Synthesis of some new imidazo[3",4":1',2'] pyrimido[4',5':4,5]thieno[2,3-*c*] pyridazines and other fused thieno[2,3-*c*]pyridazines

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5-Amino-3,4-diphenylthieno[2,3-*c*]pyridazine-6-carboxamide was prepared and used as starting material to form the novel 6-chloromethyl-3,4-diphenylpyrimido[4',5':4,5]thieno[2,3-*c*]pyridazin-8(7*H*)-one (**3**), the 6-(arylaminomethyl) compounds (**4a–c**), 7-aryl-7,8-dihydro-3,4-diphenylimidazo[3",4":1',2']pyrimido[4',5':4,5]thieno[2,3-*c*]pyridazin-10(6*H*)-ones (**5a–c**), ethyl 7,8-dihydro-8-oxopyrimido[4',5':4,5]thieno[2,3-*c*]pyridazine-6-acetate (**6**) and its carbohydrazide (**7**). The pyridazinothienopyrimidotriazepinedione **8**, pyridothienopyridazine **12** and pyridazinothienooxazepine **13** were also prepared.

Keywords: fused pyridazines, pyridines, pyrimidines, thiophenes, 1,2,4-triazepines, 1,4-oxazepines

Thienopyridazine derivatives have a broad range of biological and pharmacological effects. Thieno[2,3-*d*]pyridazine derivatives, for example, have been evaluated pharmacologically and used as potent and selective phosphodiesterase IV inhibitors,[1,2] with immunosuppressant,[3] antiarrhythmic,[4] antibiotic,[5] antiasthmatic,[6] anti-inflammatory,[7] antispasmodic,[8] antitumor,[9] potentiated pentobarbital sleep,[10] antipsychotic, anxiolytic[11] and anticonvulsant[12] activities. In continuation of our work in the chemistry of pyridazine derivatives,[13,14] herein we report the synthesis of fused heterocyclic systems including the thieno[2,3-*c*]pyridazine moiety, in the hope of discovering some with biological activity.

Many research groups have described the synthesis of imidazo[1,2-*c*]pyrimidines[15-17] and imidazo[1,2-*a*] pyrimidines,[18,19] but descriptions of the synthesis of imidazo [1,5-*a*]pyrimidines are very rare.[20] In this paper we describe a facile preparation of heterocycles containing the fused imidazo[1,5-*a*]pyrimidine system.

Results and discussion

Previous chloroacylations of amino groups were carried out either in an inert solvent such as toluene in the presence of basic catalyst[21-24] or in a basic solvent like pyridine. Here we carried out chloroacylation of the aminothieno[2,3-*c*] pyridazinecarboxamide (**1**)[25] using chloroacetyl chloride in anhydrous dioxan[26] to afford 3,4-diphenyl-5-chloroacetylaminothieno[2,3-*c*]pyridazine-5-carboxamide (**2**), while when the reaction was carried out without solvent, 6-(chloromethyl)-3,4-diphenylpyrimido[4',5':4,5] thieno[2,3-*c*]pyridazin-8-one (**3**) was produced. Compound **3** also was obtained by cyclodehydration of compound **2** using acetic anhydride. Nucleophilic displacement of the chlorine atom in compound **3** by substituted amino groups was accomplished by reaction with aromatic amines and aliphatic secondary amines in ethanol to give aryl- and alkyl-aminomethylpyrimidothienopyridazines (**4**). In the IR spectra of **4**, significant stretching bands due to N–H when present, amide C=O, C=N and C=C were observed at 3450–3400, 1660–1650, and 1583–1535 cm^{-1}, respectively. In the ^1H NMR spectra, the signal due to N-CH_2 protons, present in all compounds **4**, appeared at 3.7–4.45 ppm as singlets. The NHCO proton was observed at 9.6–10.9 ppm as a broad singlet. All other aromatic and aliphatic protons were observed in the expected regions. Compounds **4** also were obtained when 3,4-diphenyl-5-(chloroacetylamino)thieno[2,3-*c*]pyridazine-5-carboxamide (**2**) was heated with the appropriate amines. The ^{13}C NMR spectra of compounds **4** showed a signal at *ca* δ 50 for the CH_2 group.

