propylamine (5 ml) and the reaction continued for a further 15 min. following addition of $CHCl_3/H_2O$, the $CHCl_3$ extract was dried and evaporated to a residue (690 mg) which was applied to a column (silica gel, 15% acetone in benzene) to give imine **7** (94 mg, 16%), crystals from hexane, m.p. 43–44°C) and title compound **8** (244 mg, 48%), crystals from EtOAc/hexane, m.p. 103–104°C). Also eluted (74 mg, 11%) was amide **6**.

Preparation of 6-Propyl-5,7-dihydropyrrolo[3,4-b]pyridine-5,7-dione **9:** A solution of propylimino compound **7** (156 mg, 0.68 mmol) in (1 : 1) glaãal HOAc/H_2O (3 ml) was kept overnight at room temperature after which the reaction was allowed to evaporate. The residue was treated with H_2O and the crude title product **9** was collected by filtration (110 mg, 85%). Crystals from EtOAc/hexane, m.p. 100–101°C. δ_H 0.96 (3H, t, *J* = 7.4), 1.73 (2H, sextet, *J* = 7.4), 3.72 (2H, t, *J* = 7.4), 7.61 (1H, m, 3-H), 8.16 (1H, m, 2-H), 8.96 (1H, m, 4-H). Found: C, 62.90; H, 5.34; N, 14.45; *m/z* 190 (M^+, 60%, 161 (M-29, 100%). $C_{10}H_{10}N_2O_2$ requires C, 63.15; H, 5.30; N, 14.73%; M, 190.

Thieno*[3,4-b]pyridine-5,7-dione* **10:** The mother liquor of crystallised **2** (*vide supra*) was evaporated and the residue applied to a silica gel column (15% acetone in benzene). Appropriate fractions were combined and evaporated to obtain **10**. Crystals (from EtOAc/hexane); m.p. 84–86°C (lit[7]. m.p. 91°C). Found: *m/z* 165, (M^+, 100%, 105, 90%, 77, 90%). $C_7H_3NO_2S$ requires M, 165.

Effect of $SOCl_2$ on 2-Methyl-3-nitrobenzoic aãd: A mixture of the (commerãal) aãd (0.50 g, 2.76 mmol), $SOCl_2$ (5 ml) and pyridine catalyst (several drops) was refluxed for ~65 h [with TLC (benzene) monitoring]. Exhaustive evaporation of solvent (*under vacuo*) yielded a residue (450 mg, TLC benzene; one spot) of (crude) 2-methyl-3-nitro-benzoyl chloride, m.p. 59–60°C. Lassaigne sodium fusion: positive for Cl, negative for S. Treatment of the product with H_2O in dioxan gave crystals of (crude) title aãd, m.p. 179–181°C., mixture m.p. with substrate aãd unchanged). Warming the aãd chloride product with methanol formed the methyl ester; crystals (from EtOAc/hexane), m.p. 64°C. In each instance the product m.p. corresponded to the literature value.

1-Ethyl-1,4-dihydro-2-methyl-4-oxoquinolin-3-oyl-N-imidazole: **21:** A stirred mixture of aãd **12**[11] (909 mg, 3.94 mmol), 1,1[1]-carbonyldiimidazole[10] (910 mg, 5.48 mmol) and DMF (5 ml) was heated at 100°C for 2 h and afterwards chilled in ice. The preãpitate was collected, washed with EtOAc and then with Et_2O, and dried in vacuo to provide crude acylimidazole derivative **21** (960 mg, 87%). Crystals (from $CHCl_3$/EtOAc), mp 236°C**.** δ_H 1.60 (3H, t, *J* = 7.2), 2.68 (3H, s), 4.43 (2H, q, *J* = 7.2), 7.38 (1H, m), 7.54 (1H, m), 7.65 (1H, m), 7.78 (1H, m), 7.83 (1H, m), 8.39 (1H, m), 8.84 (1H, m).

Found: C, 68.84; H, 5.42; N, 14.86. $C_{16}H_{15}N_3O_2$ requires: C, 68.31; H, 5.37**;** N, 14.94.

1-Ethyl-1,4-dihydro-2,N-dimethyl-4-oxoquinoline-3-carboxamide **15:** A mixture of acylimidazole **21** (500 mg, 1.78 mmol) and methylamine gas (1.0 g, ~ 30 mmol) dissolved in DMF (6 ml) was stirred at room temperature for 3 h. The resulting reaction was chilled in ice, and the solid was collected and washed with EtOAc to give the crude title amide **15** (390 mg, 90%). Crystals (from EtOAc), m.p. 220°C. Found: C, 68.69; H, 6.57; N, 11.37. $C_{14}H_{16}N_2O_2$ requires: C, 68.79; H, 6.60; N, 11.47%.

