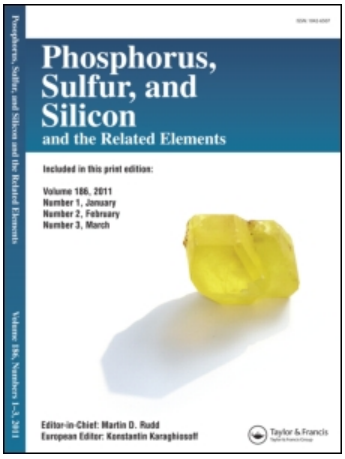

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A COMPARATIVE STUDY OF 4-THIOXO-(IMIDAZOLIDINES AND OXAZOLIDINES) AND SOME NUCLEOPHILIC REAGENTS

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A COMPARATIVE STUDY OF 4-THIOXO-(IMIDAZOLIDINES AND OXAZOLIDINES) AND SOME NUCLEOPHILIC REAGENTS

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The imidazolidines (II) were reacted with amines, H_2S and o-phenylenediamines to give 4-substituted imino derivatives (VI), thiohydantoin (VII) and 1-phenyl-3 -substituted-1H-imidazo[4,5-b]-quinoxaline-2-(3H)-ones(XIII), respectively. Interaction of the oxazolidines (V) with amines, o-phenylenediamines and o-aminophenol caused fission of the oxazole ring to produce (XIV, XVII & XIX) respectively.

Keywords: Imidazolidines; Oxazolidines; Thiohydantoin and Imidazoquinoxaline

Cyanothioformamides[1–3] which contain a potentially nucleophilic nitrogen atom α- to a cyano group are versatile reagents and find extensive applications in the synthesis of heterocyclic compounds such as imidazoles[4], oxazoles[5] and thiazoles[6]. In view of interest in the chemistry of activated nitriles[7] and cyanothioformamides[8–10], the synthesis of novel imidazolidines, oxazolidines and a comparative study between their behavior towards some nucleophilic and binucleophilic reagents are reported here.

Thus, cyanothioformainides (Ia-c & g) were reacted with different isocyanates to give 5-imino-4-thioxo-2-imidazolidinones (IIa-g). Hydrolyses of (IIa,b&d) by EtOH/HCI gave 2,5-dioxoimidazolidine-4-thiones (IIIa-c). Also, interaction of (Ia,b&f) with various aldehydes furnished

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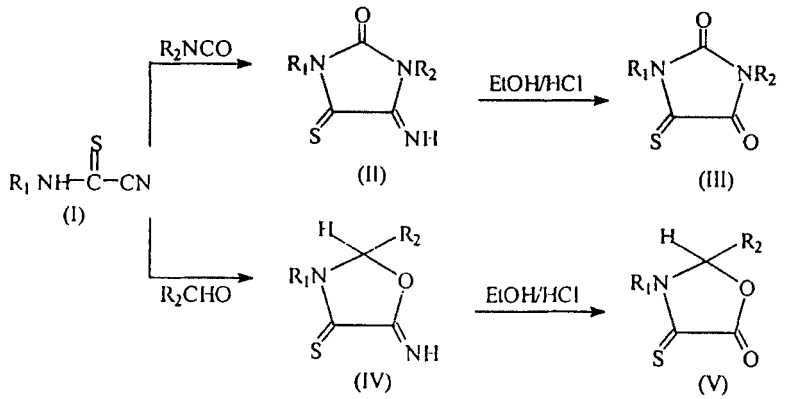
5-imino-4-oxazolidinethiones (IVa-c) which were hydrolysed to 4-thioxo-5-oxazolidinones (Va-c) (Scheme 1).



