Synthesis and Some Reactions of Quinoxalinecarboazides

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Chlorination of ethyl(quinoxalin-2(1H)one)-3-carboxylate **1** gave ethyl (2-chloroquinoxaline)-3-carboxylate **2;**thionation of **1** by P_2S_5 or **2** by thiourea yielded the same product **3**.Reaction of chloro compound **2** or thiocompound **3** with hydrazine hydrate gave pyrazolylquinoxaline **4.** The reaction of ester **1** with thiourea or hydrazine hydrate afforded pyrimidoquinoxaline **5** or carbohydrazide **6;** the reaction of **6** with carbon disulfide in basic medium followed by alkylation afforded oxadiazoloquinoxaline derivatives **7, 8a,b.** Carboazide **9** was produced by reaction of **5** with nitrous acid. Compound **9** on heating in an inert solvent,with or without amines,in alcohols or hydrolysis in H_2O undergoes Curtius rearrangments to yield **10-13**.Reaction of **13** with thiosemicarbazide gave triazoloquinoxaline **14** which on reaction with alkylhalides or hydrazine hydrate yielded **15a-c** while hydrolysis of **13** gave 3-aminoquinoxalinone **16** which was used as an intermediate to produce **17-20**.

INTRODUCTION

The chemistry of the quinoxaline system continues to attract considerable attention. Quinoxalines exhibit biological activity: pyridoquinoxaline is used as anticonvulsant,[1] and imidazoquinoxaline is used as receptor antagonsis.[2] In this context and in continuation of our work on the synthesis of some heterocyclic compounds containing quinoxaline moiety[3-9] we report the synthesis of some quinoxaline derivatives with potential biological activity.

EXPERIMENTAL

Melting points were determined on a Mel-Temp 11 melting point apparatus and are uncorrected.IR spectra were recorded on a Pye-Unicam SP3-100 spectrophotometer using KBr pellets. ^{1}H NMR spectra were measured on a Varian390-90MHz NMR spectrometer in the suitable deuterated solvent,using TMS as internal standard. Elemental analyses were performed on a Perkin-Elmer 240C microanalyzer. Spectral data are listed in Tables 1 and 2.

3-Ethoxycarbonyl-quinoxalin-2(1H)thione (3)

A mixture of **1** (0.015 mol) and P_2S_5 (0.017 mol) in pyridine (20 mL) was refluxed for 4 hr,then allowed to cool .The solid product was collected and recrystallized from ethanol as red crystals.

1,2H-(Pyrazolo[4,5-b]quinoxaline)-3-one (4)

A mixture of **2** or **3** (0.01 mol) and hydrazine hydrate (4 mL) in pyridine (15 mL) was refluxed for 4 hr and then allowed to cool.The solid product was collected and recrystallized from ethanol as yellow crystals.

1,2,3,4 Tetrahydro-4-oxo-Pyrimido[4,5-b]quinoxalin-2-thione (5)

A mixture of **1** (0.01 mol) and thiourea (0.012 mol) was refluxed in sodium ethoxide (0.5g Na/20 mL abs.ethanol) for 2 hr,the solid product which produced on heating was collected and recrystallized from acetic acid as pale yellow crystals.

3-Carbohydrazide-quinoxalin-2(1H)-one (6) Ref. [7].

3-(3'-Mercapto-1',2',4'-oxadiazol-5'-yl)quinoxalin-2(1H)-one (7)

A mixture of **6** (0.01 mol) and carbon disulfide (6 mL) in alcoholic KOH(20 mL, 10%) was refluxed for 5 hr,then allowed to cool,and poured into cold water(50 mL) and acidifed with HCl.The solid product was collected and recrystallized from ethanol as yellow crystals.

3-(3'-Alkylthio-1',2',4'-oxadiazol-5'-yl)quinoxalin-2(1H)-one (8a,b)

A mixture of **7** (0.015 mol) and alkyl halides (0.018 mol) and sodium acetate(0.02 mol) in ethanol (30 mL) was heated under reflux for 3 hr, then allowed to cool, and poured into cold water(50 mL) .The solid product was collected and recrystallized from ethanol.

