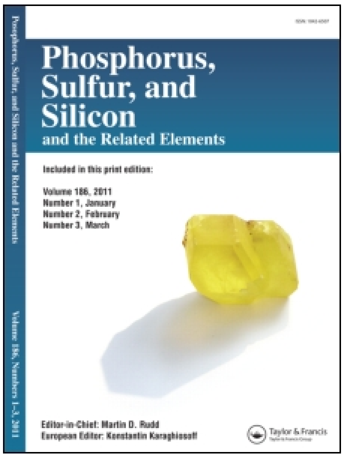

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# Synthesis of Pyrrolo[1',2':1',2']Pyrazino-[6',5':4,5]Thieno[2,3-c]Pyridazine Derivatives and Related Pentacyclic Heterocycles

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# SYNTHESIS OF PYRROLO[1",2":1',2']PYRAZINO-[6',5':4,5]THIENO[2,3-c]PYRIDAZINE DERIVATIVES AND RELATED PENTACYCLIC HETEROCYCLES

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Ethyl-5-amino-3,4-diphenylthieno[2,3-c]pyridazine-6-carboxylate(**1**) was converted into ethyl 3,4-diphenyl-5-(1-pyrrolyl)-thieno[2,3-c]pyridazine-6-carboxylate(**2**). Several derivatives of the latter compound have been synthesized. Also, the synthesis of 3,4-diphenylpyrrolo[1",2":1',2']pyrazino[6',5':4,5]-thieno[2,3-c]pyridazines and other related fused heterocycles are described.

*Key words:* Thienopyridazines; pyrrolylthienopyridazines; pyrrolopyrazinothienopyrazines.

Thienopyrrolopyrazines and benzothienopyrrolopyrazines were reported by Robba and his colleagues.[1–5] We are presently involved in a program directed to the synthesis of aza- and diaza-analogs of these foregoing heterocycles.

This work deals with the syntheses of diazabenzothienopyrrolopyrazines. The amino function of ethyl 5-amino-3,4-diphenylthieno[2,3-c]pyridazine-6-carboxylate(**1**) was easily converted to the corresponding 1-pyrrolyl group[3] via the interaction with 2,5-dimethoxytetrahydrofuran in boiling acetic acid to give (**2**). The latter pyrrolyl ester was reacted with hydrazine hydrate to give the pyrrolyl hydrazide (**3**). When (**3**) was allowed to react with phenylisothiocyanate in absolute ethanol 1-[3,4-diphenyl-5-(1-pyrrolyl)thieno[2,3-c]-pyridazin-6-oyl]-4-phenylthiosemicarbazide (**4**) was obtained, which in turn, upon dehydrative cyclization using 2N sodium hydroxide solution under reflux, yielded the 6-(4-phenyl-3-thioxo-(2H)[1,2,4]triazol-5-yl)-5-(1-pyrrolyl)-3,4-diphenylthieno[2,3-c]pyridazine (**5**). The pyrazolyl derivative (**6**) was the product of the reaction between the hydrazide (**3**) and acetyl-acetone.

The treatment of the hydrazide (**3**) with nitrous acid gave the corresponding 5-(1-pyrrolyl)-3,4-diphenyl-thieno[2,3-c]pyridazin-6-oyl azide (**7**). This acid azide is a versatile compound and could be transformed into a variety of derivatives. When (**7**) was heated in boiling ethanol the ethylcarbamate (**8**) was obtained. When it was reacted with hydrazine hydrate or aniline the products were the semicarbazides and the urea derivatives (**9**) and (**10**) respectively. Obviously these reactions went through the intermediate isocyanate (**11**) formed via Curtius rearrangement[3] of (**7**). Heating the acid azide (**7**) in a high-boiling point inert solvent such as xylene led to Curtius rearrangement with concomitant ring closure of the isocyanate intermediate (**11**) giving 3,4-diphenyl-9-oxo-9,10-dihydropyrrolo[1",2":1',2']-pyrazino[6',5':4,5]thieno[2,3-c]pyridazine (**12**). The formation of (**12**) is due to the high reactivity of the isocyanate intermediate which could not be isolated under the reaction conditions used.