Ia; $R_1 = CH_3$
b; $R_1 = C_6H_5$
c; $R_1 = C_6H_4CH_3$—p
d; $R_1 = C_6H_4OCH_3$—o
e; $R_1 = C_6H_4OCH_3$—p
f; $R_1 = C_6H_4Cl$—p
g; R_1 = α-naphthyl

SCHEME 1

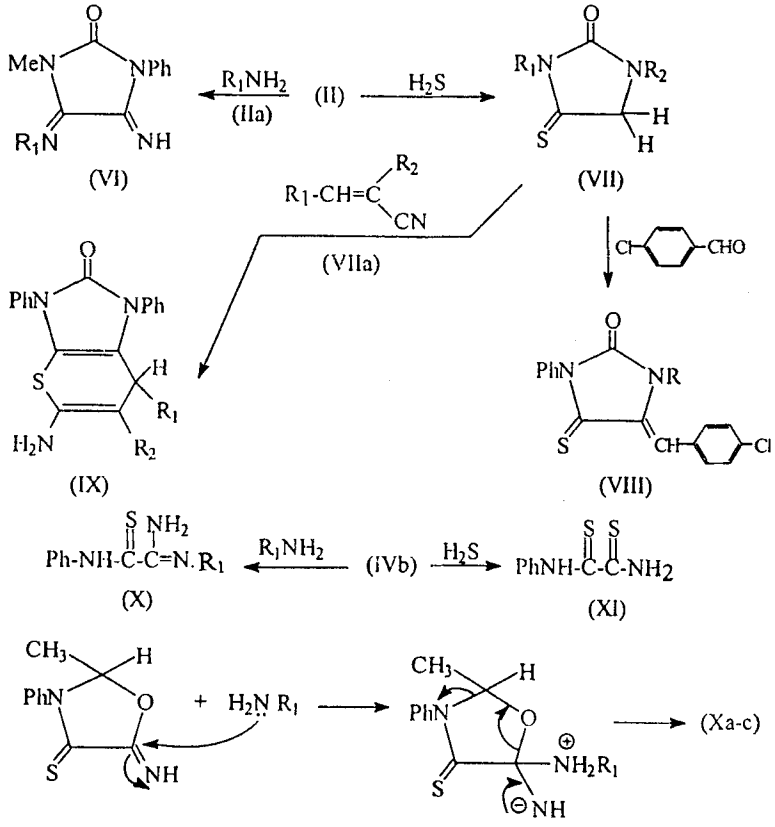
Interaction of (IIa) with different amines furnished 5-imino-4-substituted imino-2-imidazolidinones (VIa-d) (Scheme-2).

Compounds (IIb,e & g) reacted readily with excess H_2S as another nucleophile to give thiohydantoin[2] (VIIa-c) which was confirmed by its reaction with p-chlorobenzaldehyde to furnish 5-arylidine derivatives (VIIIa,b). Another piece of evidence for the thiohydantoin structure was arrived at from its reaction (VIIa) with substituted cinnamonitriles to yield 4H-thiopyrano-[2,3-d]-imidazolidinones (IXa-c). The structure (IX) was favored over the other isomer 2H-thiopyran derivative on basis of its ^{1}HNMR which revealed a singlet at δ=4.7 ppm corresponding to 4H-thiopyran[11] (Scheme 2).

Interaction of (IVb) with aromatic amines caused fission of the oxazole ring to give 2-arylimino-2-amino-N-phenylthioacetamide (Xa-c). The mechanism has been illustrated in scheme 2.

In a similar way H_2S opened the oxazole ring in (IVb) and yielded phenyldithioxamide (XI).

Interaction of (IIIa) with arylamines produced 4-arylimino-2,5-imidazolidinediones (XIIa-c). Condensation of (IIa) with o-phenylenediamine or



SCHEME 2

its derivatives as a binucleophile undergo cyclocondensation to give 3-methyl-1-phenyl-lH-imidazo[4,5-b]quinoxaline-2-(3H)-ones (XIIIa-c), (Scheme 3). In case of o-phenylenediamine itself, there are no isomers, but in the case of its p-methyl or p-chloro- derivatives the structure must be one of two isomers. The methyl group or the chlorine atom will favor structure (XIII) over the other isomer. Aromatic amines attacked the oxazole ring of (Vb) and opened it to produce N-aryl-2-phenylamino-2-thioacetamides (XIVa-c), the mechanism is similar to those discussed above. Similarly, interaction of (Vb) with o-phenylenediamine and its p-methyl derivative caused opening of the oxazole ring and recyclized it to give products which were expected to have one of the following structures

(XV-XVIII), (Scheme 3). The obtained products were found to be sulfur free which excluded structures (XV & XVIII), also ^{1}HNMR spectra of these compounds exhibited neither a quartet methine nor a doublet methyl signal which excluded structure (XVI). IR, ^{1}HNMR, mass spectra and elemental analyses of the obtained products were compatible with the quinoxaline derivative (XVII). The product that was obtained from o-phenylenediamine itself has no isomeric structures (XVIIa), but that obtained from its p-methyl derivative may be one of two structural isomers: 2-hydroxy-3-phenylamino-6-methylquinoxaline or 2-hydroxy-3-phenylamino-7-methylquinoxaline. The authors favor the first one (XVIIb) on the basis that the amino group in the p-position to the methyl group will be more reactive and will react first with the carbonyl group.

