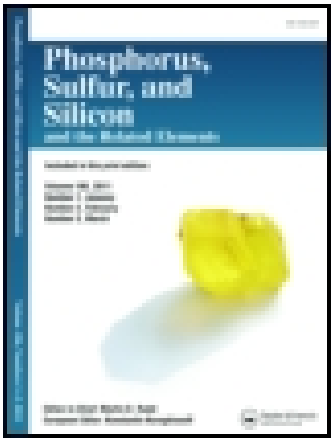

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A COMPARATIVE STUDY BETWEEN IMIDAZOLIDINEIMINOTHIONES AND4-THIOXOIMIDAZOLIDINE-2,5-DIONES TOWARDS SOME NUCLEOPHILIC AND BINUCLEOPHILIC REAGENTS: SYNTHESIS OF SOME NEW IMIDAZO(DIIMINES, DIHYDRAZONES, QUINOXALINES & AZINE) AND DIIMIDAZOLIDINONE

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A COMPARATIVE STUDY BETWEEN IMIDAZOLIDINEIMINOTHIONES AND 4-THIOXOIMIDAZOLIDINE-2,5-DIONES TOWARDS SOME NUCLEOPHILIC AND BINUCLEOPHILIC REAGENTS: SYNTHESIS OF SOME NEW IMIDAZO(DIIMINES, DIHYDRAZONES, QUINOXALINES & AZINE) AND DIIMIDAZOLIDINONE

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Reactions of 5-imino-4-thioxoimidazolidine **(II)** and 4-thioxoimidazolidine-2,5-diones **(III)** with amines, hydrazine hydrate, hydrazine derivatives, o-phenylenediamines and cupper turnings were investigated.

Keywords: Imidazolidineiminothione; imidazoquinoxaline; imidazolidinone azine and diimidazolidinone

INTRODUCTION

A variety of heterocyclic ring closure reactions with cyanothioformamides **I** [1–3] gave rise to imidazoles[4], oxazoles[5], thiazoles[6,7], pyrroles[8] and quinazolinones[9]. A part of our program in ring-closure reaction[10], activated nitriles[11] and the chemistry of cyanothioformamides[12–14]

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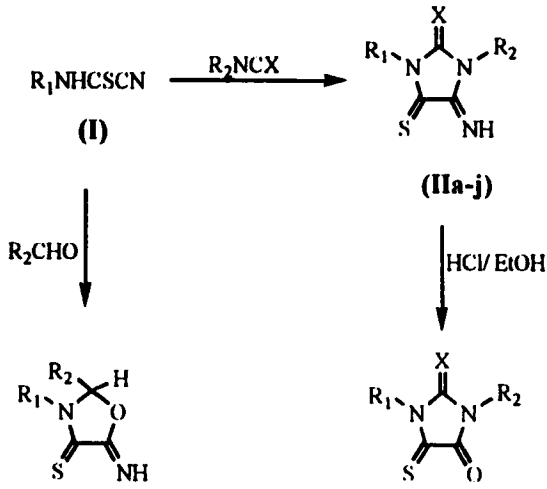
led us to investigate the behavior of the later towards some nucleophilic reagents.

Thus, interaction of **I** with isocyanates or isothiocyanates gave the corresponding imidazolidine iminothiones (**II**; Scheme-1). Imine hydrolyses of **II** furnished 4-thioxoimidazolidine-2,5-dione **III**, Scheme-1. 5-Iminoxazolidine-4-thiones **IV** were obtained[5] through interaction of **I** with aldehydes, and 1-benzoyl-5-iminoimidazolidine-2,4-dithiones **IIi,j** were produced[9] by reacting **I** with benzoyl isothiocyanate.



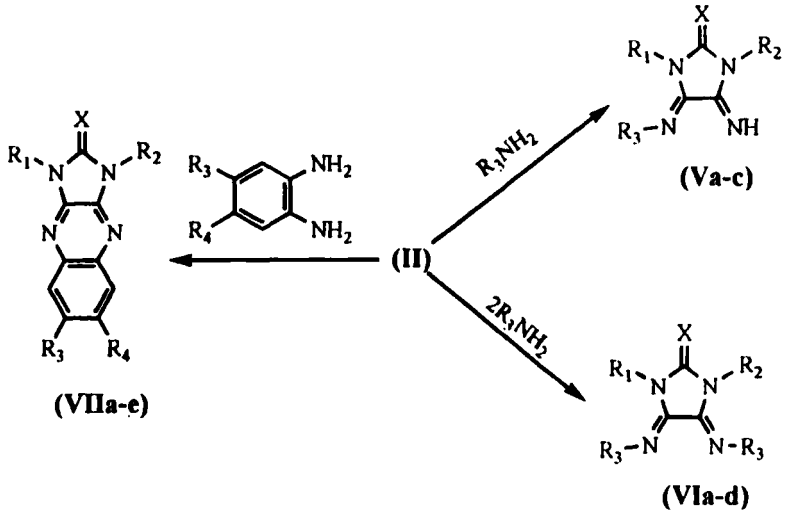
	R_1	R_2	X		R_1	R_2	X
IIa;	CH_3	C_6H_5	O	**IIg;**	C_6H_4Cl-o	C_6H_5	O
b;	CH_3	C_6H_4Cl-m	O	**h;**	C_2H_5	C_6H_4Cl-p	S
c;	C_2H_5	C_6H_5	O	**I;**	C_6H_5	COC_6H_5	S
d;	C_6H_5	C_6H_4Cl-m	O	**j,**	C_6H_4Cl-p.	COC_6H_5	S
e;	$C_6H_4OCH_3$-o	C_6H_5	O	**IIIa;**	C_2H_5	C_6H_5	O
f;	$C_6H_4OCH_3$-p	C_6H_5	O	**b;**	$C_6H_4OCH_3$-o	C_6H_5	O

SCHEME 1

The authors[9,15] carried out a comparative study between imidazolidineiminothiones **IIa-h** with both *N*-benzoylimidazolidineiminothiones **IIi,j** and oxazolidineiminothiones **IV** towards some nucleophilic and binucleophilic reagents.