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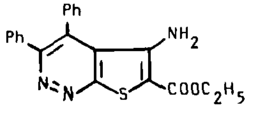
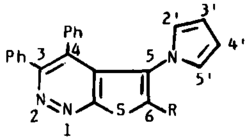
The latter oxo compound (**12**) could be transformed into the corresponding chloro derivative (**13**) by heating with phosphorylchloride under reflux. The reactivity of the chlorine atom of (**13**) was shown by its easy displacement using various nucleophilic reagents such as p-thiocresol, aniline or hydrazine hydrate to give (**14**), (**15**) and (**16**) respectively.

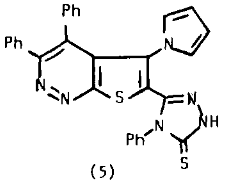
The hydrazino derivative (**16**) proved to be a useful compound for synthetics. The triazolo derivatives (**17**), (**18**) and (**19**) were produced from the reaction of (**16**) with formic acid, acetic acid and carbon disulfide respectively. The pyrazolyl



(1)



(2); R = $COOC_2H_5$
(3); R = $CONHNH_2$
(4); R = $CONHNH-\overset{S}{\overset{\|}{C}}-NH.Ph$.
(7); R = $CON_3$.
(8); R = $NHCOOC_2H_5$.
(9); R = $NHCONHNH_2$.
(10);R = NHCONHPh.



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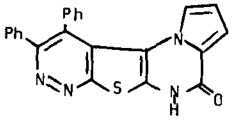

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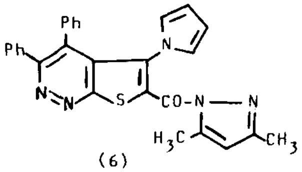

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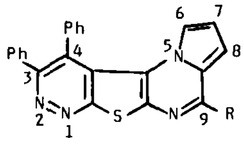
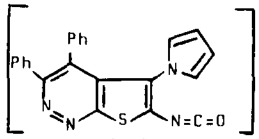


(13); R = Cl .

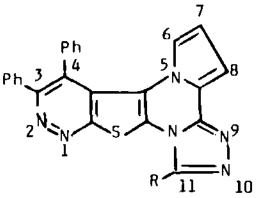
(14); R = $S.C_6H_4.CH_3$-p.

(15); R = $NHC_6H_5$.

(16); R = $NH\ NH_2$.
(21); R = $N_3$

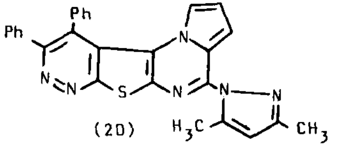


(11)

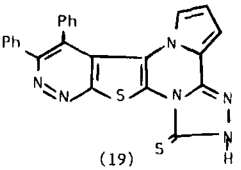


(17); R = H.

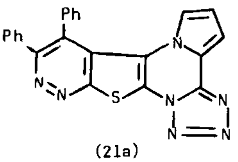
(18); R = $CH_3$.



(20)



(19)



(21a)

derivative (**20**) was obtained when (**16**) was reacted with acetyl acetone. When a solution of (**16**) in acetic acid was treated at ambient temperature with an aqueous solution of sodium nitrite the product was identified as the azido derivative (**21**). This identification was based on the IR (KBr) spectral data which showed a band at 2130 $cm^{-1}$ favoring the azido structure (**21**) and eliminating the other expected alternative tetrazolo structure (**21a**).

## EXPERIMENTAL

Melting points are uncorrected and were determined on a Mel-Temp II melting point apparatus. IR spectra were recorded on Pye-Unicam SP3-100 and Perkin-Elmer 599B spectrophotometers using KBr Wafer technique. $^1H$ NMR spectra were recorded on a Varian EM-390 90 MHz NMR spectrometer in the suitable deuterated solvent using TMS as an internal standard. Elemental analyses were determined on a Perkin-Elmer 240 C microanalyser.