Many research groups have reported the using of Mannich reaction to prepare heterocyclic compounds, for the most part using Mannich conditions catalysed in acid medium,[27] basic medium[28] or in the presence of a catalyst.[29] We applied the Mannich reaction without catalyst to the arylaminomethylpyrimidopyridazines **4a–c** with formaldehyde in ethanol to produce the imidazopyrimidothienopyridazine derivatives (**5a–c**). Formation of imidazole ring could be rationalised as attack of formaldehyde to hydroxymethylate the ArNH group followed by elimination of a water molecule to form compounds **5**. When the same reaction conditions were applied to compounds **4d,e** which have only one cyclic NH group, no reaction occurred and the starting material was recovered. The ^1H NMR spectra of compounds **5a–c** revealed the absence of signals corresponding to NH groups and showed singlet signals at 4.1–4.4 and at 5.1–5.3 corresponding to two CH_2 groups. The ^{13}C NMR showed signals at 50.0 and 62.5 for the two CH_2 groups. The mass spectrum of compound **5a** showed a molecular ion peak at *m/z* 473 and fragments at 93 for aniline and at 121 for *N,N*-dimethylaniline.

When the aminothienopyridazinecarboxamide **1**[25] was heated to reflux with diethyl malonate, the ethyl pyrimidothienopyridazinylacetate **6** was obtained, which gave the corresponding carbohydrazide **7** with hydrazine hydrate (Scheme 1). This hydrazide was cyclised using triethyl orthoformate to give the fused triazepinone **8**.

Ethyl 5-amino-3,4-diphenylthieno[2,3-*c*]pyridazine-6-carboxylate (**9**)[25] was saponified using ethanolic potassium hydroxide to afford corresponding sodium salt **10**. Hardil *et al.*[30] have reported that the reaction of sodium anthranilate with phenacyl bromide gives the corresponding phenacyl ester. When potassium 5-amino-3,4-diphenylthieno[2,3-c] pyridazine-6-carboxylate (**10**) was treated with phenacyl bromide in DMF in the presence of K_2CO_3 at 60–70 °C it afforded the ester **11**, which upon warming with polyphosphoric acid was cyclised accompanied with rearrangement to give the pyridothienopyridazine **12** (Scheme 2). When compound **10** was allowed to react with α-halogenated nitrile like chloroacetonitrile, the reaction took a different course, affording the oxazepine **13**. We expect that it formed the corresponding cyanoacetate ester, followed by spontaneous cyclisation.

The pathway of the formation of compound **12** we imagine beginning with normal condensation of carbonyl group with amino group, followed by tautomerisation of the imine group and rearrangement by acid-catalysed intramolecular attack of the enamine at the carbonyl oxygen with cleavage of the ester oxygen–carbon bond and migration of a proton (Scheme 3).

Experimental

All melting points were measured on a Fisher–Johns apparatus. Elemental analyses were determined on a Vario GmbH EL V.3

