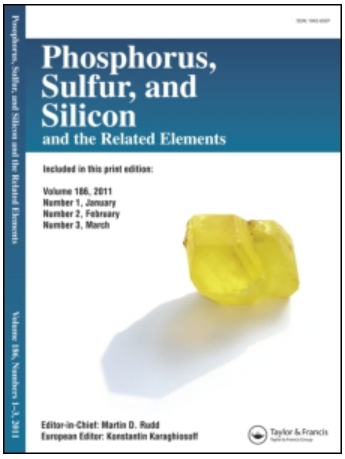

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CHEMISTRY AND CYCLIZATION REACTIONS OF 2-METHYLPYRIMIDO THIENOQUINOXALINE DERIVATIVES, PART III

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To cite this Article Badr, M. Z. A. , Mahgoub, S. A. , Geies, A. A. , Moustafa, O. S. and El-Latif, F. M. Abd(1992) 'CHEMISTRY AND CYCLIZATION REACTIONS OF 2-METHYLPYRIMIDO THIENOQUINOXALINE DERIVATIVES, PART III', Phosphorus, Sulfur, and Silicon and the Related Elements, 73: 1, 27 — 34
To link to this Article: DOI: 10.1080/10426509208034427
URL: http://dx.doi.org/10.1080/10426509208034427

Phosphorus, Sulfur, and Silicon, 1992, Vol. 73, pp. 27–34
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CHEMISTRY AND CYCLIZATION REACTIONS OF 2-METHYLPYRIMIDO THIENOQUINOXALINE DERIVATIVES, PART III†

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(Received June 9, 1992; in final form September 18, 1992)

Treatment of 2-methyl-pyrimido[4′,5′:4,5]thieno[2,3-**b**]-quinoxalin-4-one (2) with a mixture of phosphorous oxychloride phosphorous pentachloride affords 4-chloroderivatives (3). Treatment of 2 with phosphorous pentasulphide give the 4-thione derivative (4) which reacts with methyl iodide to yield the 4-methylthioderivative (6). Treatment of 3 with different nucleophiles, namely; hydrazinehydrate, aniline and dimethylamine, produce, 4-hydrazino-(5); 4-anilino-(7) and 4-dimethylamino-(8) derivatives, respectively. However, treatment of 3 with ethylglycinate gives 5-methyl imidazo[1″,2″:1′,6′]pyrimido-[4′,5′:4,5]thieno[2,3-**b**]quinoxaline-3-one (9). 4-Hydrazino-2-methylpyrimido[4′,5′:4,5]thieno[2,3-**b**]quinoxaline (5) was condensed with p-substituted benzaldehydes to produce the corresponding hydrazones (10a–c). Treatment of 5 with acetic anhydride affords the hydrazinotriacetate compound (11), while with phthalic anhydride affords the corresponding 2-(pyrimido-thienoquinoxalin-4-yl)-dihydro-1,4-phthalazine dione (12). Treatment of 5 with acetylacetone produces 4-(3,5-dimethylpyrazol-1-yl)derivative (13). 4-Hydrazino compound 5 undergoes ring closure reactions with, formic acid, carbon disulfide, benzoyl chloride, ethylchloroformate or diethylmalonate to produce the s-triazolo ring system (17) and its derivatives; 3-thio-(14); 3-one-(18) and 3-methyl ethylcarboxylate-(19), respectively. Treatment of 5 with nitrous acid affords the tetrazolo compound (20).

Key words: Pyrimido[4′,5′:4,5]thieno[2,3-**b**]quinoxalines; synthesis; reactions and antimicrobial effects.

Quinoxaline derivatives have been reported to constitute an important class of biologically active compounds,[1] as antimicrobials,[2] and also patented as anticancers drug use.[3] In continuation of our earlier work[4,5] on quinoxaline derivatives, the present investigation deals with the synthesis of new series of 2-methyl pyrimido thienoquinoxaline derivatives.