3-Carboazide-quioxalin-2(1H)-one (9): Ref. [7].

Oxazolo[4,5-b]quinoxalin-2(3H)-one (10a)

A sample of compound **9** (0.5 g) in xylene (10 mL) was heated under reflux for 30 min,then allowed to cool.The solid product was collected and recrystallized from ethanol as yel-

Table 1. Melting Points, Yields and Analytical Data of Compounds **3-20**

Comp.No	M.P °C (Yield%)	Formula Mol.Wt	Calculated / found C	H	N	S
3	187	$C_{11}H_{10}N_2O_2S$	56.41	4.27	11.96	13.67
	(68)	234	56.32	4.18	11.78	13.61
4	220-21	$C_9H_6N_4O$	58.06	3.22	30.10	- -
	(75)	186	57.95	3.16	29.89	
5	275	$C_{10}H_6N_4OS$	52.17	2.60	24.34	13.91
	(83)	230	52.00	2.51	24.23	13.83
7	290	$C_{10}H_6N_4O_2S$	48.78	2.43	22.76	13.00
	(70)	246	48.63	2.34	22.61	12.89
8a	175	$C_{11}H_8N_4O_2S$	50.76	3.07	21.53	12.30
	(77)	260	50.60	3.00	21.41	12.18
8b	164	$C_{18}H_{12}N_4O_3S$	59.34	3.29	15.38	8.79
	(70)	364	59.21	3.17	15.30	8.69
10a	335	$C_9H_5N_3O_2$	57.75	2.67	22.45	- -
	(90)	187	57.65	2.60	22.34	
10b	340	$C_{17}H_{12}N_6O_3$	58.62	3.44	24.13	- -
	(81)	348	58.56	3.35	24.04	
11a	>360	$C_9H_9N_5O_2$	49.31	4.10	31.96	- -
	(82)	219	49.25	4.00	31.89	
11b	>360	$C_{15}H_{13}N_5O_2$	61.01	4.40	23.72	- -
	(75)	295	61.22	4.37	23.61	
11c	>360	$C_{16}H_{15}N_5O_2$	62.13	4.85	22.65	- -
	(70)	309	62.01	4.83	22.56	
11d	265	$C_{14}H_{16}N_4O_2$	61.76	5.88	20.58	-
	(78)	272	61.57	5.66	20.52	
12a*	140	$C_{14}H_{15}N_4OCl$	57.83	5.16	19.27	- -
	(83)	290.5	57.71	5.04	19.11	
12b	225	$C_{14}H_{16}N_4OS$	58.33	5.55	19.44	11.11
	(70)	288	58.16	5.43	19.29	11.00
12c	285	$C_{14}H_{18}N_6O$	58.74	6.29	29.37	- -
	(80)	286	58.67	6.12	29.25	
13	218	$C_{10}H_9N_3O_3$	54.79	4.10	19.17	- -
	(85)	219	54.60	3.97	19.05	
14	>360	$C_{10}H_8N_6OS$	46.15	3.07	32.30	12.30
	(77)	260	46.00	3.00	32.24	12.13
15a	210	$C_{11}H_{10}N_6OS$	48.17	3.64	30.65	11.67
	(68)	274	48.00	3.54	30.58	11.53
15b	228	$C_{18}H_{14}N_6O_2S$	57.14	3.70	22.22	8.46
	(72)	378	57.00	3.56	22.00	8.35
15c	305	$C_{10}H_{10}N_8O$	46.51	3.87	43.41	- -
	(72)	258	46.38	3.62	43.27	
17	188	$C_{18}H_{12}N_4O_2$	68.35	3.79	17.72	- -
	(65)	316	68.23	3.64	17.60	
18a	340	$C_{15}H_{11}N_3O$	72.28	4.41	16.86	- -
	(70)	249	72.12	4.34	16.76	
18b	355	$C_{15}H_{10}N_4O_3$	61.22	3.40	19.04	- -
	(75)	294	61.15	3.27	18.89	
19	295	$C_{10}H_9N_3O_2$	59.11	4.43	20.68	- -
	(65)	203	59.00	4.32	20.52	
20	325	$C_{10}H_7N_3O$	64.86	3.78	22.70	- -
	(68)	185	64.73	3.56	22.65	