*Ethyl 5-(1-pyrrolyl)-3,4-diphenylthieno[2,3-c]pyridazine-6-carboxylate* (**2**). A mixture of ethyl 5-amino-3,4-diphenylthieno[2,3-c]pyridazine-6-carboxylate-(**1**)[6] (3.75 g, 0.01 mole) and 2,5-dimethoxy tetrahydrofuran (1.6 g, 0.01 mole) in acetic acid (50 ml) was heated under reflux for one hour. After cooling, the precipitate formed was filtered off and recrystallised from ethanol as bright yellow crystals, m.p. 178–80°C, yield 3.6 g (85%). IR: $\nu$ $cm^{-1}$ 1740, 1700 (C=O). $^1H$ NMR ($CDCl_3$): $\delta$ 1.15–1.30 (t, 3H, $CH_3$), $\delta$ 4.05–4.30 (q, 2H, $CH_2$), $\delta$ 5.75 (m, 2H, $H_3'$, $H_4'$-pyrrole ring), $\delta$ 6.15 (m, 2H, $H_2'$, $H_5'$-pyrrole ring), $\delta$ 6.65–7.20 (m, 10H, ArH).

Analysis for $C_{25}H_{19}N_3O_2S$
Calcd. C 70.56, H 4.50, N 9.87, S 7.54,
Found. C 70.30, H 4.36, N 9.60, S 7.32.

*5-(1-Pyrrolyl)-3,4-diphenylthieno[2,3-c]pyridazine-6-carbohydrazide* (**3**). To a solution of the ester (**2**) (2 g) in hot ethanol (60 ml) was added an excess of hydrazine hydrate (5 ml, 98%) and the reaction mixture was refluxed for 5 hrs. The solid product obtained was filtered off and recrystallised from acetic acid as yellow crystals, m.p. 252°C, yield 1.8 g (93%). IR: $\nu$ $cm^{-1}$ 3440–3160 (NH), 1640 (C=O). $^1H$ NMR (DMSO-$d_6$): $\delta$ 4.20–5.00 (m, 3H, $NHNH_2$), $\delta$ 5.75 (m, 2H, $H_3'$, $H_4'$-pyrrole ring), $\delta$ 6.45 (m, 2H, $H_2'$, $H_5'$-pyrrole ring), $\delta$ 6.80–7.30 (m, 10H, Ar-H).

Analysis for $C_{23}H_{17}N_5OS$
Calcd. C 67.13, H 4.16, N 17.02, S 7.79,
Found. C 66.80, H 4.15, N 16.70, S 7.62.

*1-[3,4-Diphenyl-5-(1-pyrrolyl)thieno[2,3-c]pyridazin-6-oyl]-4-phenyl thiosemicarbazide* (**4**). A mixture of (**3**) (0.82 g, 0.002 mole) and phenyl isothiocyanate (0.27 g, 0.0002 mole) in ethanol (20 ml) was heated under reflux for 4 hrs. The solid product that separated on cooling was recrystallised from ethanol to give yellow crystals, m.p. 236°C, yield 0.86 g (79%). IR: $\nu$ $cm^{-1}$ 3280–3210 (NH), 1680 (C=O), 1330 (C=S). $^1H$ NMR ($CF_3COOH$): $\delta$ 5.60 (m, 2H, $H_3'$, $H_4'$-pyrrole ring), $\delta$ 6.45 (m, 2H, $H_2'$, $H_5'$-pyrrole ring), $\delta$ 6.70–7.40 (m, 15H, Ar-H).

Analysis for $C_{30}H_{22}N_6OS_2$
Calcd. C 65.91, H 4.05, N 15.37, S 11.72,
Found. C 66.22, H 4.37, N 15.35, S 11.50.

*6-(4-Phenyl-3-thioxo(2H)[1,2,4]triazol-5-yl)-5-(1-pyrrolyl)-3,4-diphenylthieno[2,3-c]pyridazine* (**5**). A suspension of (**4**) (0.54 g, 0.001 mole) and NaOH (5 ml, 2N), was heated under reflux for one hour. After cooling, the reaction mixture was acidified with dilute HCl. The solid product obtained was filtered and recrystallised from ethanol to give yellow crystals, m.p. 280–2°C, yield 0.3 g (57%), IR: $\nu$ $cm^{-1}$ 3500–3300 (NH), 1310 (C=S). $^1H$ NMR (DMSO-$d_6$): $\delta$ 5.40 (m, 2H, $H_3'$, $H_4'$-pyrrole ring), $\delta$ 5.80 (m, 2H, $H_2'$, $H_5'$-pyrrole ring), $\delta$ 6.60–7.20 (m, 15H, Ar-H).