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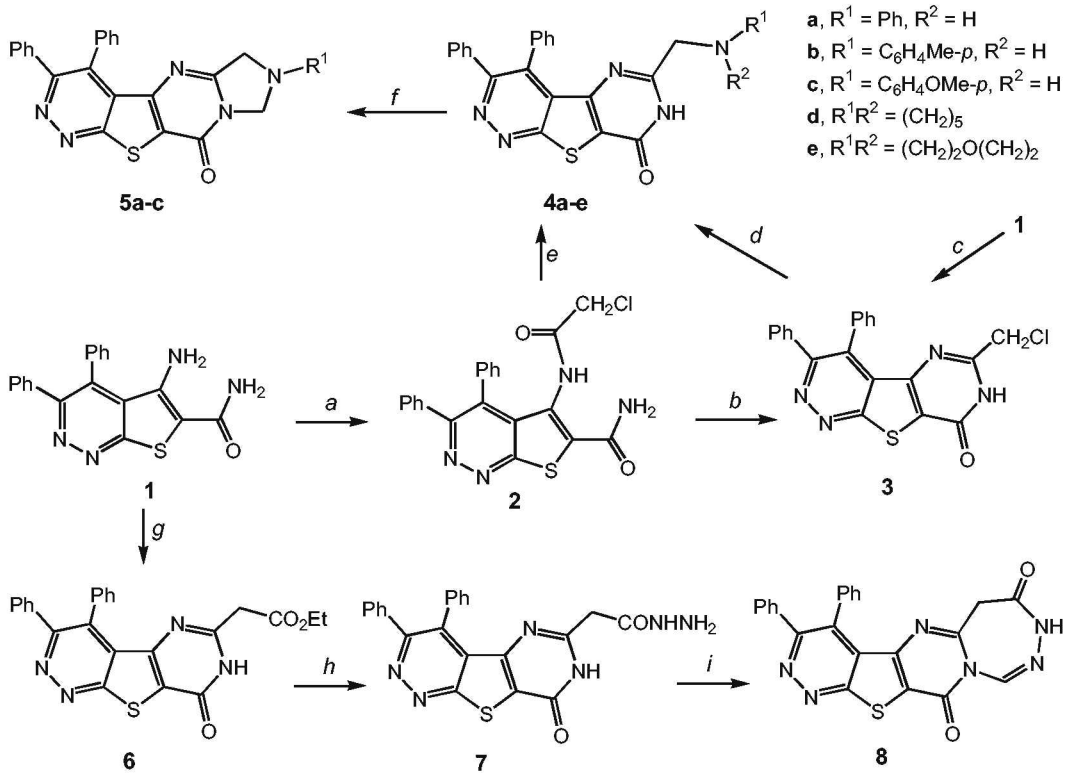
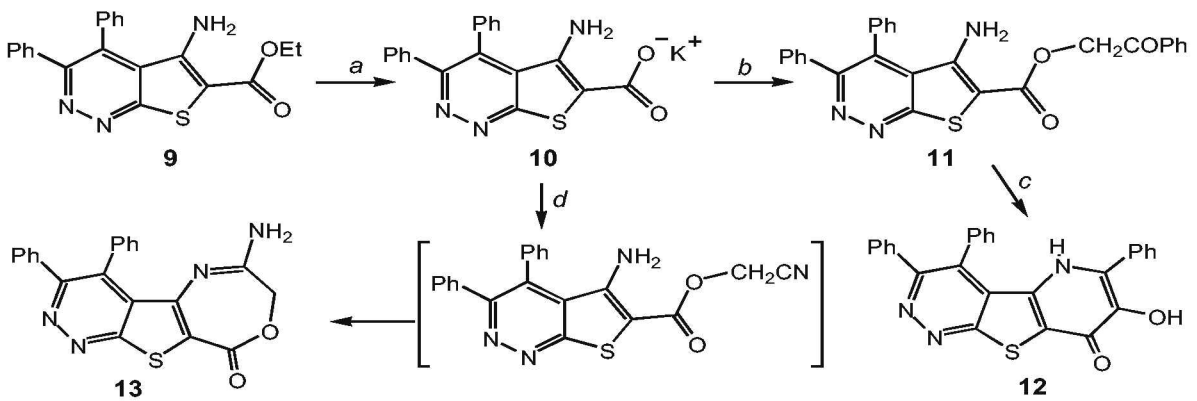