*Cl (calc.12.22, found 12.06 %)

Table 2. Spectroscopic Data of Compounds **3-20**

Compd. No.	IR(ν cm^{-1}) / ^{1}HNMR δ (ppm)
3	3400 (NH),1720 (C=O) and 1210 (C=S). ($CDCl_3$):δ 1.3-1.5 (t, 3H, CH_3), δ 4.1-4.3 (q, 2H, CH_2) δ 7.3-8 (m, 4H, Ar-H) and δ 10.3 (s, 1H, NH).
4	3300 (NH), and 1660 (C=O). (DMSO-d_6): δ 7.5-7.9 (m, 4H, Ar-H) and δ 9.8 (s, 1H, NH).
5	3250, 3150 (NH), 1665 (C=O) and 1220 (C=S). (DMSO-d_6): δ 7.4-8.1 (m,4H,Ar-H) and δ 9.5 (s, 1H, NH).
7	3100 (NH), 1670 (C=O) and 1210 (C=S). (DMSO-d_6): δ 7.6-8 (m, 4H, Ar-H) and δ 9.5 (s, 1H, NH) and δ 11.5 (s, 1H, NH of quinoxaline ring).
8a	3320 (NH), 2950 (CH-aliph.) and 1670 (C=O). ($CDCl_3$): δ 2.3 (s, 3H, CH_3), δ 7.2-7.8 (m, 4H, Ar-H) and δ 11.3 (s, 1H, NH).
8b	3400 (NH), 2970 (CH-aliph.) and 1710, 1670 (2 C=O). ($CDCl_3$): δ 4.1 (s, 2H, CH_2), δ 7.5-8.2 (m, 9H, Ar-H) and δ11.6 (s, 1H, NH).
10a	3300 (NH) and 1685 (C=O). (DMSO-d_6): δ 7.4-7.9 (m, 4H, Ar-H) and δ 9.5 (s, 1H, NH).
10b	3350-3100 (NH) and 1700-1660 (C=O). (DMSO-d_6): δ 7.6-8.3 (m, 8H, Ar-H) and δ 9.5, 11.2 (2s, 2H, 2NH).
11a	3400, 3300, 3200 (NH, NH_2) and 1690, 1660 (2C=O). (CF_3COOD): δ 7.4-8.1 (m, 4H, Ar-H).
11b	3200, 3100 (NH) and 1690, 1700 (2C=O). (DMSO-d_6): δ 7.5-8.1 (m, 9H, Ar-H) and δ 9.5, 11.4 (2s, 2H, 2NH).
11c	3300, 3220 (NH) and 1685, 1660 (2C=O). (DMSO-d_6): δ 2.2 (s, 3H, CH_3), δ 7.4-8.1 (m, 8H, Ar-H) and δ 9.3, 11.6 (2s, 2H, 2NH).
11d	3350, 3200 (NH) and 1700, 1670 (2C=O). (DMSO-d_6): δ 1.4-1.8 (s, 6H, $3CH_2$), δ 3.4 (s, 2H, CH_2) δ 3.7 (s, 2H, CH_2),δ 7.6-8.2 (m, 4H, Ar-H) and δ 9.6, 11.5 (2s, 2H, 2NH).
12a	3300 (NH) and 1670 (C=O). ($CDCl_3$): δ 1.5-1.9 (s, 6H, $3CH_2$), δ 3.3 (s, 2H, CH_2), δ 3.9 (s, 2H, CH_2), δ 7.6-8.2 (m, 4H, Ar-H) and δ 9.5 (s, 1H, NH).
12b	3320 (NH), 1680 (C=O) and 1210 (C=S). (DMSO-d_6): δ 1.5-1.9 (s, 6H, $3CH_2$), δ 3.3 (s, 2H, CH_2), δ 3.7 (s, 2H, CH_2), δ 7.5-7.9 (m, 4H, Ar-H) and δ 9.7, 11.5 (2s, 2H, 2NH).
12c	3400, 3200 (NH, NH_2) and 1670 (C=O). (CF_3COOD): δ1.4-1.7 (s, 6H, $3CH_2$), δ 3.2 (s, 2H, CH_2), δ 3.75 (s, 2H, CH_2), δ 7.3-7.9 (m, 4H, Ar-H).
13	3400, 3150 (NH) and 1720 (C=O). ($CDCl_3$): δ 2.2 (s, 3H, CH_3), δ 7.3-7.9 (m, 4H, Ar-H) and δ 9.5,11.7 (2s, 2H, 2NH).
14	3400-3100 (NH), 1660 (C=O) and 1230 (C=S). (DMSO-d_6): δ 7.3-7.9 (m, 4H, Ar-H) and δ 9.6,11.8 (2s, 2H, 2NH).
15a	3350, 3200 (NH), 2970 (CH-aliph.) and 1670 (C=O). ($CDCl_3$): δ 2.1 (s, 3H, CH_3), δ 7.6-8.1 (m, 4H, Ar-H) and δ 9.4,11.5 (2s, 2H, 2NH).
15b	3300, 3150 (NH), 2950 (CH-aliph.) and 1710, 1660 (2C=O). ($CDCl_3$): δ 4.2 (s, 2H, CH_2), δ 7.5-8.2 (m, 9H, Ar-H) and δ 9.3,11.3 (2s, 2H, 2NH).
15c	3400-3180 (NH,NH_2) and 1660 (C=O). (CF_3COOD): δ 7.4-7.9 (m, 4H, Ar-H).
17	3180 (NH), 1690 (C=O) and 1670 (N=N). (DMSO-d_6): δ 7.1-7.9 (m, 10H, Ar-H), δ 11.6 (s, 1H, NH) and δ 10.3 (s, 1H, OH).
18a	3200 (NH), 1660 (C=O) and 1620 (C=N). (DMSO-d_6): δ 7.3-8.2 (m, 9H, Ar-H), δ 11.6 (s, 1H, NH) and δ 9.5 (s, 1H, CH).
18b	3200 (NH), 1660 (C=O) and 1610 (C=N). (DMSO-d_6): δ 7.5-8.1 (m, 8H, Ar-H), δ 11.3 (s, 1H, NH) and δ 9.7 (s, 1H, CH).
19	3150 (NH) and 1660 (C=O). (DMSO-d_6): δ 2.3 (s, 3H, CH_3), δ 7.2-7.7 (m, 4H, Ar-H) and δ 9.6, 12.3 (2s, 2H, 2NH).
20	2970 (CH-aliph.) and 1600 (C=N). (DMSO-d_6): δ 2.3 (s, 3H, CH_3), δ 7.3-7.9 (m, 4H, Ar-H).