Analysis for $C_{30}H_{20}N_6S_2$
Calcd. C 68.16, H 3.81, N 15.89, S 12.12,
Found. C 68.20, H 4.12, N 16.14, S 12.10.

*2-[(3,5-Dimethylpyrazol-l-yl)carbonyl]-3-(1-pyrrolyl)-4,5-diphenylthieno[2,3-c]pyridazine* (**6**). A mixture of (**3**) (1 g) and excess of acetylacetone (10 ml) was refluxed for 5 hrs. The excess acetylacetone was eliminated in vacuo and the solid product was collected and recrystallised from ethanol as yellow crystals m.p. 228–30°C, yield 0.8 g (70%). IR: $\nu$ cm$^{-1}$ 1630 (C=O), $^1$H NMR (DMSO-d$_6$): $\delta$ 1.55, 1.65 (2s, 6H, 2 $CH_3$-pyrazole ring), $\delta$ 5.50 (m, 2H, $H'_3$, $H'_4$-pyrrole ring), $\delta$ 6.15 (m, 2H, $H'_2$, $H'_5$-pyrrole ring), $\delta$ 6.55 (s, 1H, CH-pyrazole ring), $\delta$ 6.76–7.20 (m, 10H, Ar-H).

Analysis for $C_{28}H_{21}N_5OS$
Calcd. C 70.71, H 4.45, N 14.72, S 6.74,
Found. C 70.55, H 4.50, N 15.10, S 6.60.

*5-(1-Pyrrolyl)-3,4-diphenylthieno[2,3-c]pyridazin-6-oyl azide* (**7**). To a solution of (**3**) (1.1 g) in glacial acetic acid (50 ml) a solution of sodium nitrite (0.7 g in 10 ml water) was added at room temperature with stirring. Stirring was continued for 30 minutes and the precipitate was filtered off and washed with water. Crystallisation from benzene gave yellow crystals, m.p. 149°C (dec.), yield 0.8 g (71%). IR: $\nu$ cm$^{-1}$ 2180 ($N_3$) and 1640 (C=O).

Analysis for $C_{23}H_{14}N_6OS$
Calcd. C 65.39, H 3.34, N 19.89, S 7.58,
Found. C 65.50, H 3.11, N 20.10, S 7.55.

*Ethyl 5-(1-pyrrolyl)-3,4-diphenylthieno[2,3-c]pyridazine-6-carbamate* (**8**). Compound (**7**) (0.42 g) was heated under reflux in excess absolute ethanol (30 ml) for one hour. The reaction mixture was then concentrated and left to cool. The solid product obtained was recrystallized from ethanol, m.p. 222–4°C, yield 0.38 g (86%), IR: $\nu$ cm$^{-1}$ 3380 (NH), 1730 (C=O), $^1$H NMR ($CF_3COOH$): $\delta$ 1.3–1.7 (t, 3H, $CH_3$), $\delta$ 4.3–4.8 (q, 2H, $OCH_2$), $\delta$ 6.05–6.10 (m, 2H, $H'_3$, $H'_4$-pyrrole ring), $\delta$ 6.4–6.55 (m, 2H, $H'_2$, $H'_5$-pyrrole ring), $\delta$ 6.8–7.7 (m, 10 H, Ar-H).

Analysis for $C_{25}H_{20}N_4O_2S$
Calcd. C 68.16, H 4.57, N 12.71, S 7.27,
Found. C 68.37, H 4.66, N 12.87, S 7.30.

*4-[5-(1-Pyrrolyl)-3,4-diphenylthieno[2,3-c]pyridazin-6-yl]semicarbazide* (**9**). A mixture of compound (**7**) (1 g) and hydrazine hydrate (10 ml) was refluxed for 10 minutes. On cooling the solid product obtained was filtered off, washed with ethanol and recrystallised from ethanol as yellow crystals, m.p. 240–2°C, yield 0.8 (80%), IR: $\nu$ cm$^{-1}$ 3380, 3320, 3200 (NH), 1640 (C=O), $^1$H NMR ($CF_3COOH$): $\delta$ 5.85 (m, 2H, $H'_3$, $H'_4$-pyrrole ring), $\delta$ 6.50 (m, 2H, $H'_2$, $H'_5$-pyrrole ring), $\delta$ 6.90–7.20, 7.20–7.40 (m, 10H, Ar-H).