It was found that the imidazolidine ring in **IIa-h** was still stable while the *N*-benzoylimidazolidine ring in **IIi,j** was opened with the elimination of benzamide molecule. Moreover the oxazolidine ring in **IV** was opened with the elimination of an aldehyde molecule.

As an extention of these investigation a comparison study was made between imidazolidineiminothiones **II** and 4-thioxoimidazolidine-2,5-diones **III** towards some nucleophilic and binucleophilic reagents such as amines (one mole and excess), o-phenylenediamines, hydrazine and its derivatives.



	R_1	R_2	R_3	R_4	X
Va;	CH_3	C_6H_4Cl-m	C_6H_4Cl-o		O
b;	C_6H_5	C_6H_4Cl-m	C_6H_4Cl-m		O
c;	C_6H_5	C_6H_4Cl-m	C_6H_4Br-p		O
VIa;	$C_6H_4OCH_3$-o	C_6H_5	$C_6H_4CH_3$-p		O
b;	$C_6H_4OCH_3$-p	C_6H_5	$C_6H_4CH_3$-p		O
c;	$C_6H_4OCH_3$-p	C_6H_5	$C_6H_4OCH_3$-p		O
d;	$C_6H_4OCH_3$-p	C_6H_5	C_6H_4F-p		O
VIIa;	C_2H_5	C_6H_5	H	H	O
b;	C_2H_5	C_6H_5	H	CH_3	O
c;	C_2H_5	C_6H_5	H	Cl	O
d;	C_2H_5	C_6H_5	NO_2	H	O
e;	C_2H_5	C_6H_4Cl-p	H	H	S

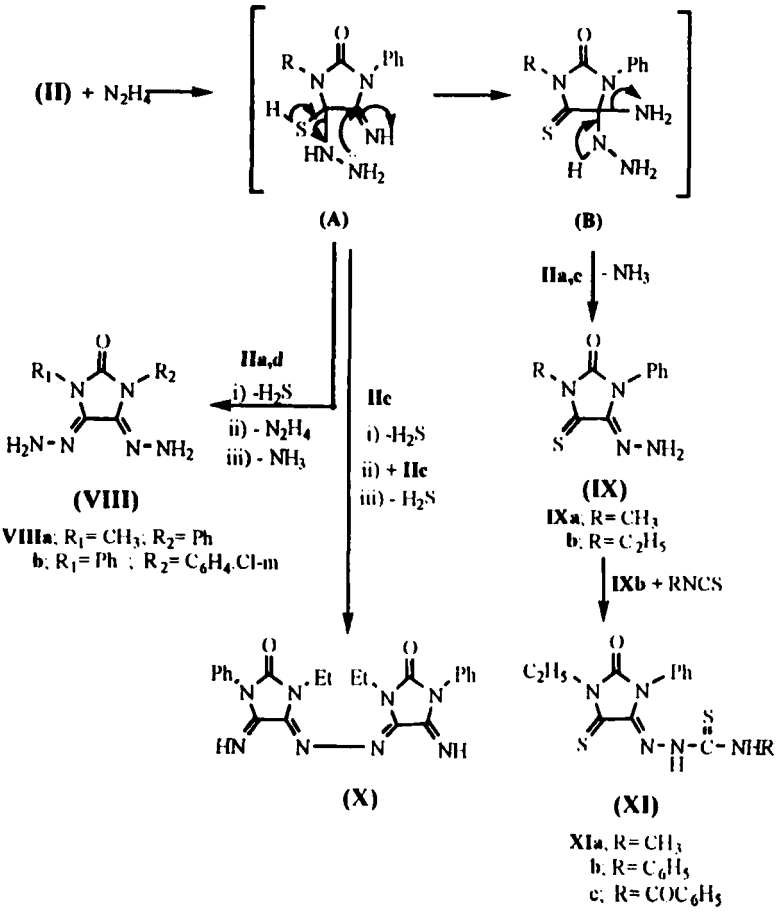
SCHEME 2

Thus, interaction of **II** with one mole of amine in ethanol produced H_2S along with the formation of 4-substituted imino-5-iminoimidazolidine **V**, while using an excess of amines and longer reaction times led to the formation of 4,5-disubstituted iminoimidazolidines **VI** through elimination of H_2S and NH_3. Moreover, condensation of **II** with o-phenylenediamines induced cyclization through elimination of H_2S and NH_3 to afford products with analytical and spectral data compatible with imidazo[4,5-b] quinoxalines **VII**. In the case of o-phenylenediamine, there were no isomers, but the case of (4-methyl-4-chloro and 4-nitro)-1,2-phenylenediamine, the products were one isomer and the authors favour structures **VIIb,c** for 4-methyl and 4-chloro in each and **VIId** (for 4-nitro) (Scheme 2).