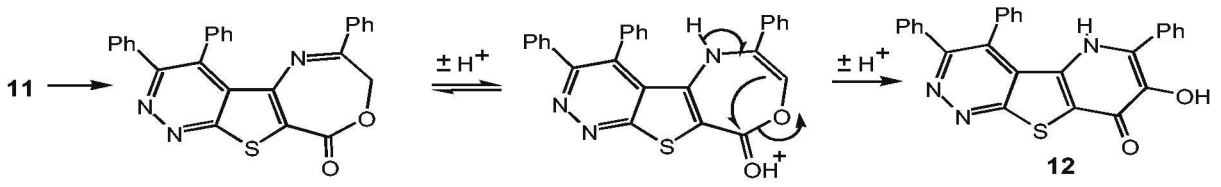
Reagents: *a*, $ClCH_2COCl$/dioxan; *b*, Ac_2O; *c*, $ClCH_2COCl$ (neat); *d*, R^1NHR^2/EtOH; *e*, R^1NHR^2(neat); *f*, CH_2O/EtOH; *g:* $CH_2(CO_2Et)_2$; *h:* $N_2H_4.H_2O$; *i:* $CH(OEt)_3$

Scheme 1



Reagents: a: KOH/EtOH; *b:* $PhCOCH_2Br$/DMF/K_2CO_3;*c:* PPA;*d:* $ClCH_2CN$/DMF

Scheme 2



Scheme 3

microanalyser in the central lab of Assiut University. Chlorine analyses were performed using a standard method through combustion followed by titration with mercury nitrate in presence of diphenylcarbazole as indicator. IR spectra were recorded on a Pye-Unicam Sp-100 spectrophotometer using the KBr wafer technique. NMR spectra were recorded on Varian EM-390 90 MHz and Jeol 400 MHz spectrometers in a suitable deuterated solvent using TMS as internal standard (chemical shifts in ppm). Mass spectra were recorded on a JEOL JMS-600 apparatus.

5-Amino-3,4-diphenylthieno[2,3-*c*]pyridazine-6-carboxamide (**1**) and ethyl 5-amino-3,4-diphenylthieno[2,3-*c*]pyridazine-6-carboxylate (**9**) were prepared from 4-cyano-5,6-diphenyl-pyridazin-3(2*H*)-thione using chloroacetamide and ethyl chloroacetate respectively, according to the literature method.[25]

5-(Chloroacetylamino)-3,4-diphenylthieno[2,3-c]pyridazine-5-carboxamide (**2**)

A mixture of thieno[2,3-*c*]pyridazine **1** (1 g) and chloroacetyl chloride (1 ml) in dioxan (10 ml) was heated on a steam bath for 3 hours. Upon cooling, the mixture was diluted with water and the product obtained was filtered off and recrystallised (ethanol) to give **3** (0.98 g, 80%), m.p.176–178 °C. IR: ν_{max} 3450, 3300 (NH), 1630, 1620 cm^{-1} (2 C=O). NMR ($CDCl_3$): δ_H 3.7 (s, 2H, CH_2), 4.5 (s, 2H, NH_2), 4.8 (s, 1H, NH) and 7.3–7.9 (m, 10H, ArH). Anal. Calcd for $C_{21}H_{15}ClN_4O_2S$ (422.89): C; 59.64; H; 3.58; Cl, 8.38; N, 13.25; S, 7.58. Found: C, 59.42; H, 3.52; N, 13.11; S, 7.66; Cl, 8.12%.

6-Chloromethyl-3,4-diphenylpyrimido[4',5':4,5]thieno[2,3-c]pyridazin-8-one (**3**)

Method a: A mixture of thieno[2,3-*c*]pyridazine **1** (1 g) and chloroacetyl chloride (5 ml) was heated on a steam bath for 3 hours, then allowed to cool. The mixture was cautiously diluted with water and neutralised with sodium carbonate. The product so obtained was filtered off and recrystallised from acetic acid to afford **3** (73%), m.p.> 300 °C.