Refluxing 2-methyl-4H[1,3]oxazin[4′,5′:4,5]thieno[2,3-**b**]-quinoxalin-4-one (1) in ethanol with ammonium acetate and acetic acid gave the corresponding pyrimido thieno quinoxalinone (2). Its IR spectrum showed bands at 3050–3200 cm^{-1} (NH), at 1740 cm^{-1} (C=O) and at 1620 cm^{-1} (C=N). Its mass spectrum showed mol. ion peak at m/e = 268 in agreement with its mol. formula ($C_{13}H_8N_4OS$). Treatment of 2-methylpyrimido[4′,5′:4,5]thieno[2,3-**b**]quinoxalin-4-one (2) with mixture of phosphorous oxychloride and phosphorous pentachloride and/or with phosphorous pentasulphide in dry pyridine gave the corresponding 4-chloroderivative (3) and/or 2-methylpyrimido[4′,5′:4,5]-thieno[2,3-**b**]quinoxalin-4(3H)thione (4), respectively. The IR spectrum of 4 showed the C=N band at 1640 cm^{-1} and the C=S band at 1230 cm^{-1}. Treatment of 4 with methyl iodide in ethanol and fused sodium acetate gave 2-methyl-4-methylthiopyrimido[4′,5′:4,5]thieno[2,3-**b**]quinoxaline (6).

†Presented in Part at the 15th International Symposium on Organic Sulphur Compounds, Caen, France, June 28–July 4, p. 315 of Abstract.

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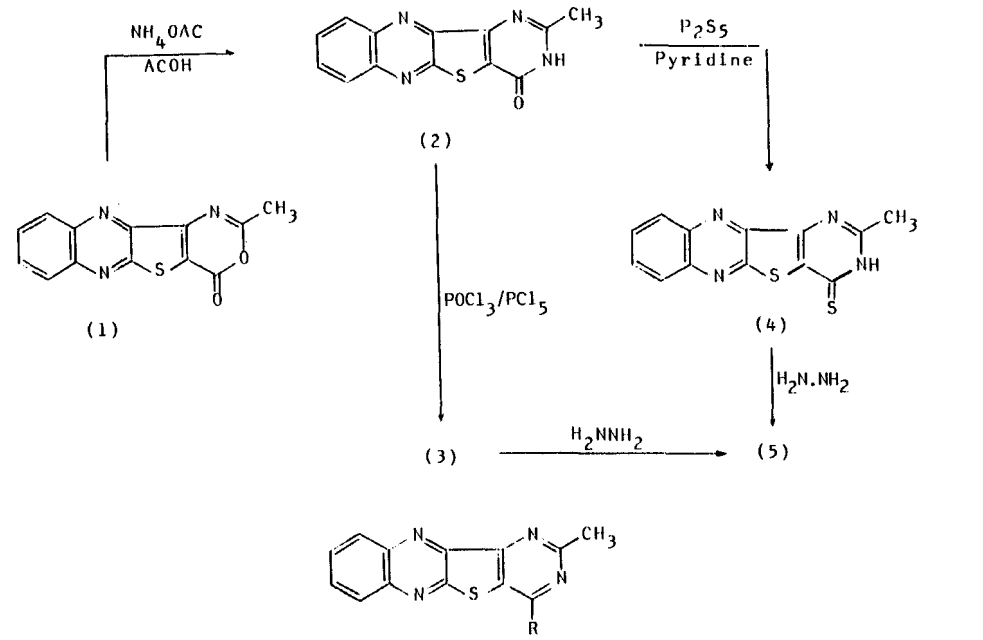
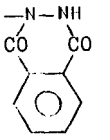


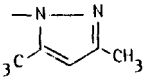
3; R = Cl
6; R = SCH_3
7; R = NHPh
8; R = $N(CH_3)_2$

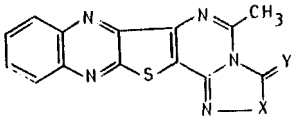
5 ; R = $NHNH_2$
10a; R = $NHN{=}CHC_6H_5$
10b; R = $NHN{=}CHC_6H_4OCH_3(P)$
10c; R = $NHN{=}CHC_6H_4NO_2(P)$
11 ; R = $N(COCH_3)\text{-}N(COCH_3)_2$

12; R =

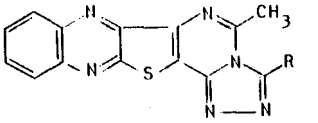


13; R=

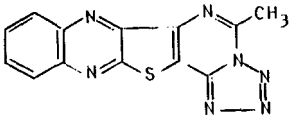




9; X = CH_2 ; Y=O
14; X = NH ; Y=S
18; X = NH ; Y=O



15; R = SC_2H_5
16; R = Ph
17; R = H
19; R = $CH_2COOC_2H_5$



(20)