Interaction of **IIa** with excess of hydrazine hydrate in ethanol at room temperature furnished a product, which was analysed as the dihydrazone derivative **VIIIa** (through elimination of H_2S and NH_3). On the other hand repating this reaction using equimolar amounts of the reactants furnished an abnormal product which contained sulphur, and was formulated as 5-hydrazono-4-thioxoimidazolidine-2-one **IXa** based on elemental and spectral data. The postulated mechanism can be proceed as described in our publication[16] and which nucleophilic addition of hydrazine to the thioxo group proceeded to give an intermediate **A** which underwent rearrangement to the intermediate **B** followed loss of ammonia to afford **IXa**. On the other hand, upon reaction of **IIc** with hydrazine hydrate under the same conditions, two products could be isolated. The major product was confirmed as 5-hydrazono-4-thioxoimidazolidine derivative **IXb** while the minor one was identified as bis-(3-ethyl-5-imino-2-oxo-1-phenyl-imidazolin-4-yl)azine (**X**). The reaction pathway is thus assumed to involve interaction of the intermediate **A** with another molecule of **IIc** with the elimination of two molecules of H_2S to furnish **X** (Scheme3). In addition, **IId** was reacted with excess of hydrazine hydrate to produce the dihydrazone derivative **VIIIb** (Scheme3).

Compounds (**VIII-X**) were confirmed by elemental and spectral data. The structure of **IX** was also demonstrated by interaction of **IXb** with isothiocyanate to afford the corresponding thiosemicarbazone derivatives **XIa-c** (Scheme-3).

It is a point of interest that although the reaction of the iminothione **II** with one mole of hydrazine hydrate furnished the abnormal product **IX**, interaction of **II** with one mole of hydrazine derivatives such as phenylhydrazine, 2,4-dinitrophenylhydrazine, acetyl or benzoylhydrazine or thi-

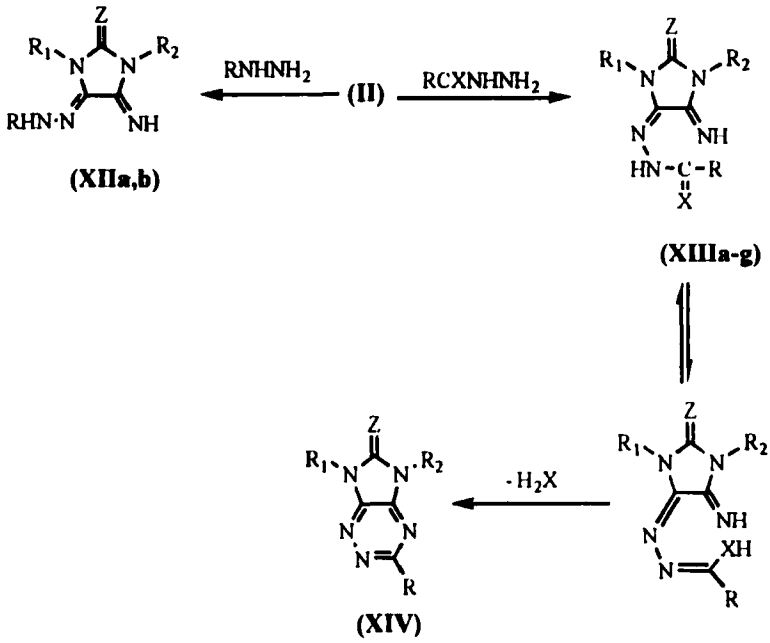


SCHEME 3

osemicarbazide proceeded via elimination of H_2S to produce the normal products 5-imino-4-substituted hydrazono-imidazolidines **XIIa,b** and **XIIIa-f** (Scheme-4).

In the case of acetyl, benzoyl hydrazine or thiosemicarbazide, it was expected to produce the imidazotriazine derivatives **XIV** through furthur cyclization of **XIII**, but unfortunately **XIV** could not be isolated.

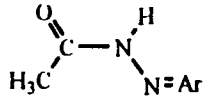
The ^1H NMR spectrum of **XIIIa** in $CDCl_3$ exhibited the presence of two isomers in the ratio of 2:1. The predominate isomer is deduced to have the



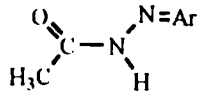
	R	R_1	R_2	X	Z
XIIa;	C_6H_5	C_2H_5	C_6H_5	O	O
b;	$C_6H_3(NO_2)$-2,4	C_2H_5	C_6H_5	O	O
XIIIa;	CH_3	CH_3	C_6H_5	O	O
b;	CH_3	C_2H_5	C_6H_5	O	O
c;	C_6H_5	C_2H_5	C_6H_5	O	O
d;	CH_3	C_6H_4Cl-p	C_6H_5	O	O
e;	NH_2	C_2H_5	C_6H_5	O	O
f;	NH_2	C_2H_5	C_6H_5	S	O
g;	NH_2	C_2H_5	C_6H_4Cl-p	S	S

SCHEME 4

bulkier group in trans position to the carbonyl group[17,18] on the bases that the trans coupling is larger than the cis one[19,20] The coupling constants were identified as J (CH_3-H) = 0.4 Hz (in trans form) and J (CH_3-H)= 0.0 Hz (in cis form). The spectrum of the trans isomer showed signals at δ 2.37 (3H, s, $COCH_3$), 3.35 (3H, s, N-CH_3), 7.7–8.0 (5H, m, Ar-H) and 8.7 (2H, hump, 2NH; cancelled with D_2O). The cis isomer exhibited a shift to upfield for the acetyl and aromatic protons, but the shift was to the downfield for N-CH_3 protons.