Analysis for $C_{23}H_{18}N_6OS$
Calcd. C 64.77, H 4.25, N 19.70, S 7.51,
Found. C 64.90, H 4.33, N 20.08, S 7.54.

*1-[5-(1-Pyrrolyl)-3,4-diphenylthieno[2,3-c]pyridazin-6-yl]-3-phenylurea* (**10**). An equimolar mixture of the azide (**7**) (0.42 g, 0.001 mole) and aniline (0.093 g, 0.001 mole) in dry benzene was heated under reflux for one hour. The solid product obtained after cooling was filtered off and recrystallised from ethanol as cream crystals m.p. 340°C (dec.), yield 0.4 g (87%). IR: $\nu$ cm$^{-1}$ 3500–3300 (NH). $^1$H NMR (DMSO-d$_6$): $\delta$ 5.90 (m, 2H, $H'_3$, $H'_4$-pyrrole ring), $\delta$ 6.40 (m, 2H, $H'_2$, $H'_5$-pyrrole ring), $\delta$ 9.6, 9.70 (2s, 2H, 2NH).

Analysis for $C_{29}H_{21}N_5OS$
Calcd. C 71.43, H 4.34, N 14.36, S 6.57,
Found. C 71.55, H 4.35, N 14.12, S 6.39.

*3,4-Diphenyl-9-oxo-9,10-dihydropyrrolo[1",2":1',2']pyrazino-[6',5':4,5]thieno[2,3-c]pyridazine* (**12**). A solution of compound (**7**) (0.5 g) in xylene (15 ml) was refluxed for one hour and then allowed to cool. The formed product was filtered off and recrystallised from benzene-ethanol mixture to give white crystals, m.p. >350°C, yield 0.36 g (78%). IR: $\nu$ cm$^{-1}$ 3500–3400 (NH), 1630 (C=O). $^1$H NMR ($CF_3COOH$): $\delta$ 5.75 (m, 1H, $H_7$), $\delta$ 6.30 (m, 2H, $H_6$, $H_8$), $\delta$ 7.10–7.55 (m, 10H, Ar-H).

Analysis for $C_{23}H_{14}N_4OS$
Calcd. C 70.03, H 3.57, N 14.20, S 8.12,
Found. C 70.32, H 3.43, N 14.35, S 8.20.

*9-Chloro-3,4-diphenylpyrrolo[1",2":1',2']pyrazino[6',5':4,5]-thieno[2,3-c]pyridazine* (**13**). A suspension of (**12**) (2 g) in phosphoryl chloride (25 ml) was heated under reflux for 3 hours. The cold reaction mixture was poured into ice-water mixture, the residual solid product was worked up in an ammonium hydroxide-ice mixture, filtered, washed with water and recrystallised from ethanol-benzene as orangeyellow crystals, m.p. 258–60°C, yield 1.8 g (86%). IR: $\nu$ cm$^{-1}$ 3100, 1570, 1450, 1070, 760 (C—Cl). $^1$H NMR ($CF_3COOH$): $\delta$ 5.95 (m, 1H, $H_7$), $\delta$ 6.70 (m, 2H, $H_6$, $H_8$), $\delta$ 7.10–7.60 (m, 10H, Ar-H).

Analysis for $C_{23}H_{13}ClN_4S$
Calcd. C 66.90, H 3.17, Cl 8.58, N 13.56, S 7.76,
Found. C 66.87, H 3.35, Cl 8.85, N 13.77, S 7.39.