Method b: The carboxamide **2** (1 g) was heated under reflux in acetic anhydride (10 ml) for 4 h. After cooling, the mixture was diluted with water. The solid product was filtered off and recrystallised from acetic acid to afford **3** (0.54 g, 56%). IR: ν_{max} 3100 (NH); and 1650 cm^{-1} (C=O). ^{1}H NMR (CF_3CO_2D): δ_H 3.8 (s, 2H, CH_2Cl) and 7.3–7.6 (m, 10 H, ArH). Anal. Calcd for $C_{21}H_{13}ClN_4OS$ (404.87): C, 62.30; H, 3.24; Cl, 8.76; N, 13.84; S, 7.92%. Found: C, 62.05; H, 3.12; Cl, 8.63; N, 13.67; S, 7.88%.

6-(Substituted-aminomethyl)-3,4-diphenylpyrimido[4',5':4,5]thieno[2,3-c]pyridazin-8-ones (**4a–e**), *general procedure*

The chloromethyl compound **3** (0.4 g, 1 mmol) or chloroacetylamino-amide **2** (0.42 g, 1 mmol) was heated under reflux for 2 h with an excess of the appropriate amine (11 mmol). Ethanol (20 ml) was then added and the mixture was refluxed for an additional 1 h. After cooling, the solid product obtained was filtered off and recrystallised to afford the amines **4a–e**.

6-(Anilinomethyl)-3,4-diphenylpyrimido[4',5':4,5]thieno[2,3-c]pyridazin-8-one (**4a**): Using aniline (1 ml), compound **3** (0.4 g, 0.001 mol) gave **4a**, yellowish crystals (0.37 g, 81%), m.p. 156–158 °C, from dioxan. IR: ν_{max} 3400 (NH), 1650 cm^{-1} (C=O). NMR (CF_3CO_2D): δ_H 4.1 (s, 2 H, CH_2) and 6.7–7.7 (m, 15 H, ArH). Anal. Calcdfor.$C_{27}H_{19}N_5OS$ (461.54): C, 70.26; H, 4.15; N, 15.17; S, 6.95. Found: C, 69.98; H, 4.08, N, 15.06; S, 6.88%.

3,4-Diphenyl-6-(p-toluidinomethyl)pyrimido[4',5':4,5]thieno[2,3-c]pyridazin-8-one (**4b**): Compound **3** (0.4 g, 1 mmol) and *p*-toluidine (1.07 g) afforded **4b** (0.34 g, 72%), m.p. 196 °C (from dioxan). IR: ν_{max} 3400 (NH), 1650 cm^{-1} (C=O). NMR (DMSO-d_6): δ_H 2.1 (s, 3H, CH_3), 4.3 (s, 2 H, CH_2), 6.6–7.8 (m, 14 H, ArH), 9.9 and 10.5 (2 s, 2H, 2 NH). Anal. Calcd for $C_{28}H_{21}N_5OS$ (475.57): C, 70.72; H, 4.45; N, 14.73; S, 6.74. Found: C, 70.98; H, 4.08; N, 15.06; S, 6.88%.

6-(p-Anisidinomethyl)-3,4-diphenylpyrimido[4',5':4,5]thieno[2,3-c]pyridazin-8-one (**4c**): *p*-Anisidine (1.23 gm, 0.01 mol) and compound **3** (0.4 g, 1 mmol) gave the product **4c** as white crystals (0.34 g, 69%) m.p. 226–228 °C (from dioxan). IR: ν_{max} 3400 (NH), 1650 cm^{-1} (C=O). NMR (DMSO-d_6): δ_H 2.1 (s, 3H, CH_3), 4.3 (s, 2 H, CH_2), 6.6–7.8 (m, 14 H, ArH), 9.9 and 10.5 (2 s, 2H, 2 NH). Anal. Calcd for $C_{28}H_{21}N_5O_2S$ (491.57): C, 69.42; H, 4.31; N, 14.25; S, 6.52. Found: C, 69.26; H, 4.08 N, 14.06; S, 6.38%.