Scheme 1

The IR spectrum showed a C=N band at 1550 cm^{-1} with the disappearance of band due to the thione group. However, production of 6 does not exclude existence of 4 in solution as cyclic thioamide together with the 3-mercapto tautomer as observed from the large red shift in electronic absorption at λ_{max} 470 nm due to n-π transition of (C=S) group when compared to that of methylthio product (6) at λ_{max} 400 nm (Table III). The ^{1}H-NMR spectrum ($CDCl_3$) of 6 showed signals

at δ2.7 (s, 3H, S—CH_3), δ2.9 (s, 3H, CH_3 pyrimidine) and at δ7.7–8.5 (m, 4H, ArH).

Compound 3 was reacted with hydrazine hydrate in ethanol to give 4-hydrazino-2-methylpyrimido[4′,5′:4,5]thieno[2,3-**b**]-quinoxaline (5) and which was alternatively produced by refluxing 6 with hydrazine hydrate. The IR spectrum of 5 showed NH and NH_2 bands at 3300–3400 cm^{-1}, and a C=N band at 1620 cm^{-1}. Reaction of 3 with aniline and/or dimethylamine gave 2-methyl-4-*N*-phenylamino-pyrimido-[4′,5′:4,5]thieno[2,3-**b**]quinoxaline (7) and its 4-*N*-dimethylaminopyrimido derivative (8) respectively. The IR spectrum of 7 showed the N—H band at 3240 cm^{-1} and the C=N band at 1605 cm^{-1}. Its ^{1}H-NMR spectrum ($CDCl_3$) showed signals, at δ2.8 (s, 3H, CH_3), δ8.9 (s, 1H, NH) and at δ7.2–8.4 (m, 9H, ArH). The IR spectrum of 8 showed the C=N band at 1610 cm^{-1}. Its ^{1}H-NMR spectrum ($CDCl_3$) showed signals at δ2.7 (s, 3H, CH_3), δ3.5 (s, 6H, $(CH_3)_2$) and at δ7.7–8.5 (m, 4H, ArH). However, when 3 was reacted with ethylglycinate, it gave 5-methyl-imidazo[1″,2″:1′,6′]-pyrimido[4′,5′:4,5]thieno[3,2-**b**]quinoxaline-3-one (9). Its IR spectrum showed a C=O band at 1650 cm^{-1} and a C=N band at 1670 cm^{-1}.

Condensation of 5 with benzaldehyde, p-methoxy benzaldehyde and p-nitro benzaldehyde, gave the corresponding, 2-methyl-4-arylidine hydrazonopyrimido[4′,5′:4,5]thieno[2,3-**b**]quinoxalines (10a–c) respectively. Their IR spectra showed NH band at range 3300–3200 cm^{-1} and C=N bands at range 1640–1580 cm^{-1}. The ^{1}H-NMR spectrum ($CDCl_3$) of 10b showed signals, at δ2.8 (s, 3H, CH_3), δ3.8 (s, 3H, OCH_3), δ9.8 (s, 1H, CH), δ7.5 (s, 1H, NH) and at δ6.8–8.5 (m, 8H, ArH). Treatment of 5 with acetic anhydride gave, 2-methyl-4-triacetyl hydrazino-pyrimido[4′,5′:4,5]-thieno[2,3-**b**]quinoxaline (11). Its ^{1}H-NMR spectrum ($CDCl_3$) showed signals, at δ2.9 (s, 3H, CH_3 pyrimidine), at δ2.5 (s, 6H, $(COCH_3)_2$) and δ2.6 (s, 3H of —$COCH_4$) and at δ7.8–8.6 (m, 4H, ArH). Reaction of 5 with phthalic anhydride gave 2-(3,4-dihydro-2-methylpyrimido-[4′,5′:4,5]thieno[2,3-**b**]quinoxalin-4-yl)-1,4-phthalazin-1,4(3H)dione (12). Its IR spectrum showed NH band at 3500 cm^{-1} and 1,4-dione band at 1790–1750 cm^{-1} and C=N band at 1610 cm^{-1}. On the other hand, treatment of 5 with acetylacetone gave 4-(3,4-dimethylpyrazol-1-yl)-2-methylpyrimido[4′,5′:4,5]thieno[2,3-**b**]quinoxaline (13). Its ^{1}H-NMR spectrum ($CDCl_3$) showed signals, at δ2.3 (s, 3H, CH_3) and at δ3 (s, 3H, CH_3) both of pyrazol ring, at δ2.8 (s, 3H, CH_3 of pyrimidine), at δ6 (s, 1H, CH) and at δ7.7–8.5 (m, 4H, ArH).