Attempted interaction of the oxazole (Vb) with o-aminophenol hoping to obtain another cyclic structure of type (XX or XXI) was unsuccessful and instead the intermediate (XIX) was isolated. The non-cyclization of (XIX) can be attributed to the phenolic (OH) which is a weak nucleophile, (Scheme 3).

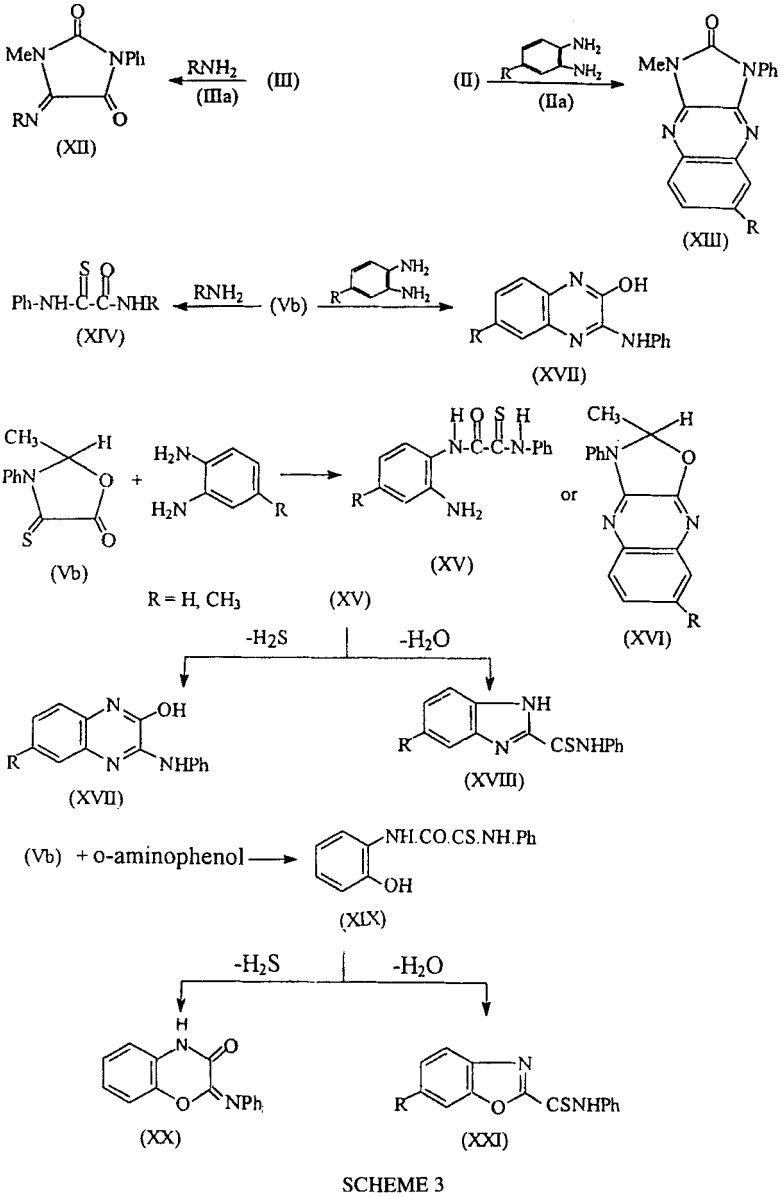
EXPERIMENTAL

Melting points are uncorrected. Elemental analyses were carried out in the microanalytical laboratories of the Faculty of Science, Cairo University. IR spectra (KBr) were measured on a Shimadzu IR 440 spectrophotometer, ^{1}HNMR spectra on a JEOL FX 90Q (90 MHz) spectrophotometer and mass spectra on a Shimadzu GC-MS-QP 1000 EX spectrophotometer using a direct-inlet system.