3,4-Diphenyl-6-(piperidinomethyl)pyrimido[4',5':4,5]thieno[2,3-c]pyridazin-8-one (**4d**): Following the general procedure, **3** (0.5 g) and piperidine (3 ml) afforded **4d**, which recrystallised from ethanol as yellowish-white crystals (0.41 g, 73%), m.p. 152–154 °C. IR: ν_{max} 3450 (NH), 1660 cm^{-1} (C=O). NMR (CF_3CO_2D): δ_H 2.2–2.4 (m, 6H, piperidine); 2.7–2.9 (m, 2H, piperidine); 3.2–3.4 (m, 2H, piperidine), 3.7 (s, 2H, CH_2), 7.1–7.7 (m, 10H, ArH). Anal. Calcd for $C_{26}H_{23}N_5OS$ (453.56):C, 68.85; H,5.11; N, 15.44; S, 7.07. Found: C, 68.55; H, 4.99; N, 15.11; S, 6.95%.

6-(Morpholinomethyl)-3,4-diphenylpyrimido[4',5':4,5]thieno[2,3-c]pyridazin-8-one (**4e**): From **3** and morpholine, the product **4e** (73%), m.p. 320 °C, crystallised from ethanol, was obtained. IR: ν_{max} 3450 (NH), 1660 cm^{-1} (C=O). NMR (DMSO-d_6): δ_H 2.75–2.85 (m, 4H, 2 CH_2, morpholine); 3.5–3.65 (m, 4H, 2 CH_2, morpholine); 3.8 (s, 2H, CH_2), 7.1–7.8 (m, 10H, ArH), 9.9 (s, 1H, NH). Anal. Calcd for $C_{25}H_{21}N_5O_2S$ (455.53): C, 65.92; H, 4.65; N, 15.37; S, 7.04. Found: C, 65.75; H, 4.87; N, 15.51; S, 7.15%.

7,8-Dihydro-3,4,7-triphenylimidazo[3"4":1',2']pyrimido[4',5':4,5]thieno-[2,3-c]pyridazin-9(6H)-one (**5a**): *typical procedure*

Formalin (5 ml, 30%) was added with stirring to a suspension of compound **4a** (0.46 g, 1 mmol) in ethanol (15 ml). Stirring was continued for 3 hours and the product thus obtained was filtered off and recrystallised from ethanol to give **5a** as white crystals (0.31 g, 65%), m.p. 256–258 °C. IR: ν_{max} 1680 cm^{-1} (C=O). NMR (DMSO-d_6): δ_H 4.4 (s, 2H, CH_2); 5.3 (s, 2H, CH_2) and 6.7–7.8 (m, 15 H, ArH); δ_C 50.0, 60.5 (2CH_2), 158 (carbonyl carbon), 116–160 (aromatic carbons). M.S: *m/z* 473 (M^+, 20%). Anal. Calcd for.$C_{28}H_{19}N_5OS$ (473.55): C, 71.02; H, 4.04; N, 14.79; S, 6.77. Found: C, 70.88; H, 3.89; N, 14.67; S, 6.69%.

7,8-Dihydro-3,4-diphenyl-7-p-tolylimidazo[3",4":1',2']pyrimido[4',5':4,5]thieno[2,3-c]pyridazin-9(6H)-one (**5b**): product (0.28 g, 58%), m.p. 296–298 °C, obtained from 4b following the procedure described for **5a**. NMR (DMSO-d_6): δ_H 2.3 (s, 3H, CH_3), 4.1, 5.2 (2 s, H, 2CH_2), and 6.6–7.8 (m, 14H ArH). Anal. Calcd for $C_{29}H_{21}N_5OS$ (487.58): C, 71.44; H, 4.34; N, 14.36; S, 6.58. Found: C, 71.28; H, 4.19; N, 14.51; S, 6.49%.