1-Ethyl-1,4-dihydro-2-methyl-4-oxo-N-phenylquinoline-3-carboxamide **14:** A mixture of acylimidazole **21** (319 mg, 1.14 mmol), aniline (197 mg, 2.1 mmol) and pyridine catalyst (1.5 ml) was heated (~120°C) for 24 h. The reaction was evaporated under reduced pressure and the residue (190 mg, 54%) of crude title amide **14** was crystallised from methanol; m.p. 214–215°C. Found: C,74.27; H, 6.00; N, 9.14. $C_{19}H_{18}N_2O_2$ requires C, 74.49; H, 5.92; N, 9.14%.

3,3-Dichloro-4-ethylthieno[3,4-b]quinoline-1,9-dione ***17*** *from $SOCl_2$ acting on acylimidazole* **21:** A mixture of **21** (325 mg, 1.16 mmol) and $SOCl_2$ (5 ml) was stirred at room temperature with TLC monitoring which revealed a slow transformation of **21** to dichlorothiolactone **17** accompanied by increasing darkening of the reaction. After 4 days the solution was evaporated and the residue was washed with aqueous $NaHCO_3$, and extracted into $CHCl_3$. Evaporation gave a dark, tarry solid (230 mg) which was chromatographed (silica gel, 20% EtOAc/$CHCl_3$) to obtain **17** (150 mg, 48%), m.p. 187–189°C, identified by comparison (mixture m.p., TLC and HPLC) with authentic[9] compound **17**.

3,3,9-Trichlorothieno[3,4-b]quinolin-1-one ***1*** *from $SOCl_2$ acting on acylimidazole* ***21*** *and on methyl ester* **16:** A mixture of **21** (330 mg, 1.17 mmol) and $SOCl_2$ (5 ml) was refluxed for 1.5 h. Evaporation gave a residue which was extracted into $CHCl_3$. Removal of solvent gave a dark gummy material which was extracted with boiling EtOAc to give crystals of title compound **1** (200 mg, 56%), m.p. 200–202°C (from dioxan), identified by mixture m.p., TLC and HPLC comparison with authentic[9] **1:** Refluxing a mixture of methyl ester **16** (150 mg, 0.61 mmol) and $SOCl_2$ (5 ml) for 1.5 h also provided thiolactone **1** (30 mg, 16%), m.p. 198–201°C, likewise identified

Action of hydrogen chloride on acylimidazole **21:** Acylimidazole **21** (51 mg, 0.18 mmol) was added with stirring to a dioxan solution [10 ml, containing ~10% (by weight) hydrogen chloride gas]. Monitoring of the reaction (at room temperature) by TLC (30% acetone and 5% Et_3N in benzene) showed little remaining substrate **21** after ~10 min. The sticky product which had separated was filtered (45 mg) and treated with aqueous $NaHCO_3$ to provide aãd **12** (25 mg, 60%) and some unchanged acylimidazole **21**.

9-Chloro-2-phenylpyrrolo[3,4-b]quinoline-1,3-dione **22:** A mixture of *N*-phenylquinoline-3-carboxamide **14** (116 mg, 0.38 mmol) and $SOCl_2$ (5 ml) was refluxed for 2.5 h. Evaporation gave a residue which was chromatographed (silica gel, 10% acetone in $CHCl_3$) to give (62 mg, 53%) product **22** containing minor impurities. Crystals (from EtOAc), m.p.242–244°C. δ_H 7.45–7.60 (5H, m), 7.91 (1H, m), 8.03 (1H, m), 8.48 (1H, m), 8.55 (1H, m). Found: *m/z* 308 (100%, Cl isotopic ratio, ~3 : 1), 324 (~5%,Cl isotopic ratio: *ca* 3 : 1). M, 308.03587. $C_{17}H_9ClN_2O_2$ requires: M, 308.03525.

X-ray crystallographic analysis for **2**

Intensity data were collected on a Bruker SMART IK CCD area detector diffractometer with graphite monochromatated Mo Kα radiation (50kV, 30 mA). The collection method involved ω-scans of width 0.3°. Data reduction was carried out using the program *SAINT* + (Bruker, 1999).[12] The crystal structure was solved by direct methods using *SHELXTL* (Bruker, 1999).[13] Diagrams and publication material were generated using *SHELXTL* and *PLATON* +(Spek, 2003).[14]

Crystal data for **2**.

EF $C_7H_3Cl_2NOS$, FW 220.06, crystal system: orthorhombic, space group: Pnma, unit cell dimensions: a = 11.407(2)Å, b = 6.861(5)Å, c = 10.382(2)Å, volume: 812.5(6)Å^3, Z = 4, D_{calc} = 1.799 Mg m^{-3}, μ = 0.996 mm^{-1}, T = 293(2)K, F(000) = 440, crystal size = 0.40 × 0.27 × 0.22 mm, unique reflections 1062[R(int) = 0.0226]. The final refinement converged to R_1 = 0.0298 and wR_2 = 0.0726 for observed data and R_1 = 0.0341, wr_2 = 0.756 for all data with residuals (max. peak/hole) of 0.486 and –0.348 eÅ^{-3}. Full crystallographic details for structure **2** have been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 640183). Any request to the CCDC for this material should quote the full literature ãtation.

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