Cyanothioformamides (Ia-g) were prepared according to reported methods[1–3].

5-Imino-4-thioxo-2-imidazolidinones (IIa-g)

Compound (IIa; R_1 = Me, R_2= Ph) was prepared according to ref. 6 and (IIb; $R_1 = R_2$ = Ph) according to ref. 3, 4. Compounds IIc-g were similarly prepared (75–80%) (Table I). IIe; $\nu_{max/cm^{-1}}$, 3190 (NH), 2990 (aliph. CH), 1715 (CO), 1480, 1225 (N-CS-, amide II, amide I), 6H ($CDCl_3$), 4.0 (3H, 5, OCH_3), 7.2–8 (9H, m, Ar-H), 10.5 (1H,s,NH; eliminated with D_2O), UV (DMF, 2 × 10^{-4} M), λ_{max} 276 nm (ϵ = 8233.5). IIg; $\nu_{max/cm^{-1}}$, 3195 (NH), 1710 (CO), 1490, 1220 (N-CS-), m/z 332 (M^+, 18%), 331(100), 304 (19), 268 (6), 225 (25), 169 (40), 134 (12), 111(50), 75 (60).



SCHEME 3

TABLE I Physical Data for Compounds of Scheme 1*

Compd. No.	R_1	R_2	*M.P. T/°C*	*TLC*		*Formula*	*Analyses Required / Found*			
				Eluent	R_f		*N*		*S*	
IIc	$C_6H_4CH_3$-p	C_6H_5	132–3	E/H (1 : 3)	0.75	$C_{16}H_{13}N_3OS$	14.24	(14.10)	10.85	(10.90)
d	$C_6H_4OCH_3$-o	C_6H_5	145–7	E/H (1 : 3)	0.64	$C_{16}H_{13}N_3O_2S$	13.51	(13.20)	10.29	(10.40)
e	$C_6H_4OCH_3$-p	C_6H_5	110–11	E/H (1 : 4)	0.61	$C_{16}H_{13}N_3O_2S$	13.51	(13.30)	10.29	(10.30)
f	α-naphthyl.	C_6H_5	125–6	E/H (1 : 3)	0.62	$C_{19}H_{13}N_3OS$	12.69	(12.50)	6.67	(6.90)
g	C_6H_5	C_6H_4.Cl-p	138–9	E/H (1 : 3)	0.71	$C_{15}H_{10}N_3OS$ Cl	13.31	(13.50)	10.14	(10.00)
IIIa	CH_3	C_6H_5	180–1	E/H (1 : 3)	0.21	$C_{10}H_8N_2O_2S$	12.73	(12.50)	14.55	(14.70)
c	$C_6H_4OCH_3$-o	C_6H_5	190–1	E/H (1 : 3)	0.7	$C_{16}H_{12}N_2O_3S$	8.97	(8.70)	10.26	(10.30)
IVa	CH_3	C_6H_4.Cl-p	90–91	E/H (1 : 2)	0.7	$C_{10}H_9N_2OS$ Cl	11.64	(11.70)	13.31	(13.50)
b	C_6H_5	CH_3	135–7	E/H (1 : 1)	0.64	$C_{10}H_{10}N_2OS$	13.59	(13.70)	15.53	(15.60)
c	C_6H_4Ci-p	CH_3	137–9	E/H (1 : 2)	0.56	$C_{10}H_9N_2OS$ Cl	11.64	(11.90)	13.31	(13.40)
Va	CH_3	C_6H_4.Cl-p	120–1	E/H (1 : 3)	0.41	$C_{10}H_8NO_2S$ Cl	5.79	(5.90)	13.25	(13.30)
b	C_6H_5	CH_3	155–6	E/H (1 : 1)	0.80	$C_{10}H_9NO_2S$	6.76	(6.70)	15.46	(15.70)
c	C_6H_4Cl-p	CH_3	160–1	E/H (1 : 2)	0.40	$C_{10}H_8NO_2S$ Cl	5.79	(5.90)	13.25	(13.30)

* All the compounds gave satisfactory C & H analyses.
E = ethyl acetate H = n-hexane

2, 5-Dioxoimidazolidine-4-thiones (IIIa-c)

Compound IIIb (R_1=R_2=Ph) was prepared according to the method of ref. 4. Compounds IIIa,c were similarly prepared (60–65%) (Table I). IR spectra revealed the disappearance of ν NH and the appearance of νCO at 1730 cm^{-1}.