(trans)



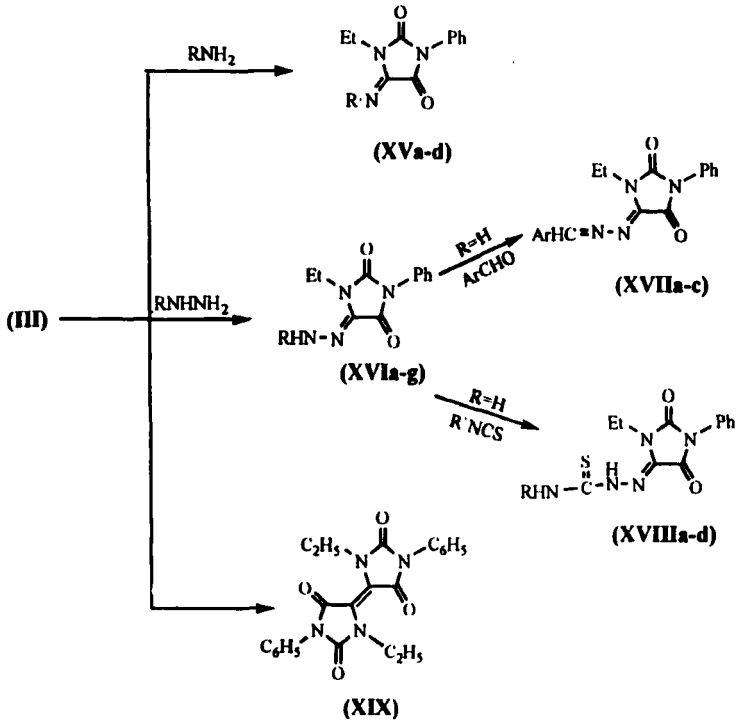
(cis)

In contrast to the above data, ^{1}H NMR spectrum of **XIIIdCDCl$_3$** exhibited the absence of isomers. Compounds **XIIIa-f** were confirmed by IR, ^{1}H NMR, MS and elemental analyses. Similarly, interaction of **IIh** with thiosemicarbazide gave 5-imino-4-thiosemicarbazono-1-(4′-chlorophenyl)-2-thioxo-3-ethylimidazolidine **XIIIg**.On the other hand 4-thioxoimidazolidine-2,4-dione **III** was reacted with the same reagents to compare **III** with imidazolidineiminothiones **II.**

Thus, interaction of **IIIa** with amines either (one mole or excess) furnished only one product which was formulated as 4-substituted imino-3-ethyl-1-phenylimidazolidine-2,5-diones **XVa-d.** Hydrazine hydrate, or its derivatives with **IIIa** produced only one product in each case, and were given structures **XVIa-g** based on elemental analyses and spectral data. These data showed that 4-thioxoimidazolidine-2,5-diones **III** possess only one active center, which is the thioxo group, and the reactions proceeded through it with the libaration of H_2S. While the imidazolidineiminothions **II** possess two active centers (the thioxo and the imino groups). The 4-hydrazono derivative **XVIa** were further confirmed by condensations with aromatic aldehydes to give the corresponding azino derivatives **XVIIa-c** and also by reaction with isothiocyanates to yield substituted thiosemicarbazone derivatives **XVIIIa-d.** On addition **IIIa** refluxed with copper turnings in gave **XIX** and cupper sulphide, compounds **XV-XVIII** (Scheme5).

EXPERIMENTAL

Melting points are uncorrected. Elemental analyses were carried out in the microanalytical unit at Cairo University. IR spectra (KBr) were measured on a Shimatzu 440 spectrometer, ^{1}H-NMR spectra on a JEOL FX 90 Q (90 MHz) spectrometer, and mass spectra on a Shimadzu GC-MSQP 1000 EX spectrometer using a direct-inlet system.



	R		Ar
XVa;	CH_2Ph	XVIIa;	$C_6H_4CH_3$-p
b;	$C_6H_4CH_3$-p	b;	C_6H_4Cl-p
c;	$C_6H_4OCH_3$-p	c;	$C_6H_4NO_2$-p
d;	C_6H_4Cl-p		R'
XVIa;	H	XVIIIa;	CH_3
b;	$COCH_3$	b;	C_6H_5
c;	COPh	c;	C_6H_4Cl-p
d;	$CONH_2$	d;	COPh
e;	$CSNH_2$		
f;	C_6H_5		
g;	$C_6H_4NO_2$-p		

SCHEME 5

Synthesis of 5-imino-4-thioxoimidazolidines IIa-h

A mixture of cyanothioformamide **(I)** (0.01 mol) in dry ether (20 ml), aryl isocyanate or isothiocyanate (0.01 mol), and triethylamine (0.5 ml) was stirred at room temperature for 30 min. The solid obtained was recrystallized from benzene/chloroform (1:4) to give **IIb-h** (Table I), **IIa** [3] and **IIi&j**[9].

TABLE I Physical data of various compounds prepared

No.	Yield [%]	M.P. [°C]	TLC [a] Eluent		Molecular Formula (M. Wt)	Analyses Required/ Found	
			Ratio E/H	R_f		C	H
	60	135	1:3	0.60	$C_{10}H_8ClN_3OS$	47.34	3.18
					(253.71)	47.30	3.10
	80	65	1:3	0.40	$C_{11}H_{11}N_3OS$	56.63	4.75
					(233.29)	56.60	4.70
	65	105	1:2	0.51	$C_{15}H_{10}ClN_3OS$	57.05	3.19
					(315.78)	57.00	3.20
	79	145	1:3	0.60	$C_{16}H_{13}N_3O_2S$	61.72	4.21
					(311.36)	61.90	4.40
	77	110	1:4	0.61	$C_{16}H_{13}N_3O_2S$	61.72	4.21
					(311.36)	61.90	4.40
	80	167	1:3	0.50	$C_{15}H_{10}ClN_3OS$	57.05	3.19
					(315.78)	57.20	3.00
	72	93	1:3	0.60	$C_{11}H_{10}ClN_3S_2$	46.55	3.55
					(283.80)	46.52	3.51
	65	127	1:2	0.40	$C_{11}H_{10}N_2O_2S$	56.40	4.29
					(234.28)	56.39	4.30
	84	170	1:3	0.70	$C_{16}H_{12}N_2O_3S$	61.53	3.87
					(312.35)	61.60	3.80
	70	215	1:2	0.50	$C_{16}H_{12}Cl_2N_4O$	55.48	3.48
					(346.39)	55.30	3.40