*9-(p-Tolulyl thio)-3,4-diphenylpyrrolo[1″,2″:1′,2′]pyrazino-[6′,5′:4,5]thieno[2,3-c]pyridazine* (**14**). To a well stirred mixture of (**13**) (0.41 g, 0.001 mole) and p-thiocresol (0.24 g, 0.002 mole) in dimethyl sulphoxide (10 ml), triethylamine (1 ml) was added. The reaction mixture was then heated at 160°C for 30 minutes. After cooling it was poured onto crushed ice and the solid product was collected, washed with water and recrystallised from ethanol-benzene into bright yellow crystals, m.p. 236–8°C, yield 0.3 g (60%). IR: $\nu$ cm$^{-1}$ 1560, 1430, 1170, 1060, 700. $^1$H NMR ($CF_3COOH$): $\delta$ 2.6 (s, 3H, $CH_3$), $\delta$ 6.2–6.3 (m, 1H, $H_7$), $\delta$ 6.4–6.7 (m, 2H, $H_6$, $H_8$), $\delta$ 7.2–7.8 (m, 14H, Ar-H).

Analysis for $C_{30}H_{20}N_4S_2$
Calcd. C 71.97, H 4.02, N 11.19, S 12.80,
Found. C 72.12, H 4.32, N 10.88, S 13.12.

*9-Anilino-3,4-diphenylpyrrolo[1″,2″:1′,2′]pyrazino[6′,5′:4,5]thieno[2,3-c]pyridazine* (**15**). A mixture of (**13**) (0.5 g) and excess aniline (5 ml) was heated under reflux for one hour. The product obtained on cooling was filtered off, washed with pet.ether and recrystallised from acetic acid to give yellow crystals, m.p. 304–6°C, yield 0.45 g (79%). IR: $\nu$ cm$^{-1}$ 3500–3300 cm$^{-1}$ (NH), 1600, 1460, 700.

Analysis for $C_{29}H_{19}N_5S$
Calcd. C 74.17, H 4.07, N 14.91, S 6.82,
Found. C 74.32, H 3.95, N 15.13, S 6.70.

*9-Hydrazino-3,4-diphenyl pyrrolo[1″,2″:1′,2′]pyrazino[6′,5′:4,5]thieno[2,3-c]pyridazine* (**16**). A mixture of (**13**) (1 g) and hydrazine hydrate (4 ml, 98%) in ethanol (25 ml) was heated under reflux for 4 hours. The product obtained after cooling was filtered, washed with water and recrystallised from ethanol-benzene to give dark yellow crystals, m.p. 278–80°C, yield 0.8 g (80%). IR: $\nu$ cm$^{-1}$ 3400–3180 (NH). $^1$H NMR (DMSO-$d_6$): $\delta$ 3.65 (m, 2H, $NH_2$), $\delta$ 5.45 (m, 1H, $H_7$), $\delta$ 6.15 (m, 2H, $H_6$, $H_8$), $\delta$ 7.10–7.60 (m, 10H, Ar-H), $\delta$ 8.05 (s, 1H, NH).

Analysis for $C_{23}H_{16}N_6S$
Calcd. C 67.63, H 3.94, N 20.57, S 7.84,
Found. C 67.52, H 4.13, N 20.76, S 8.10.

*3,4-Diphenyl[1,2,4]triazolo[3″,4″:3′,4′]pyrrolo[1″,2″:1′,2′]-pyrazino[6′,5′:4,5]thieno[2,3-c]pyridazine* (**17**). A solution of (**16**) (0.5 g) in formic acid was heated under reflux for 5 hours. The reaction mixture was concentrated in vacuo and the solid product was collected, washed with water and recrystallised from ethanol as yellow crystals, m.p. 306–8°C, yield 0.35 g (70%). IR: $\nu$ cm$^{-1}$ 1610 (C═N), 1320, 1160, 690. $^1$H NMR (DMSO-$d_6$): $\delta$ 5.70 (m, 1H, $H_7$), $\delta$ 6.20 (m, 1H, $H_8$), $\delta$ 6.40 (m, 1H, $H_6$), $\delta$ 6.60–7.00, 7.10–7.60 (2 m, 10H, Ar-H), $\delta$ 6.80 (s, 1H, CH-triazole ring).

Analysis for $C_{24}H_{14}N_6S$
Calcd. C 68.88, H 3.37, N 20.08, S 7.66,
Found. C 69.12, H 3.35, N 20.13, S 7.50.