5-Imino-4-oxazolidinethiones (IVa-c)

A solution of cyanothioformamide (I; 0.01 mol) in dry ether (20 ml) was treated with the requisite aldehyde (0.012 mol) and triethylamine (3 drops). The reaction mixture was magnetically stirred for 15 minutes and the obtained solid was recrystallized from ethanol to give IVa-c (60–65%) (Table I). IVa; $\nu_{max/cm^{-1}}$ 3150 (NH), 1670 (C=N), 1470, 1250 (-CS-N< amide II & amide I); δH ($CDCl_3$) 3.3 (3H, S, CH_3), 6.5 (IH, S, C-H), 7.5–7.9 (4H, q, AB system), 9.2 (1H, br.s, NH, eliminated by D_2O).

4-Thioxo-5-oxazolidinones (Va-c)

To a solution of (IVa-c; 0.01 mol) in boiling ethanol (20 ml), conc. HCI (4 ml) was added. The obtained product was recrystallized from ethanol to give Va-c (50–60%) (Table I). Vb $\nu_{max/cm^{-1}}$, 1780 (-CO-O-), 1475 & 1260 (-CS-N< amide II & amide I); δH ($CDCl_3$) 1.60 (3H, d, CH_3), 6.27–6.4 (IH, q, CH), 7.9 (5H, m, Ar-H); m/z 207 (M^+, 44%), 175 (100%).

5-Imino-3-methyl-1-phenyl-4-substitutedimino 2-imidazolidinones (VIa-d)

A mixture of (II; 0.01 mol) and the requisite amine (0.012 mol) in ethanol (30 ml) was heated under reflux (2–3 hr). Concentration of the reaction mixture furnished a product, which was recrystallized from ethanol to give VIa-d *(50–55%)* (Table II). VIb, $\nu_{max/cm^{-1}}$ 3190 (NH), 2950 (CH aliphatic), 1710 (CO), 1660 (C=N), 6H (CD_3COCD_3), 3.2 (3H, S, NCH_3), 5.5 (2H, S, N-CH_2), 7.2–7.9 (1OH, m, Ar-H), 8.8 (1H, br.s, NH, eliminated with D_2O), m/z 292 (M^+, 100%), 277 (4.4), 204 (7.1) & 119 (5.2).

1 3-Diaryl-4-thiohydantoin derivatives (VIIa-c)

To a suspension of (II; 0.01 mol) in 30 ml absolute ethanol, 0.5 ml of triethylamine was added then a stream of H_2S was passed in until the solu-

tion became clear. The obtained product was recrystallized from benzene to give VIIa-c; (VIIa[2]; R_1=R_2=Ph) (50–55%) (Table II). VIIb, $\nu_{max/cm^{-1}}$ revealed the disappearance of ν NH indicating that the amino group was involved in the reduction, 6H ($CDCl_3$) 4.0 (3H, S, OCH_3), *5.1* (2H, S, CH_2), 7.2–8.0 (9H, m, Ar-H), m/z 298 (M^+100%), 299 *(19.5),* 149 (80.6), 139 (39.6), 107 (3.2), 77 (33.6).

5-Arylidine derivatives (VIIIa, b)

A mixture of (VIIa or c; 0.01 mol), p-chlorobenzaldehyde (0.01 mol) and fused sodium acetate (0.1 gm) in Ac_2O, AcOH mixture (10, 20 ml) was refluxed for 2hr. The obtained product was recrystallized from benzene/light petroleum (40–60°) to give VIIIa,b (60%) (Table II). VIIIb, $\nu_{max/cm^{-1}}$ 2950 (CH aliph.), 1690 (CO), 1480, 1280 (-CS-N, amide II & amide I), δH ($CDCl_3$) 6.1 (1H, S, arylidine CH-), 6.8–8 (13H, m, Ar-H). VIIIa, m/z 390 (94.2), 389 (100; base peak), 391 (49.5), 392 (46.1), 393 (21), 77 (23.6).