lowish crystals.

N,N'[bis(quinoxalin-2(1H)-one-3-yl)] urea (10b)

A sample of compound **9** (0.5 g) was heated in (20 mL) of water for 3 hr. The solid product was collected and recrystallized from acetic acid as yellow crystals.

3-Semicarbazido-quinoxalin-2(1H)-one (11a)

A mixture of **9** or **10a** (0.01 mol)and hydrazine hydrate(4 mL) in ethanol (15 mL) was refluxed for 2 hr and then allowed to cool.The solid product was collected and recrystallized from ethanol as pale yellow crystals.

3-Phenylsemicarbazido-quinoxalin-2(1H)-one (11b)

A mixture of **9** (0.01 mol) and phenylhydrazine (5 mL) in ethanol (15 mL) was refluxed for 3 hr .The solid product was collected and recrystallized from ethanol as yellow crystals.

3-(*P*-Tolylurea)quinoxalin-2(1H)-one (11c)

A mixture of **9** (0.01 mol) and *p*-toludine (0.01 mol) in ethanol (15 mL) was refluxed for 4 hr. The solid product was collected and recrystallized from ethanol as red crystals.

3-Piperidinocarbonylamino-quinoxalin-2(1H)-one (11d)

A mixture of **9** (0.01 mol) and piperidine (5 mL) in ethanol (20 mL) was refluxed for 3 hr. The solid product was collected and recrystallized from acetic acid as red crystals.

2-Chloro-3-piperidinocarbonylaminoquinoxaline (12a)

A sample of compound **11d** (0.5 g) was refluxed in $POCl_3$ (20 mL) for 3 hr,then allowed to cool, and poured into cold water (50 mL) .The solid product was collected and recrystallized from ethanol as white crystals.

3-Piperidinocarbonylaminoquinoxalin-2(1H)-thione (12b)

A mixture of compound **11d** (0.005 mol) and thiourea (0.01 mol) in ethanol(30 mL) was refluxed for 3 hr, allowed to cool, then the solid product was collected and dissolved in sodium hydroxide (15 mL,10%) followed by acidifaction with HCl . The solid product was collected and recrystallized from ethanol as red crystals.

2-Hydrazino-3-piperidinocarbonylaminoquinoxaline (12c)

The title compound was prepared by treatment of chloro compound **12b**(0.015 mol) and hydrazine hydrate (0.02 mol,99%) in ethanol (25 mL) and refluxed for 2 hr.The solid product was collected and recrystallized from ethanol as pale yellow crystals.

3-Methoxycarbonylamino-quinoxalin-2(1H)-one (13)

A sample of compound **9** (0.5 g) was heated in methanol (20 mL) for 3 hr; the solid product which seperated on heating was collected and recrystallized from methanol as white crystals.

3-(Amino-3'-thio-1',2',4'-triazolo-5'-yl)quinoxalin-2(1H)-one (14)

A mixture of **13** (0.015 mol) and thiosemicarbazide (0.017 mol) in pyridine (20 mL) was refluxed for 3 hr .The solid product was collected and recrystallized from acetic acid as red crystals.

3-(Amino-3'-alkyl(aralkyl)thio-1',2',4'-triazolo-5'-yl)-quinoxalin-2(1H)-one (15a,b)

A mixture of **14** (0.02 mol) and methyl iodide or phenathyl bromide (0.025 mol) in ethanol (40 mL) in presence of fused sodium acetate (1.5 g) was refluxed for 3 hr, by addition of water (35 mL) a solid separated ,which was collected and recrystallized from ethanol as yellow needles.

3-(Amino-3'-hydrazino-1',2',4'-triazolo-5'-yl)quinoxalin-2(1H)-one (15c)

A solution of compound **14** (0.5 g) and hydrazine hydrate (0.01 mol,99%) in ethanol (25 mL) was refluxed for 6 hr.The hot reaction mixture was filtred , then cooled and the resulting solid was dried and recrystallized from ethanol as pale yellow crystals.

3-Aminoquinoxalin-2(1H)-one (16) Ref. [11].

3-(Quinoxalin-2(1H)-one-yl)-azo-β-naphthol (17)

The title compound was prepared by treatment of **16** (0.015 mol) with hydrochloric acid (20 mL) while adding dropwise sodium nitrite solution (20 mL) at -5°C and stirring for one hour, β-naphthol (0.015 mol) was added to the reaction mixture. The solid product was collected and recrystallized from ethanol /acetic as pale red crystals.