Compound 5 underwent several cyclization reactions. Thus, treatment of 5 with carbon disulphide in presence of potassium hydroxide gave 3-mercapto-5-methyl-2-triazolo[4″,3″:1′,6′]pyrimido[4′,5′:4,5]-thieno[2,3-**b**]quinoxaline (14) which was alkylated with ethyliodide in presence of sodium acetate to give the corresponding 3-ethylthio derivative (15). The IR spectrum of 14 showed C=N band at 1610 cm^{-1} and C=S band at 1220 which disappeared in that of 15. The ^{1}H-NMR spectrum ($CDCl_3$) of 15 showed signals at δ1.4–1.6 (t, 3H, —CH_3), at δ3.3–3.6 (q, 2H, CH_2), at δ2.9 (s, 3H, CH_3 pyrimidine) and at δ7.8–8.5 (m, 4H, ArH). Refluxing of 5 with benzoyl chloride gave 5-methyl-3-phenyl-s-triazolo[4″,3″:1′,6′]-pyrimido[4′,5′:4,5]thieno-[2,3-**b**]quinoxaline (16). Treatment of 5 with formic acid in glycerol gave 5-methyl-s-triazolo[4″,3″:1′,6′]pyrimido[4′,5′:4,5]thieno[2,3-**b**]-quinoxaline (17). The ^{1}H-NMR spectrum (DMSO) showed signals at 2.7 (s, 3H, CH_3), at δ8.7 (s, 1H, CH triazole ring) and at δ7.7–8.2 (m, 4H, ArH). Reaction of 5 with ethylchloroformate in pyridine gave 5-methyl-s-triazolo[4″,3″:1′,6′]-

pyrimido[4′,5′:4,5]thieno[2,3-**b**]quinoxaline-3(2H) one (18). Its IR spectrum showed a C=O band at 1650 cm^{-1} and a C=N band at 1590 cm^{-1}. Similarly, refluxing of 5 with diethylmalonate gave 3-ethoxycarbonyl-5-methyl-s-triazolo[4″,3″:1′,6′]-pyrimido-[4′,5′:4,5]thieno[2,3-**b**]quinoxaline (19). Its IR spectrum showed a C=O band at 1730 cm^{-1} and a C=N band at 1610 cm^{-1}. The ^{1}H-NMR spectrum ($CDCl_3$) showed signals at δ1.1–1.4 (t, 3H, CH_3), at δ2.9 (s, 3H, CH_3 pyrimidine), at δ4.2–4.5 (q, 2H, CH_2), at δ3.8 (s, 2H, CH_2CO) and at δ7.8–8.5 (m, 4H, ArH). Finally, reaction of 5 with sodium nitrite in hydrochloric acid gave the cyclization product, 5-methyltetrazolo[4″,3″:1′,6′]pyrimido[4′,5′:4,5]thieno[2,3-**b**]-quinoxaline (20). Its IR spectrum showed the C=N band at 1610 cm^{-1}.

EXPERIMENTAL

Melting points reported are uncorrected. IR (KBr wafer) spectra were recorded on a Beckman 408-26 spectrophotometer. UV spectra were recorded on Shimadzu 200S spectrophotometer and NMR spectra were recorded on a Varian EM-390-90 MHz. The mass spectra of the solid samples were analyzed by a high resolution double focussing mass spectrometer model M.S. -902, AET, England.

*2-Methyl[1,3]oxazino[4′,5′:4,5]thieno[2,3-**b**]quinoxalin-4-one* (1): The title compound was prepared by saponification of ethyl-3-aminothieno[2,3-**b**]quinoxalin-2-carboxylate[5] (2.5 g, 0.01 mol) in ethanolic NaOH solution (20 ml 10%) by boiling for 30 min. The separated sodium salt was boiled with acetic anhydride (20 ml) for 1 hr. The solid separated was recrystallized from ethanol and identified as in Table I.