Thiopyranoimidazolidinones (IXa-c)

A mixture of thiohydantoin (VIIa; 0.01 mol), substituted cinnamonitrile (0.01 mol) and piperidine (0.5 ml) in absolute ethanol (30 ml) was refluxed for 3hr. The reaction mixture was then cooled, poured on to crushed ice, neutralized with dil. HCl and the obtained product was recrystallized from EtOH/H_2O to give IXa-c (55%) (Table II). IXa, $\nu_{max/cm^{-1}}$ 3415, 3300 (NH_2), 2175 (-C≡N), 1700 (C=O), δH ($CDCl_3$) 4.7 (1H, s, 4-H thiopyran), 4.9 (2H, s, NH_2, eliminated with D_2O), 7.3–7.9 (15H, m, Ar-H), m/z 422 (M^+, 18.7), 77 (100%), 423 (16.7), 424 (6), 425 (1.9), 427 (6.3), 428 (5.7), 375 (73.4), 357 (28.2), 355 (61.5), 154 (20.4).

2-Arylimino-2-amino-N-phenyl-thioacetamide (Xa-c)

A solution of (IVb; 0.01 mol) in ethanol (30 ml) was treated with the requisite amine (0.012 mol) then refluxed for 3hr. The solvent was concentrated and the obtained product was recrystallized from ethanol to give Xa-c (50%) (Table II). Xa, $\nu_{max/cm^{-1}}$ 3400, 3300 (NH_2), 3100 (NH), 1640 (C=N), 1480, 1300 (-CS-N), 6H ($CDCl_3$) 6.0–6.5 (2H, br.s, NH_2, eliminated with D_2O), 7.4–7.7 (5H, m, Ar-H), 7.0–7.3, 8.2–8.4 (4H, q, AB system), 12.2 (1H, br.s, NH, eliminated with D_2O). m/z 289 (M^+; 55.8), 290 (23.8), 291(19.9). 271(27.4), 155(33.9), 153 (100), 104 (93.4), 77 (98.7), 51(71.4).

TABLE II Physical Data for the Compounds of Scheme 2*

Compd. No.	R_1	R_2	*M.P. T/°C*	*TLC*		*Formula*	*Analyses Required / Found*	
				Eluent	R_f		*N*	*S*
VIa	C_6H_{11}-cyclo		130–1	C/M (1 : 5)	0.76	$C_{16}H_{20}N_4O$	19.72 (19.50)	
b	C_6H_5-CH_2-		90–1	E/H (1 : 3)	0.42	$C_{17}H_{16}N_4O$	19.18 (19.30)	
c	C_6H_4-CH_3-p		133–4	E/H (1 : 4)	0.50	$C_{17}H_{16}N_4O$	19.18 (19.20)	
d	C_5H_4-N-p		200–1	E/H (1 : 4)	0.55	$C_{15}H_{13}N_5O$	25.09 (25.00)	
VIIb	$C_6H_4OCH_3$-p	C_6H_5	195–6	E/H (1: 3)	0.56	$C_{16}H_{14}N_2O_2S$	9.39 (9.50)	10.74 (10.90)
c	C_6H_5	C_6H_4.Cl-p	225–6	E/H (1 : 3)	0.51	$C_{15}H_{11}N_2OSCl$	9.26 (9.30)	10.58 (10.50)
VIIIa	C_6H_5		190–1	E/H (1 : 3)	0.72	$C_{22}H_{15}N_2OSCl$	7.17 (7.30)	8.19 (8.00)
b	C_6H_4Cl-p		230–1	E/H (1 : 3)	0.38	$C_{22}H_{14}N_2OSCl_2$	6.59 (6.70)	7.53 (7.50)
IXa	C_6H_5	CN	165–6	E/H (1 : 3)	0.40	$C_{25}H_{18}N_4OS$	13.27 (13.50)	7.58 (7.70)
b	$C_6H_4OCH_3$-p	CN	110–1	E/H (1 : 3)	0.31	$C_{26}H_{28}N_4O_2S$	12.39 (12.50)	7.08 (7.00)
c	C_6H_4-$N(CH_3)_2$-p	$CO_2C_2H_5$.	100–1	E/H (1 : 3)	0.40	$C_{29}H_{20}N_4O_3S$	10.94 (11.00)	6.25 (6.20)
Xa	C_6H_4-Cl-p		92–3	E/H (1 : 2)	0.80	$C_{14}H_{12}N_3SCl$	14.51 (14.30)	11.05 (11.00)
b	C_6H_4-Br-p		215–6	E/H (1 : 4)	0.32	$C_{14}H_{12}N_3SBr$	12.57 (12.70)	9.58 (9.30)
c	$C_6H_4OCH_3$-p		200–1	E/H (1 : 2)	0.70	$C_{15}H_{15}N_3OS$	14.74 (14.90)	11.23 (11.00)