7,8,-Dihydro-7-(p-methoxyphenyl)-3,4-diphenylimidazo[3",4":1',2']pyrimido[4',5':4,5]thieno[2,3-c]pyridazin-9-one (**5c**): Product (0.32 g, 63%), m.p. >300 °C, obtained from **4e** following the procedure described for **5a**. NMR (DMSO-d_6): δ_H 3.7 (s, 3H, OCH_3), 4.1, 5.1 (2 s, H, 2CH_2), and 6.6–7.8 (m, 14H, ArH). Anal. Calcd for $C_{29}H_{21}N_5O_2S$ (503.58): C, 69.17; H, 4.20; N, 13.91; S, 6.37. Found: C, 69.08; H, 3.99; N, 13.77; S, 6.49%.

Ethyl 2-(7,8-dihydro-8-oxo-3,4-diphenylpyrimido[4',5':4,5]thieno[2,3-c]pyridazin-6-yl)-acetate (**6**)

5-Amino-3,4-diphenylthieno[2,3-*c*]pyridazine-6-carboxamide (**1**) (1.73 gm. 5 mmol) in an excess of diethyl malonate (1.6 ml, 0.01 mol) was gently refluxed for 2 hours. Ethanol (15 ml) was then added and the reflux was continued for additional 1 h. The product obtained on cooling was filtered off and recrystallised from dioxan to give **6** (1.53 g, 67%), m.p. 271–273 °C. IR: ν_{max} 3450 (NH), 1720 (C=O, ester) and 1660 cm^{-1} (C=O, pyrimidine). NMR (DMSO-d_6): δ_H 1.1–1.3 (t, 3H, CH_3), 3.5 (s, 2H, CH_2), 4.1–4.3 (q, 2H, OCH_2), 6.8–7.6 (m, 10H, ArH) and 7.8 (s, 1H, NH). Anal. Calcd for $C_{24}H_{18}N_4O_3S$ (442.25): C, 65.12; H, 4.1; N, 12.66; S, 7.24. Found: C, 64.89; H, 3.98; N, 12.45; S, 7.12%.

2-(7,8-Dihydro-8-oxo-3,4-diphenylpyrimido[4',5'; 4,5]thieno[2,3-c]pyridazin-6-yl)acetohydrazide (**7**)

The ester **6** (2.2 g, 5 mmol) and hydrazine hydrate (0.5 ml, 0.01 mol) were heated to reflux for 2 h in ethanol (10 ml). The product that separated on cooling was filtered off and recrystallised from dioxan to give **7** (1.2 gm, 56%), m.p. 273–275 °C. IR: ν_{max} 3450, 3300 (NH), 1690, 1620 cm^{-1} (2C=O). NMR (CF_3CO_2D): δ_H 4.1 (s, 2H, CH_2) and 7.1–7.7 (m, 10H, ArH). Anal. Calcd for: $C_{22}H_{16}N_6O_2S$ (428.24): C, 61.65; H, 3.76; N, 19.62; S, 7.48%. Found: C, 61.45; H, 3.66; N, 19.45; S.7.23%.

3,4-Diphenylpyridazino[3",4":4,5']thieno[2',3':5,4]pyrimido[1,2-d][1,2,4]triazepin-7(8H),12(6H)-dione (**8**)

The carbohydrazide **7** (0.42 g, 1 mmol), triethyl orthoformate (3 ml, 0.02 mol) and a few drops of acetic acid were heated to reflux for 3 h. The product obtained on cooling was filtered off and recrystallised from acetic acid to afford **8** (0.43 g, 78%), m.p. >300 °C. IR: ν_{max} 3450 (NH), 1690 and 1650 cm^{-1} (2 C=O). NMR (CF_3CO_2D): δ_H 4.1 (s, 2H, CH_2) and 7.1–7.7 (m, 10H, 10-H, ArH) and at 8.9 (s, 1H, N(8)-H). Anal. Calcd for: $C_{23}H_{14}N_6O_2S$ (438.23): C, 62.98; H, 3.21; N, 19.17; S, 7.31. Found: C, 62.67; H, 3.01; N, 18.98; S, 7.12%.