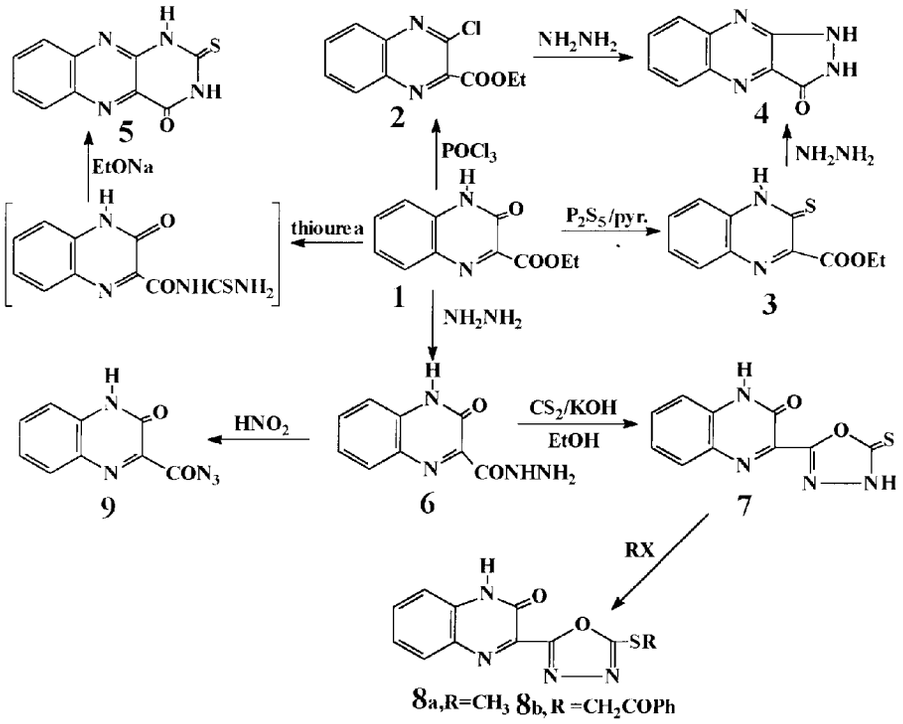
3-Aryldeneamino-quinoxalin-2(1H)-one (18a,b)

A mixture of **16** (0.025 mol) and aromatic aldehydes (0.025 mol) in ethanol (30 mL) and a few drops of piperidine was refluxed for 2 hr.The solid product was collected and recrystallized from ethanol .

3-Acetylamino-quinoxalin-2(1H)-one (19)

A sample of compound **16** (0.4 g) was refluxed in acetic anhydride (20 mL) for 5 hr,then allowed to cool.The solid product was collected and recrystallized from ethanol as yellowish crystals.

Scheme I



2-Methyl-oxazolo[4,5-b]quinoxaline (20)

A sample of compound **19** (0.3 g) was refluxed in $POCl_3$ (20 mL) for 5 hr,then allowed to cool, and poured into ice/water(100 g). The solid product was collected and recrystallized from ethanol as white crystals.