* All the compounds gave satisfactory C & H analyses.
C = chloroform E = ethyl acetate H = n-hexane M = methanol

Formation of phenyldithioxoamide (XI)

Through a suspension of (IVb; 0.01 mol) in 20 ml of absolute ethanol containing 0.5 ml of triethylamine was passed a stream of hydrogen sulfide The reaction mixture became clear and darkened slightly. Dilution with an equal volume of water gave (XI), m.p. and m.m.p. with authentic sample[12] 98–99°C.

3-Methyl-1-phenyl-4-arylimino-2,5-imidazolidinediones (XIIa-c)

A solution of (IIIa; 0.01 mol) in ethanol (30 ml) was treated with the appropriate amine and refluxed for 3hr. Concentration and recrystallization of the obtained product from ethanol gave XIIa-c (65%) (Table III). IR spectra showed the absence of νCS and the presence of ν C=N at 1650 cm^{-1}.

3-Methyl-1-phenyl-1H-imidaza[4, 5-b]quinoxaline-2-(3H)ones (XIIIa-c)

A mixture of (IIa; 0.01 mol) and o-phenylenediamine or its derivatives (0.012 mol) in ethanol (30 ml) was refluxed for 24 hr. The obtained product was recrystallized from ethanol to give XIIIa-c (60%) (Table III). IR spectrum of XIIIb exhibited niether ν CS nor ν NH, δH ($CDCl_3$), 2.5 (3H, 5, Ar-CH_3), 3.5 (3H, 5, N-CH_3), 7.2–7.8 (8H, m, Ar-H).

N-Aryl-2-phenylamino-2-thioxoacetamide (XIVa-c)

Were prepared by the same procedure used for compounds (X). XIVc $\nu_{max/cm^{-1}}$ 3260 (NH), 1675 (C=O), 1530, 1250 (N-CS-), δH($CDCl_3$), 3.9 (3H,s,OCH_3), 7.1–8.5 (9H, m, Ar-H), 12.1 (2H, br.s, 2xNH,eliminated with D_2O), m/z 286 (M^+, 100%), 136 (80.4), 104 (49.4), 77 (79.7), 51(40.2).

2-Hydroxy-3-phenylaminoquinoxalines (XVIIa,b)

A mixture of (Vb; 0.01 mol) and o-phenylenediamine or its p-methyl derivative (0.01 mol) in ethanol (30 ml) was refluxed for 10 hr. Concentration gave a product which was recrystallized from ethanol to give XVIIa,b (50%) (Table III). XVIIb $\nu_{max/cm^{-1}}$ broad band around 3390 (OH, NH), 1650 (>C=N), 6H ($CDCl_3$) 2.5 (3H, s, CH_3), 7.2–8.4 (8H, m, Ar-H), 1.6 (1H, s), 8.6 (1H, br.s, eliminated with D_2O, OH, NH), m/z 251 (M^+, 73%), 250 (100), 222(31.3), 77(12), 51(13).