No.	Yield [%]	M.P. [°C]	TLC [a] Eluent		Molecular Formula (M. Wt)	Analyses Required/ Found	
			Ratio E/H	R_f		C	H
	65	195	1:3	0.81	$C_{21}H_{14}Cl_2N_4O$	61.85	3.45
					(409.46)	61.60	3.40
	67	150	1:3	0.41	$C_{21}H_{14}BrClN_4O$	55.69	3.11
					(454.73)	55.60	3.11
	81	70	1:3	0.61	$C_{30}H_{26}N_4O_2$	75.93	5.52
					(474.57)	75.80	5.40
	87	65	1:3	0.60	$C_{30}H_{26}N_4O_2$	75.93	5.52
					(474.57)	75.70	5.70
	83	80	1:3	0.51	$C_{30}H_{26}N_4O_4$	69.70	4.18
					(506.56)	69.50	4.30
	88	73	1:3	0.57	$C_{28}H_{20}F_2N_4O_2$	69.70	4.17
					(482.49)	69.50	4.30
	70	189	1:2	0.60	$C_{17}H_{14}N_4O$	70.33	4.86
					(290.33)	70.30	4.82
	80	168	1:2	0.50	$C_{18}H_{16}N_4O$	71.04	5.30
					(304.35)	71.00	5.20
	65	142	1:2	0.65	$C_{17}H_{13}ClN_4O$	62.87	4.03
					(324.77)	62.80	4.00
	75	198	1:2	0.60	$C_{17}H_{13}N_5O_3$	60.89	3.91
					(335.32)	60.80	3.80
	65	128	1:3	0.45	$C_{17}H_{13}ClN_4S$	59.91	3.84
					(340.84)	59.80	3.80

No.	Yield [%]	M.P. [°C]	TLC [a] Eluent		Molecular Formula (M. Wt)	Analyses Required/ Found	
			Ratio E/H	R_f		C	H
	60	210	1:1	0.63	$C_{10}H_{12}N_6O$	51.72	5.21
					(232.25)	51.70	5.00
	65	183	1:3	0.55	$C_{15}H_{13}ClN_6O$	54.80	3.99
					(328.76)	54.80	3.90
	70	212	1:4	0.36	$C_{10}H_{10}N_4OS$	51.27	4.30
					(234.28)	51.20	4.20
	65	206	1:2	0.60	$C_{11}H_{12}N_4OS$	53.00	4.86
					(248.31)	53.10	4.80
	70	188	1:2	0.40	$C_{22}H_{22}N_8O_2$	61.39	5.15
					(430.47)	61.30	5.10
	55	90	1:2	0.30	$C_{13}H_{15}N_5OS_2$	48.58	4.70
					(321.43)	48.50	4.60
	60	208	1:2	0.50	$C_{18}H_{17}N_5OS_2$	56.38	4.47
					(383.50)	56.30	4.40
	65	190	1:3	0.50	$C_{19}H_{17}N_5O_2S_2$	55.47	4.16
					(411.51)	55.30	4.10
	60	105	1:3	0.40	$C_{17}H_{16}N_5O$	66.43	5.58
					(307.36)	66.50	5.20
	65	195	1:3	0.50	$C_{17}H_{15}N_7O_5$	51.39	3.81
					(397.35)	51.40	3.50
a	65	213	1:2	0.33	$C_{12}H_{13}N_5O_2$	55.59	5.05
					(259.27)	55.60	5.00

No.	Yield [%]	M.P. [°C]	TLC [a] Eluent		Molecular Formula (M. Wt)	Analyses Required/ Found	
			Ratio E/H	R_f		C	H
b	55	188	1:3	0.50	$C_{13}H_{15}N_5O_2$	57.13	5.53
					(273.30)	57.10	5.50
c	70	246	1:3	0.40	$C_{18}H_{17}N_5O_2$	64.47	5.11
					(335.37)	64.30	5.00
d	60	90	1:3	0.60	$C_{17}H_{14}ClN_5O_2$	57.39	3.97
					(355.79)	57.30	3.80
e	62	166	1:3	0.50	$C_{12}H_{14}N_6O_2$	52.55	5.14
					(274.28)	52.50	5.10
f	65	192	1:3	0.30	$C_{12}H_{14}N_6OS$	49.64	4.86
					(290.35)	49.60	4.80
g	60	235	1:3	0.50	$C_{12}H_{13}ClN_6S_2$	42.29	3.84
					(340.86)	42.20	3.80
	60	183	1:3	0.40	$C_{18}H_{17}N_3O_2$	70.34	5.55
					(307.35)	70.20	5.50
	55	120	1:3	0.50	$C_{18}H_{17}N_3O_2$	70.34	5.58
					(307.35)	70.20	5.50
	65	91	1:3	0.60	$C_{18}H_{17}N_3O_3$	66.86	5.30
					(323.35)	66.70	5.23
	55	270	1:3	0.30	$C_{17}H_{14}ClN_3O_2$	62.30	4.31
					(327.77)	62.20	4.20
a	65	162	1:3	0.60	$C_{11}H_{12}N_4O_2$	56.89	5.21
					(232.24)	56.80	5.10