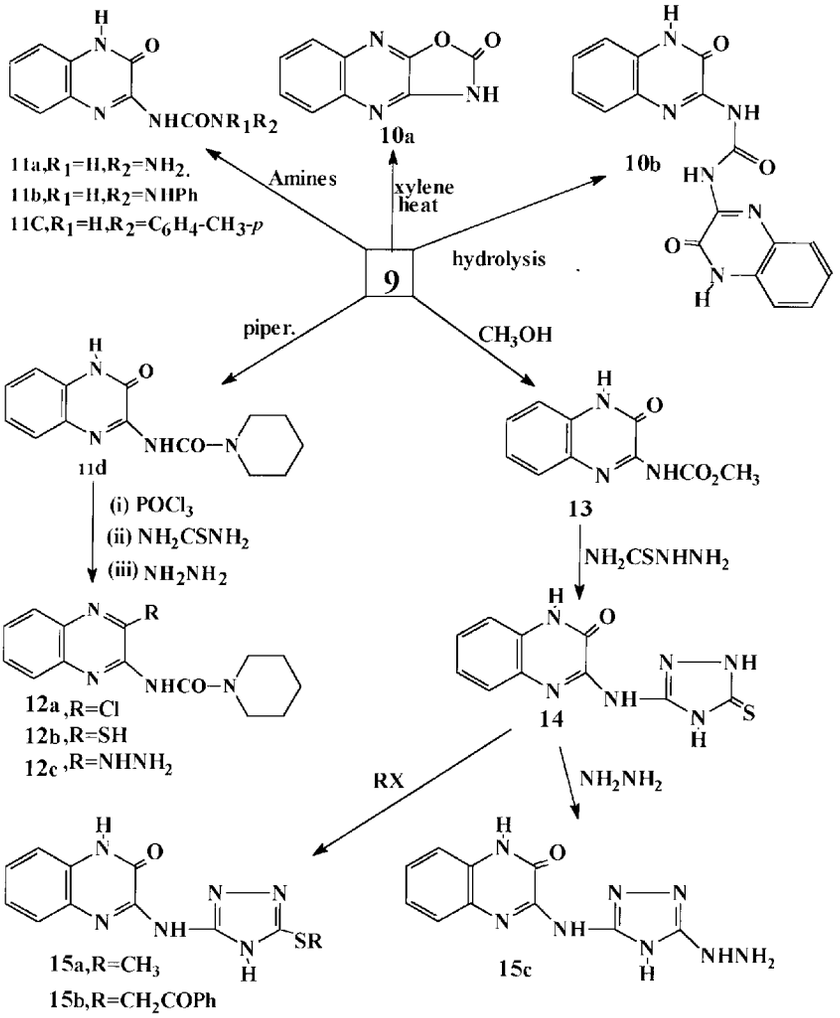
RESULTS AND DISCUSSION

3-Ethoxycarbonyl(quinoxalin-2(1H)-one)[10] **1** was chlorinated by $POCl_3$ or thionated by P_2S_5 and gave 3-ethoxycarbonyl(2-chloroquinoxaline) **2**[11] or 3-ethoxycarbonyl-quinoxalin-2(1H)-thione **3.**The latter compounds **2** or **3** when refluxed with hydrazine hydrate gave 1,2H (pyrazolo[4,5-b]quinoxaline)-3-one **4**, reaction of ester **1** with thiourea followed by ring closure in the presence of sodium ethoxide gave 1,2,3,4,tetrahydro-4-oxo-pyrimido[4,5-b]-quinoxalin-2-thione **5** .Carbohydrazide[7] **6** was refluxed with carbon disulfide in alcoholic KOH to gave thiooxadiazolylquin-quinoxaline **7** which smoothly alkylated in the presence of sodium acetate to afford the corresponding S-alkyl derivatives **8a**,**b**. Carboazide[7] **9** was obtained by diazotization of carbohydrazide **6** (Scheme I).

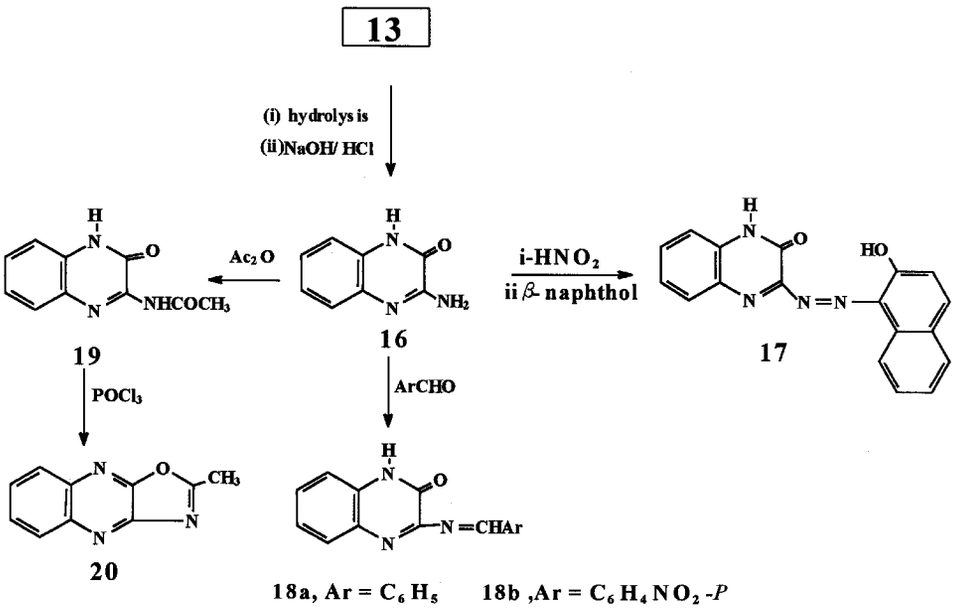
The latter compound **9** was used as a key intermediate to produce other fused heterocyclic compounds: when heated in an inert solvent(e.g.xylene) it undergoes ring-closure to give oxazolo[4,5-b]quinoxaline **10a.** Hydrolysis of **9** by boiling in H_2O yielded urea derivative **10b.** The carboazide **9** on thermal Curtius rearrangments by refluxing with different amines (e.g. hydrazine hydrate,phenyl hydrazine, *p*-toludine, piperidine) or abs. alcohol (e.g.methyl alcohol) gave the corresponding products, semicarbazido derivatives **11a**,**b**,urea derivative **11c,** piperidino derivative **11d** or carbamate **13,** respectively .The semicarbazido derivative **11a** was also produced by reactions of **10a** or **13** with hydrazine hydrate (Scheme II). Chlorination of **11d** by $POCl_3$ gave 2-chloroquinoxaline derivative **12a.**Thionation of the latter chloro compound **12a** by thiourea yielded quinoxalinthione derivative **12b** which was reacted with hydrazine hydrate to produce 2-hydrazino-3-piperidinoquinoxaline derivative **12c** .Condensation of carbamate **13** with thiosemicarbazide in boiling pyridine via initial nucleophilic attack of the amino group to the ester carbonyl without attack at the Carbonyl of the pyrazine ring followed by cyclization to give triazolylquinoxaline[9] **14** which was alkylated or hydrazonated to yield the corresponding S-alkyl (S-aralkyl)or hydrazino derivatives **15a**,**b** ,**15c,** respectively (Scheme II).