*2-Methyl-pyrimido[4′,5′:4,5]thieno[2,3-**b**]quinoxalin-4(3H)-one* (2): A mixture of 1 (2.7 g, 0.01 mol) in absolute ethanol (30 ml) and ammonium acetate (0.77 g, 0.01 mol) in acetic acid was refluxed for 3 hr. The separated solid was recrystallized from acetic acid and analyzed as in Table I.

*4-Chloro-2-methyl-pyrimido[4′,5′:4,5]thieno[2,3-**b**]quinoxaline* (3): A mixture of 2 (2.68 g, 0.01 mol) and phosphorous pentachloride (2.68 gm) and phosphorous oxychloride (3 ml) was refluxed for 3 hr. The mixture was poured over ice and solid separated was recrystallized and analyzed as in Table I.

*2-Methyl-pyrimido[4′,5′:4,5]thieno[2,3-**b**]quinoxalin-4(3H)-thione* (4): A mixture of 2 (2.68 g, 0.01 mol) and phosphorous pentasulphide (1.9 g, 0.01 mol) in dry pyridine was refluxed for 4 hr. The solid separated on water addition was filtered, recrystallized and analyzed as in Table I.

*4-Hydrazino-2-methylpyrimido[4′,5′:4,5]thieno[2,3-**b**]quinoxaline* (5): The title compound was prepared by refluxing hydrazine hydrate (5 ml) with either 3 (2.9 g, 0.01 mol) in absolute ethanol (30 ml) for 1 hr or with 4 (2.98 g, 0.1 mol) for 3 hr. The solid separated was washed with ethanol and analyzed as in Table I.

*2-Methyl-4-methylthio-pyrimido[4′,5′:4,5]thieno[2,3-**b**]quinoxaline* (6): A mixture of 4 (2.84 g, 0.01 mol) in ethanol (20 ml) and fused sodium acetate (2 gm) was treated with methyl iodide (5 ml) while stirring for 1 hr. The solid separated on water addition (50 ml) was filtered, recrystallized and analyzed as in Table I.

2-Methyl-4-N-phenylamino-pyrimido[4′,5′:4,5]thieno[2,3-**b**]*quinoxaline* (7): A mixture of 3 (0.29 g, 0.001 mol) and aniline (0.001 mol) in ethanol (20 ml) was refluxed for 3 hr. The solid separated was recrystallized and analyzed as in Table I.

2-Methyl-4-N-dimethylamino-pyrimido[4′,5′:4,5]thieno[2,3-**b**]*quinoxaline* (8): A mixture of 3 (0.029 g, 0.001 mol) and dimethylamine (5 ml) in ethanol (20 ml) was refluxed for 3 hr. The solid separated was recrystallized and analyzed as in Table I.

*5-Methylimidazo[1″,2″:1′,6′]pyrimido[4′,5′:4,5]thieno[2,3-**b**]quinoxaline-3-one* (9): A mixture of 3 (0.29 g, 0.001 mol) and ethylglycinate (0.103 g, 0.001 mol) in ethanol (30 ml) was refluxed for 3 hr. The solid separated was recrystallized and analyzed as in Table I.

*2-Methyl-4-arylidine hydrazonopyrimido[4′,5′:4,5]thieno[2,3-**b**]quinoxalines* (10a–c): A mixture of 5 (0.57 g, 0.002 mol) and benzaldehyde, p-methoxybenzaldehyde and/or p-nitrobenzaldehyde (0.002 mol) in ethanol (20 ml) and drops of piperidine was refluxed for 4 hr. The separated solid in each case was recrystallized from ethanol and analyzed as in Table II.

TABLE I

Characterization data of the compounds 1–9

Comp. No.	m.p. °C[a]	Yield %[b] Colour	Mol. Formula	Analysis Calcd./Found C	H	N	S
1	278-79	80 Yellow	$C_{13}H_7N_3O_2S$	57.99 57.78	2.60 2.51	15.61 15.50	11.90 11.81
2	360	90 Yellow	$C_{13}H_8N_4OS$	58.20 58.20	2.98 2.93	20.89 20.86	11.94 11.89
3[c]	234-35	70 Pale yellow	$C_{13}H_7N_4SCl$	54.45 54.32	2.44 2.46	19.54 19.42	11.16 11.21
4	324-25	75 Yellow	$C_{13}H_8N_4S_2$	54.92 54.83	2.81 2.73	19.71 19.67	22.53 22.45
5	280-81	85 Yellow	$C_{13}H_{10}N_6S$	55.31 55.42	3.54 3.60	29.78 29.68	11.34 11.23
6	220-21	70 Yellow	$C_{14}H_{10}N_4S_2$	56.37 56.26	3.35 3.29	18.79 18.62	21.47 21.36
7	281-82	70 Yellow	$C_{19}H_{13}N_5S$	66.47 66.35	3.79 3.68	20.40 20.53	9.32 9.26
8	274-75	60 Yellow	$C_{15}H_{13}N_5S$	61.00 60.94	4.40 4.52	23.72 23.64	10.84 10.72
9	330	65 Lemon yellow	$C_{15}H_9N_5OS$	58.63 58.53	2.93 3.10	22.80 22.86	10.42 10.37