No.	Yield [%]	M.P. [°C]	TLC [a] Eluent		Molecular Formula (M. Wt)	Analyses Required/ Found		
			Ratio E/H	R_f		C	H	
	60	100	1:2	0.40	$C_{13}H_{14}N_4O_3$	56.93	5.14	
					(274.28)	56.90	5.10	
	65	164	1:2	0.50	$C_{18}H_{16}N_4O_3$	64.28	4.79	
					(336.35)	64.20	4.70	
	70	186	1:2	0.55	$C_{12}H_{13}N_5O_3$	52.36	4.76	
					(275.27)	52.30	4.70	
	65	218	1:2	0.45	$C_{12}H_{13}N_5O_2S$	49.47	4.50	
					(291.33)	49.40	4.50	
	55	99	1:2	0.60	$C_{17}H_{16}N_4O_2$	66.22	5.23	
					(308.34)	66.20	5.20	
	60	213	1:2	0.50	$C_{17}H_{15}N_5O_4$	57.79	4.28	
					(353.34)	57.80	4.30	
a	65	123	1:2	0.55	$C_{19}H_{18}N_4O_2$	68.19	5.43	
					(334.38)	68.10	5.30	
b	55	152	1:3	0.45	$C_{18}H_{15}ClN_4O_2$	60.87	4.26	
					(354.80)	60.70	4.20	
c	60	155	1:2	0.55	$C_{18}H_{15}N_5O_4$	59.18	4.14	
					(365.35)	59.10	4.10	
a	65	176	1:1	0.55	$C_{13}H_{15}N_5O_2S$	51.14	4.95	
					(305.36)	51.10	4.80	
b		55 208	1:1	0.60	$C_{18}H_{17}N_5O_2S$	58.84	4.66	
					(367.43)	58.80	4.60	

No.	Yield [%]	M.P. [°C]	TLC [a] Eluent		Molecular Formula (M. Wt)	Analyses Required/ Found	
			Ratio E/H	R_f		C	H
1c	60	213	1:1	0.65	$C_{18}H_{16}ClN_5O_2S$	53.80	3.01
					(401.87)	53.70	3.90
1d	70	207	1:1	0.50	$C_{19}H_{17}N_5O_3S$	57.71	4.33
					(395.44)	57.60	4.30
	67	175	1:3	0.30	$C_{22}H_{20}N_4O_4$	65.34	4.98
					(404.43)	65.30	4.90

uent used in all experiment is ethylacetate/hexane

IR of **IIc** exhibited the following bands: ν_{NH} at 3250, $\nu_{CH\cdot\ aliphat\cdot}$ at 2990, $\nu_{C=O}$ at 1780 and $\nu_{C=N}$ at 1630 cm^{-1}. **IIe**: ν_{NH}at 3200, $\nu_{C=O}$ at 1772, $\nu_{C=N}$ at 1660 and $\nu_{C=S}$ at 1450 and 1250 cm^{-1}. ^1H NMR spectrum **IIc** ($CDCl_3$) exhibited the following signals: 1.3 (3H, t, CH_3), 4.1 (2H, q, CH_2), 7.2–7.3 (5H, m, Ar-H), 9.3 ppm (1H, s, NH; cancelled with D_2O). **IIe** ($CDCl_3$): 4.0 (3H, s, OCH_3), 7.2–8.10 (9H, m, Ar-H) and 9.45 (1H, s, NH; cancelled with D_2O). The mass spectrum of **IIe** assigned a molecular ion peak at m/z 311 (61%) together with a base peak at m/z 161 (100%). Other significant peaks were observed at m/z: 278 (95.8%), 162 (82%), 122 (48%) and 91 (27%).

Hydrolysis of II

To a solution of **IIc** or **IIe** (0.01 mol) in boiling ethanol (20 ml) was added conc. HCl (5 ml). The product was recrystallized from ethanol to give **IIIa** and **IIIb**, respectively (Table I). IR spectra of **IIIa,b** showed the absence of ν_{NH}.

Condensation of II with aromatic amines

A mixture of **II** (0.01 mol) and aromatic amine (0.01 mol) in ethanol (30 ml) was heated under reflux for 3 h. The product was recrystallized from ethanol to give **Va-c**, (Table I).

The IR spectrum of **Vc** showed ν_{NH} at 3355, $\nu_{C=O}$ at 1725 and $\nu_{C=N}$ at 1580 cm^{-1}. The δ: ^1H NMR spectrum of **Va** ($CDCl_3$) 3.5 (3H, s, N-CH_3), 7.7–8.1 (8H, m, Ar-H) and 9.7 (1H, hump, NH, disappeared by D_2O).

1,3-Diaryl-4,5-bis[arylamino] 2-imidazolidinones VIa-d

A mixture of **II** (0.01 mol) and aromatic amine (0.02 mol) in absolute ethanol (20 ml) was heated under reflux (20–24 h.). The mixture was cooled, pour into crushed ice and neutralized with hydrochloric acid. The solid obtained was recrystallized from chloroform/pet.ether (40–60) to give **VI**, (Table I).

The IR spectrum of **VIb** exhibited the following bands $\nu_{CH\text{-}arom\cdot}$ at 3054, $\nu_{CH\text{-}\ aliph\cdot}$ at 2905, $\nu_{C=O}$at 1732 and $\nu_{C=N}$ at 1663, 1665 cm^{-1}. **VIc**: $\nu_{CH\text{-}arom\cdot}$ at 3030, $\nu_{CH\text{-}aliph}$ at 2915, $\nu_{C=O}$ at 1732 and $\nu_{C=N}$ at 1650, 1613

cm^{-1}. **VId**: $\nu_{CH\text{-}arom.}$ at 3050, $\nu_{CH\text{-}aliph.}$ at 2910, $\nu_{C=O}$ at 1732 and $\nu_{C=N}$ at 1668, 1590 cm^{-1}. The ^1H NMR spectrum of **VIa** ($CDCl_3$) exhibited the following signals δ: 2.2 (3H, s, CH_3), 2.4 (3H, s, CH_3), 4.0 (3H, s, OCH_3) and 6.6–8.10 (17H,m,Ar-H). **VIb**($CDCl_3$): 2.3 (3H, s, CH_3), 2.5 (3H, s, CH_3), 4.0 (3H, s, OCH_3), 6.6–8.20 (17H, m, Ar-H). **VId** ($CDCl_3$) δ: 4.10 (3H, s, OCH_3), 6.61–8.10 (17H, m, Ar-H). The mass spectrum of **VIa** exhibited a molecular ion peak at m/z 474 (23%) together with a base peak at m/z 386 (100%). Other significant peaks were observed at m/z: 473 (23%), 388 (3.7%), 385 (83%0, 236 (93%) and 132 (30%).