Potassium5-amino-3,4-diphenylthieno[2,3-c]pyridazine-6-carboxylate (**10**)

The thieno[2,3-*c*]pyridazine derivative **9**[25] (1.87 gm, 5 mmol) was refluxed for 2 hours with potassium hydroxide (0.56 g, 0.01 mol) in ethanol (10 ml). The solid product obtained on cooling was filtered off to give the salt **10** (78% yield), m.p. >300 °C, used without further purification. IR: ν_{max} 3450, 3350 cm^{-1}(NH_2) and 1680 cm^{-1} (C=O). Anal. Calcd for $C_{19}H_{12}KN_3O_2S$ (385.19): C, 59.19; H, 3.13; N, 10.90; S, 8.32. Found: C, 58.88; H, 3.02; N, 10.67; S, 8.11%.

Reaction of the salt **10** *with phenacyl bromide: formation of the phenacyl ester* **11.**

A mixture of salt **10** (0.78 g, 2 mmol), phenacyl bromide (0.4 g, 2 mol) and potassium carbonate (0.41 g 3 mmol) in DMF (15 ml) was heated in a steam bath for 3 hours, then allowed to cool and diluted with water (100 ml). The solid product was filtered off and recrystallised from ethanol to afford **11** in 76% yield, m.p. 205–207 °C. IR: ν_{max} 3450, 3340 (NH) and 1720, 1690 cm^{-1} (2 C=O). Anal. Calcd for

$C_{27}H_{19}N_3O_3S$ (465.25): C, 69.64; H, 4.11; N, 9.03; S, 6.89. Found: C, 69.34; H, 4.01; N, 8.98; S, 6.82%.

7-Hydroxy-3,4,6-triphenylpyrido[2,3:4,5]thieno[2,3-c]pyridazin-8(5H)-one (**12**)

Compound **11** (1 g) in polyphosphoric acid (20 g) was heated on a steam bath for 3 h. It was then allowed to cool, diluted with water, and neutralised with aqueous ammonia. The solid product was filtered off and recrystallised from dioxan to afford **12** (0.60 g, 63% yield, m.p. >300 °C. IR: ν_{max} 3400, 3300 (NH, OH) and 1620 cm^{-1} (C=O). NMR (CF_3CO_2D): δ_H 7.1–7.6 (m, 15H, ArH). M.S: *m/z* 447 (100%). Anal. Calcd for $C_{27}H_{17}N_3O_2S$ (447.23): C,60.37; H, 3.83; N, 9.39; S, 7.16. Found: C, 60.02; H, 3.78; N, 9.12; S, 6.98%.

6-Amino-3,4-diphenylpyridazino[3',4':5,4]thieno[3,2-e][1,4]oxazepin-9(7H)-one (**13**)

Chloroacetonitrile (0.7 g, 2 mmol) was added with stirring at room temperature to the salt **10** (0.78 g, 2 mmol) in DMF (15 ml). Stirring was continued for 3 hours, then the mixture was diluted with water and the solid product was filtered off and recrystallised from ethanol to afford **13** in 81%, m.p.216–218 °C. IR: ν_{max} 3500, 3400 (NH_2) and 1680 cm^{-1} (C=O). NMR ($CDCl_3$): δ_H 4.8 (s, 2H, CH_2), 5.6 (s, 2H, NH_2) and 7.1–7.6 (m, 10H, ArH). Anal. Calcd for $C_{21}H_{14}N_4O_2S$ (386.21): C, 65.25; H, 3.65; N, 14.50; S, 8.30. Found: C, 65.01; H, 3.59; N, 14.34; S, 8.13%.

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