(a) All compounds were recrystallized from ethanol 95% except 2 which was recrystallized from acetic acid.

(b) After recrystallization.

(c) Cl; Calcd 12.20; Found 12,30.

*2-Methyl-4-triacetylhydrazino-pyrimido[4',5':4,5]thieno[2,3-***b***]quinoxaline* (11): A mixture of 5 (0.57 g, 0.002 mol) and acetic anhydride was refluxed for 3 hr. The solid separated was recrystallized and analyzed as in Table II.

*2-(3,4-Dihydro-2-methylpyrimido[4',5':4,5]thieno[2,3-***b***]quinoxaline 4-yl)phthalazin-1,4(3H)dione* (12): A mixture of 5 (0.57 g, 0.002 mol) and phthalic anhydride (0.296 g, 0.002 mol) in acetic acid (20 ml) was refluxed for 3 hr. The separated solid was recrystallized and analyzed as in Table II.

*2-Methyl-4(3,5-dimethyl-pyrazol-l-yl)pyrimido[4',5':4,5]thieno[2,3-***b***]quinoxaline* (13): A mixture of 5 (0.57 g, 0.002 mol) and acetylacetone (0.005 mol) in ethanol (20 ml) was refluxed for 2 hr. The separated solid was recrystallized and analyzed as in Table II.

TABLE II

Characterization data of the compounds 10–20

Comp. No.[(a)]	m.p. °C	Yield %[(b)] Colour	Mol. Formula	Analysis Calcd./Found C	H	N	S
10a	239-240	85 Orange	$C_{20}H_{14}N_6S$	64.86 64.74	3.78 3.64	22.70 22.63	8.64 8.52
10b	320	80 Yellow	$C_{21}H_{16}N_6OS$	63.00 62.78	4.00 3.92	21.00 20.91	8.00 7.90
10c	325	75 Yellow	$C_{20}H_{13}N_7O_2S$	57.83 57.92	3.13 3.24	23.61 23.53	7.71 7.62
11	224-225	70 Yellow	$C_{19}H_{16}N_6O_3S$	55.88 55.71	3.92 4.10	20.58 20.47	7.84 7.71
12	245-246	57 Yellow	$C_{21}H_{12}N_6O_2S$	61.16 60.95	2.91 2.86	20.38 20.25	7.76 7.69
13	294-295	60 Yellow	$C_{18}H_{14}N_6S$	62.42 62.45	4.04 4.13	24.27 24.17	9.24 9.11
14	325-326	70 Red	$C_{14}H_8N_6S_2$	51.85 51.95	2.46 2.52	25.92 25.92	19.75 19.62
15	169-170	75 Reddish	$C_{16}H_{12}N_6S_2$	54.54 54.65	3.40 3.32	23.86 23.71	18.18 18.02
16	255-256	63 Yellow	$C_{20}H_{12}N_6S$	65.21 65.14	3.26 3.19	22.82 22.84	8.69 8.56
17	260	65 Red	$C_{14}H_8N_6S$	57.53 57.54	2.73 2.69	28.76 28.67	10.95 10.82
18	289-290	55 Brownish	$C_{14}H_8N_6OS$	54.55 54.49	2.60 2.64	27.27 27.18	10.39 10.32
19	270-271	60 Red	$C_{18}H_{14}N_6O_2S$	57.14 54.02	3.70 3.59	22.22 22.12	8.46 8.31
20	295-296 (dec.)	65 Brown	$C_{13}H_7N_7S$	53.24 53.16	2.38 2.30	33.44 33.29	10.92 10.86

(a) All compounds were recrystallized from ethanol 95% except 11,12 and 16 which were recrystallized from acetic acid.