Formation of imidazoquinoxalines VIIa-e

To a solution of **II** (0.01 mol) in ethanol (20 ml) was added o-phenylenediamine or its derivatives (0.012 mol). The solution was refluxed for 4 hr, and the solid that obtained was recrystallized from ethanol to give **VIIa-e**, (Table I). IR measurements of **VIIa-e**, which showed the absence of NH. ^1H NMR spectrum of **VIIb** ($CDCl_3$) exhibited the following signals δ: 1.32 (3H, t, CH_3), 2.6 (3H, s, CH_3), 4.10 (2H, q, CH_2), 7.6–8.3 ppm (8H, m, Ar-H). ^1H NMR spectrum of **VIIe** ($CDCl_3$): 1.4 (3H, t, CH_3), 4.21 (2H, q, CH_2) and 7.8–8.2 ppm (8H, m, Ar-H).

Formation of dihydrazones VIIIa,b

A mixture of **IIa** or **d** (0.01 mol) and hydrazine hydrate (0.03 mol) in ethanol (30 ml) was stirred for 10 min. at room temperature. The product was recrystallized from ethanol/ benzene to give **VIIIa,b**, (Table I).

IR measurements of **VIIIab** showed a strong broad band at 3300, 3150 cm^{-1} corresponding to two NH_2 group, $\nu_{C=O}$ at 1700 and $\nu_{C=N}$ at 1690 cm^{-1}. IR spectrum of **VIIIb**: ν_{NH2}at 3370, 3280, $\nu_{C=O}$ at 1690 cm^{-1}. The mass spectrum of **VIIIa** showed the following peaks: 232 (M^+, 28.1%), 104 (28.1%), 77 (47.8%), 68 (67.8%) and 42 (100%) The mass spectrum of **VIIIb**: 329 (M^+, 79%), 330 (M+1; 26%), 300 (19%), 270 (7%), 201 (1.6%), 164 (13%), 137 (33%), 119 (36%) and 77 (100%).

Formation of the monohydrazones IXa

To a solution of **IIa** (0.01 mol) in ethanol (30 ml) was added hydrazine hydrate (0.01 mol), and the reaction mixture was stirred at room tempera-

ture for 15 min. The product was recrystallized from ethanol to give **IXa** (Table I). The IR spectrum of **IXa** showed ν_{NH2} at 3250, 3100, $\nu_{C=O}$at 1700, $\nu_{C=N}$ at 1690 and $\nu_{C=S}$ at 1460, 1200 cm^{-1}. The ^1H NMR spectrum of **IXa** ($CDCl_3$) exhibited signals at δ1.8 (2H, s, NH_2; which disappeared by D_2O), 3.3 (3H, s, N-CH_3), 7.5–7.9 (5H, m, Ar-H); The mass spectrum of **IXa** reveled a molecular ion peak at m/z 234 (2.8%); other significant peaks were observed at 235 (M+1), 70%), 190 (100%; base peak), 150 (64%) and 77 (52.1%).

Interaction of IIc with hydrazine hydrate

A mixture of **IIc**; (0.01 mol) and hydrazine hydrate (0.01 mol) in ethanol (30 ml) was stirred at room temperature for 15 min. The product was filtered off and recrystallized from ethanol to give **IXb** (Table I). Concentration of the alcohol mother-liquor furnished another product which recrystallized from benzene to give **X**; (Table I).

The IR spectrum of **IXb**: ν_{NH2} at 3350, 3151, $\nu_{C=O}$ at 1720 cm^{-1}. The ^1H NMR spectrum of **IXb** ($CDCl_3$) δ 1.3 (3H, t, CH_3), 1.9 (2H, s, NH_2, which disappeared by D_2O), 4.1 (2H, q, CH_2), 7.52–7.94 (5H, m, Ar-H). The mass spectrum of **IXb** gave a molecular ion peak at m/z 248 (M^+; 100%), along with other peak at 232 (M-NH_2; 17%), 204 (17%), 187 (20%), 161 (25%) and 135 (40%).

IR measurements of **X** afforded $\nu_{CH\ aliph.}$ (2900), $\nu_{C=O}$ (1780) and $\nu_{C=N}$ (1630) cm^{-1}; ^1H NMR of (**X**; $CDCl_3$): δ1.30 (6H, t, $2CH_3$), 3.91 (4H, q, $2CH_2$), 7.6–7.8 (10H, m, Ar-H). The mass spectrum of **X** exhibited a molecular ion peak at m/z 430 (17%) along with other peaks at, 255 (100%), 402 (66%), 373 (14%), 331 (21%) and 119 (83%).

Interaction of IXb with isothiocyanates

A mixture of **IXb** (0.01 mol) the isothiocyanate (0.01 mol) and triethylamine (0.5 ml) in ethanol (30 ml) was refluxed for 3h. The solid obtained was recrystallized from ethanol to give **XIa-c**, (Table I).

IR spectrum of **XIb** showed bands at 3230, 3180 (NH), 1750 (C=O) cm^{-1}. The mass spectrum of **XIc** exhibited m/z at 411 (M^+; 33%), 233 (11.53%) and 105 (100%).