TABLE III Physical Data for the Compounds of Scheme 3*

Compd. No.	*R*	*M.P. T/°C*	*TLC*		*Formula*	*Analyses Required / Found*	
			Eluent	R_f		*N*	*S*
XIIa	C_6H_4-CH_3-p	160–1	E/H (1 : 3)	0.61	$C_{17}H_{15}N_3O_2$	14.33 (14.50)	-
b	C_6H_4-OCH_3-p	120–1	C/P (6 : 4)	0.36	$C_{17}H_{15}N_3O_3$	13.59 (13.50)	-
c	C_6H_4-Br-p	145–1	E/H (1 : 3)	0.61	$C_{16}H_{12}N_3O_2Br$	11.73 (11.90)	-
XIIIa	H	200–1	E/H (1 : 2)	0.89	$C_{16}H_{12}N_4O$	20.29 (20.10)	-
b	CH_3	215–7	E/H (1 : 5)	0.55	$C_{17}H_{14}N_4O$	19.31 (19.50)	-
c	Cl	195–7	E/H (1 : 3)	0.58	$C_{16}H_{11}N_4OCl$	18.04 (18.00)	-
XIVa	C_6H_4-Cl-p	140–1	E/H (1 : 3)	0.75	$C_{14}H_{11}N_2OSCl$	9.64 (9.50)	11.02 (11.00)
b	$C_6H_4CH_3$-p	145–7	E/H (1 : 2)	0.76	$C_{15}H_{14}N_2OS$	10.37 (10.50)	11.85 (11.70)
c	$C_6H_4OCH_3$-p	110–1	E/H (1 : 2)	0.64	$C_{15}H_{14}N_2O_2S$	9.79 (9.70)	11.19 (11.00)
XVIIa	H	235–7	E/H (1 3)	0.49	$C_{14}H_{11}N_3O$	17.72 (17.50)	-
b	CH_3	235–6	E/H (1 : 2)	0.42	$C_{15}H_{13}N_3O$	16.73 (16.50)	-
XIX	-	235–6	E/H (1 : 1)	0.23	$C_{14}H_{12}N_2O_2S$	10.29 (10.30)	11.76 (11.50)

* All the compounds gave satisfactory C & H analyses.
E = ethyl acetate H = n-hexane C = chloroform P = pet. ether 40/60

Interaction of Vb with o-aminophenol

A solution of (Vb; 0.01 mol) in ethanol (20 ml) was treated with o-aminophenol (0.01 mol) and the mixture was refluxed for 12 hr. Concentration furnished a product which was recrystallized from ethanol to give XIX (40%) (Table III), $\nu_{max/cm^{-1}}$ broad band around 3100 (OH, NH), 1670 (CO), m/z 272 (M^+, 10.3%), 109 (100), 254 (31.6), 225 (7.3), 136 (37).

References

[1] Dieckmann, W. and Kammerer, H. : a) Chem. Ber.; 1905, 38, 2977. b) Chem. Ber; 1907, 40, 13737.
[2] Walter, W., Bode, K.D. Justus Leibigs Ann. Chem. 698, 131,1966.
[3] Papadopoulos, B.P.; J. Org. Chem. 1979, 44, 3858.
[4] Keteham, R. and Schaumann, E., J. Org. Chem. 1980, 45, 3748.
[5] Ketcham, R.; Schaumann, E. and Niemer, T., Synthesis 1980, 869.
[6] Ismail, K.; Ketcham, R., Schaumann, E. and Adiwidjaja, G., J. Org. Chem. 1985, 50, 19, 3431.
[7] Ammar, Y.A.; EI-Sharief, A.M.Sh.; Zahran, M.A.; El-Said, M.Z. and El-Said U.H.; J. Chem. Research(S), 1995, 324.
[8] El-Sharief, A.M.Sh., Ketcham, R. and Schaumann, E.; Phosphorus, Sulfur and Silicon, 1989, 36, 83.
[9] Mohamed, A.M. El-Shariet, A.M. Sh.; Ammar, Y.A. and Aly, MM.; Die Pharmazie, 1989,44,H. 11.
[10] Mohamed, Y.A.; Ammar, UY.A.; El-Sharief, A.M.Sh. and Aly, M.M.; J. Chinese Chemical Society, 1990, 37, 511.
[11] Mohamed, Y.A.; Zahran, M.A.; Aly, M.M.; El-Agrody, A.M. and El-Said, U.H., J. Chem. Research(S), 1995, 322.
[12] Kumelj, B. and Tisler, M.; Vestnir Solven Remi. drustra, 5, 69, (1958); C.A. 54, 22426F (1960).