(b) After recrystallization.

*3-Mercapto-5-methyl-2-triazolo[4",3":1',6']pyrimido[4',5':4,5]thieno[2,3-**b**]quinoxaline* (14): A mixture of 5 (0.57 g, 0.002 ml) and carbon disulphide (10 ml) in dry pyridine (15 ml) was refluxed for 4 hr. The solid separated on water addition was recrystallized and analyzed as in Table II.

*5-Methyl-3-ethylthio-s-triazolo[4",3":1',6']pyrimido[4',5':4,5]thieno[2,3-**b**]quinoxaline* (15): A mixture of 14 (0.065 g, 0.002 mol) and fused sodium acetate in ethanol and ethyliodide (10 ml) was stirred for 1 hr. The solid separated on addition of water was recrystallized and analyzed as in Table II.

*5-Methyl-3-phenyl-s-triazolo[4",3":1',6']pyrimido[4',5':4,5]thieno[2,3-**b**]quinoxaline* (16): A mixture of 5 (2.82 g, 0.01 mol) and benzoyl chloride (20 ml) was refluxed for 4 hr. The separated solid was recrystallized and analyzed as in Table II.

*5-Methyl-s-triazolo[4",3":1',6']pyrimido[4',5':4,5]thieno[2,3-**b**]quinoxaline* (17): A mixture of 5 (0.57 g, 0.002 mol) and formic acid (5 ml) in glycerol (20 ml) was refluxed for 3 hr. The separated solid on water addition was recrystallized and analyzed as in Table II.

TABLE III

UV spectral measurements for compounds 4 and 6

Comp.(a) No.	Band 1		Band 2		Band 3		Band 4	
	max_{nm}	max	max_{nm}	max	max_{nm}	max	max_{nm}	max
4	470	$0.4x10^6$	440	$0.5x10^6$	395	$0.96x10^6$	355	$0.92x10^6$
6	400	$0.56x10^6$	355	$2.24x10^6$	345	$2.2 x10^6$	285	$4 x 10^6$

(a) In $CDCl_3$ (5×10^{-5}M).

TABLE IV

Bactericidal and fungicidal activities of selected synthesized compounds

Comp. No.	Zone of inhibition* (nm)							
	B.c.	S.a.	E.c.	K.sp.	P.n.	A.fl.	A.fu.	F.s.
1	6	-	9	-	-	-	-	-
2	-	-	7	6	-	-	-	-
3	7	-	7	-	7	6	6	5
4	-	-	-	6	-	-	-	-
5	6	-	6	9	-	-	-	-
6	6	-	7	-	-	-	12	-
7	-	-	8	9	10	7	10	7
8	6	-	-	9	-	-	-	-
11	6	-	9	9	-	-	-	-
18	-	-	8	9	-	-	-	-

* B.c. = Bacillius cereus; S.a. = Staphylococcus aureus; E.c. = Esherichia coil; K.sp. = Klebsiella sp.; P.n. = Penicillium nigricans; A.fl. = Aspergillus flavas; A.fu. = Aspergillus fumigatus; F.s. = Fusarium solani.; most compounds showed remarkable bactericidal activity with considerable antifungal activity for some, as resulted of agar diffusion test.

*5-Methyl-s-triazolo[4",3":1',6']pyrimido[4',5':4,5]thieno[2,3-***b***]quinoxaline-3(2H)-one* (18): A mixture of 5 (0.57 g, 0.002 ml) and chloroethylformate (3 ml) in dry pyridine (10 ml) was refluxed for 5 hr. The solid separated was recrystallized and analyzed as in Table II.

*3-Ethoxycarbonyl-5-methyl-s-triazolo[4",3":1',6']pyrimido[4',5':4,5]thieno[2,3-***b***]quinoxaline* (19): A mixture of 5 (0.57 g, 0.002 mol) and diethylmalonate (10 ml) was refluxed for 3 hr. The solid separated was recrystallized and analyzed as in Table II.

*5-Methyl-tetrazolo[4",3":1',6']pyrimido[4',5':4,5]thieno[2,3-***b***]quinoxaline* (20): The title compound was prepared by treatment of 5 (0.57 g, 0.002 mol) and hydrochloric acid while dropping with sodium nitrite solution (10 ml) at 0°C and stirred for 30 minutes. The solid separated was recrystallized and analyzed as in Table II.

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