Formation of hydrazone derivatives XIIa,b and XIIIa-g

A mixture of **II** (0.01 mol) and the appropriate hydrazine derivatives (0.01 mol) in ethanol (20 ml) was heated under reflux for 3 h. The product was recrystallized from ethanol to give **XIIa,b** or **XIIIa-g**, Table (I).

The IR spectrum of **XIIIa**: ν_{NH} at 3220, 3100, $\nu_{C=O}$ at 1725, 1715 and $\nu_{C=N}$ at 1650 cm^{-1}. IR spectrum of **XIIId**: ν_{NH} at 3300, $\nu_{C=O}$ at 1750, 1700 cm^{-1}. The IR spectrum of **XIIIe**: ν_{NH2} at 3470, 3400, ν_{NH} at 3290, $\nu_{C=O}$at 1760, 1700 cm^{-1}. The ^1H NMR spectrum of **XIIIb** ($CDCl_3$) showed signals at δ 1.4 (3H, t, CH_3), 2.5 (3H, s, $COCH_3$), 3.9 (2H, q, CH_2), 7.6–8.3 (7H, m, Ar-H), 8.2–8.3 (2H, 2s, 2NH; cancelled with D_2O). The ^1H NMR of **XIIIc**; ($CDCl_3$): δ1.4 (3H, t, CH_3), 4.10 (2H, q, CH_2), 7.7–8.2 (10H, m, Ar-H), 9.3 ppm (2H,s,NH). ^1H NMR of **XIIIg** ($CDCl_3$): δ 1.4 (3H, t, CH_3), 4.2 (2H, q, CH_2), 7.8–8.3 (4H, AB-system, Ar-H), 8.3, 9.1, 12.3 (3s, NH_2, NH). The mass spectrum of **XIIIa** exhibited a molecular ion peak at m/z 259 (31.41%)along with other peaks at 188)59%), 119 (100%) and 77 (22.4%).

Interaction of III with amines

A mixture of **III** (0.01 mol) and the requisite amine compounds (0.01 mol) in ethanol (30 ml) was heated under reflux for 2 h., The reaction mixture was concentrated and the product was recrystallized from ethanol/benzene to give **XVa-d** (Table I).

The IR spectrum of **XVb**, showed bands at 2290 (CH-aliphatic), 1750, 1720, (C=O), 1630 cm^{-1} (C=N). The ^1H NMR spectrum of **XVb** (DMSO-d_6): δ 1.4 (3H, t, CH_3-C), 2.2 (3H, s, CH_3-Ar), 3.9 (2H, q, CH_2) and 7.6–8.1 (9H, m, Ar-H).

Formation of hydrazone, derivatives XVIa-g

A mixture of **III** (0.01 mol) and hydrazine or its derivatives in ethanol was refluxed for 1 hr. The solid obtained was recrystallized from ethanol to give **XVIa-g**, (Table I).

IR spectrum of **XVIa** showed bands at 3420, 3340 (NH_2), 1750, 1720 cm^{-1} (C=O). The IR spectrum of **XVId**, revealed bands at 3500, 3400 (NH_2), 1780, 1720 cm^{-1} (C=O). The ^1H NMR spectrum of **XVIb** ($CDCl_3$)

showed signals at δ 1.4 (3H, t, CH_3), 2.3 (3H, s, $COCH_3$), 4.1 (2H, q, CH_2), 7.6–8.0 (5H, m, Ar-H) and 8.0 (1H, s, NH). The mass spectrum of **XVIe** afforded a molecular ion peak at m/z 291′ (100%) along with other peaks at, 274 (23%), 232 (25 %), 189 (69%), 129 (12%) and 119 (15 %).

Interaction of XVIa with aromatic aldehydes

A mixture of **XVIa** (0.01 mol) and aromatic aldehydes (0.01 mol) in ethanol (20 ml) was heated under reflux for 1 h., The solid that obtained was recrystallized from ethanol/ benzene to give **XVIIa-c**, (Table (I).

The IR spectrum of **XVIIa** exhibited the complete disappearance of NH_2 bands. The ^1H NMR spectrum of **XVIIa**; (DMSO-d_6) showed signals at δ 1.5 (3H, t, CH_3-C), 2.3 (3H, s, CH_3-Ar), 4.5 (2H, q, CH_2), 7.4–8.2 (9H, m, Ar-H) and 8.5 ppm (1H, s, N=CH).

Interaction of XVIa with isothiocyanates

A solution of **XVIa** (0.01 mol) in ethanol (30 ml) was treated with aryl isothiocyanates (0.01 mol), and the mixture was heated under reflux for 3 h. The obtained product was recrystallized from ethanol/benzene to give **XVIIIa-d** (Table I).

The IR spectrum of **XVIIIc** showed the absence of NH_2 and the presence of two ν_{NH} at 3215, 3150, ν_{CO} at 1750, 1720, $\nu_{C=N}$ at 1630 and $\nu_{CS\text{-}N}$ at 1450, 1170 cm^{-1}. The mass spectrum of **XVIIId** exhibited a molecular ion peak at m/z 395 (1.2%) with a base peak at m/z 105 (100%, COC_6H_5) and other significant peaks at m/z 324 (1.1%), 274 (3.3%), 323 (2.3%), 159 (2.6%) and 147 (3.8%).

Interaction of III with Cu/Decaline

A mixture of **III** (0.01 mol) in decaline (15 ml) and copper turnings (1 gm) was refluxed for 1 h to give **XIX** (Table I). The mass spectrum of **XIX** exhibited a molecular ion peak at m/z 404 (100%) along with other peaks at, 274 (20%), 348 (1.3%), 284 (1.8%), 243 (70%), 218 (13.84%), 162 (1.1%) and 119 (2.1%).

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