*11-Methyl-3,4-diphenyl[1,2,4]triazolo[3″,4″:3′,4′]pyrrolo[1″,2″:1′,2′]pyrazino[6′,5′:4,5]thieno[2,3-c]pyridazine* (**18**). This was prepared using a similar procedure to that of (**16**), using glacial acetic acid instead of formic acid. The product was recrystallised from acetic acid to yield yellow crystals. m.p. >350°C, yield 0.3 g (57%). IR: $\nu$ cm$^{-1}$ 1620 (C═N), 1390, 720. $^1$H NMR ($CF_3COOH$): $\delta$ 3.2 (s, 3H, $CH_3$), $\delta$ 6.1–6.2 (m, 1H, $H_7$), $\delta$ 6.4–6.7 (m, 2H, $H_6$, $H_8$), $\delta$ 7.15–7.85 (m, 10H, Ar-H).

Analysis for $C_{25}H_{16}N_6S$
Calcd. C 69.59, H 3.73, N 19.47, S 7.43,
Found. C 69.88, H 3.62, N 19.23, S 7.40.

*3,4-Diphenyl-11-thioxo-10,11-dihydro[1,2,4]triazolo[3″,4″:3′,4′]pyrrolo[1″,2″:1′,2′]pyrazino[6′,5′:4,5]thieno[2,3-c]pyridazine* (**19**). A mixture of (**16**) (0.6 g), carbon disulfide (3 ml) in ethanol and two pellets of potassium hydroxide was heated on a water bath for 5 hours. The solid product obtained was dissolved in water and then acidified with acetic acid. Recrystallization from acetic acid gave greenish-yellow crystals m.p. >350°C, yield 0.4 g (61%). IR: $\nu$ cm$^{-1}$ 3300–3100 (NH), 1630 (C═N), 1190 cm$^{-1}$

(C═S). $^1$H NMR ($CF_3COOH$): δ 5.95–6.1 (m, 1H, $H_7$), δ 6.2–6.5 (m, 2H, $H_6$, $H_8$), δ 7.2–7.9 (m, 10H, Ar-H).

Analysis for $C_{24}H_{14}N_6S_2$
Calcd. C 63.98, H 3.13, N 18.65, S 14.23,
Found. C 64.12, H 2.98, N 18.55, S 14.25.

*9-(3,5-Dimethyl pyrazol-1-yl)-3,4-diphenylpyrrolo[1″,2″:1′,2′]pyrazino[6′,5′:4,5]thieno[2,3-c]pyridazine* (**20**). A mixture of (**16**) (1g) and excess acetylacetone (25 ml) was heated under reflux for 3 hours. The solid product obtained after cooling was filtered off, washed with pet.ether and recrystallised from acetic acid as yellow crystals, m.p. 218–20°C, yield 0.9 g (78%). $^1$H NMR ($CF_3COOH$): δ 2.70 (s, 6H, 2 $CH_3$), δ 6.10 (m, 1H, $H_7$), δ 6.75 (m, 3H, $H_6$, $H_8$, CH-pyrazole ring), δ 7.10–7.60 (m, 10H, Ar-H).

Analysis for $C_{28}H_{20}N_6S$
Calcd. C 71.16, H 4.26, N 17.78, S 6.78,
Found. C 71.25, H 4.23, N 17.59, S 6.70.

*9-Azido-3,4-diphenyl pyrrolo[1″,2″:1′,2′]pyrazino[6′,5′:4,5]-thieno[2,3-c]pyridazine* (**21**). To a well stirred solution of (**16**) (1 g) in glacial acetic acid (40 ml) was added at room temperature a solution of sodium nitrite (1 g in 10 ml water) and stirring was continued for one hour. The solid obtained was filtered off, washed with water and recrystallised from acetic acid to give brown crystals, m.p. 212–4°C, yield 0.6 g (60%). IR: $\nu$ cm$^{-1}$ 2130 ($N_3$), 1620 (C═N). $^1$H NMR ($CF_3COOH$): δ 5.80 (m, 1H, $H_7$), δ 6.45 (m, 2H, $H_6$, $H_8$), δ 7.05–7.55 (m, 10H, Ar-H).

Analysis for $C_{23}H_{13}N_7S$
Calcd. C 65.86, H 3.12, N 23.37, S 7.64,
Found. C 66.10, H 3.37, N 23.35, S 7.80.

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