3-Aminoquinoxalin-2(1H)one[12] **16** was obtained when carbamate **13** was heated with alcoholic sodium hydroxide (10%).Diazotization of aminoquinoxaline **16** by nitrous acid followed by coupling with β-naphthol yielded 3-(quinoxalin-2(1H)one-yl)-azo-β-napthol **17**. Condensation of aminoquinoxalinone **16** with aromatic aldehydes gave the corresponding Shiff base **18a**,**b**. Finally acylation of **16** through

Scheme II



Scheme III



boiling in acetic anhydride afforded 3-acetylaminoquinoxalinone **19** which was cyclized to 2-methyl-oxazolo-[4,5,-b]quinoxaline **20** by refluxing with $POCl_3$ (Scheme III).

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Key Words

Azide; Oxazoloquinoxaline; Triazolo; Pyrimidoquinoxaline.

REFERENCES

1. Lonard, J.; Susan,A. *J. Med. Chem*. **1995,** *38*, 3720.
2. Lone, J. (11 Feb **1994**, patent); *C. A*. **1996,** *124*, 8850b.
3. Badr, M. Z. A.; Mahgoub, S. A.; Moustafa,O. S.; Geies A. A. *Phosphorus, Sulfur and Silicon*. **1993,** 79, 77.
4. Moustafa, O. S.; Bachiet, E. A.; Badr, M. Z. A. *Afinidad* **1998,** *476*, 285.
5. Moustafa, O. S.; Badr, M. Z. A. *Phosphorus,Sulfur and Silicon*. **1996,** *119*, 127.
6. Moustafa, O. S. *Phosphorus, Sulfur and Silicon*. **1997,** *131*, 49.
7. Badr, M. Z. A.; Mahgoub, S. A.; Atta, F. M.; Moustafa,O. S. Abd-El-Latif, F. M. *J. Indian Chem. Soc*. **1994,** *71*, 617.
8. Moustafa, O. S. *Phosphorus, Sulfur and Silicon*.**1999**, *148*, 131.
9. Moustafa, O. S. *Bull. Fac. Sci. Assiut, Univ*. **1995,** 24(I-B), 289.
10. Gowenlock, A. H.; Newbold, G. T.; Spering, F. S. *J. Chem. Soc*. **1945,** 622.
11. Fernandes, P. S.; Sonar.T. M. *J. Indian Chem. Soc*. **1986**, 427-429.
12. Stevens, J. R.; Pfister, K.; Wolf, F. J. *J. Amer. Chem. Soc*. **1946,** *68,* 1035.