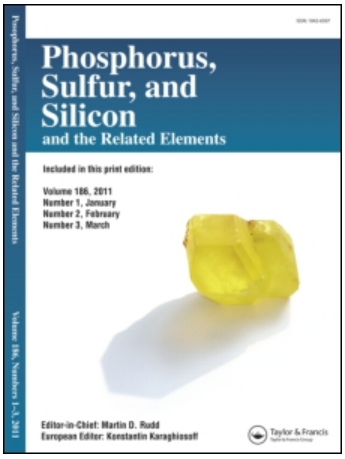

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SOME REACTIONS WITH p-ETHOXYPHENYLCYANO-THIOFORAMIDE: SYNTHESIS OF PYRROLE, PYRROLO[2,3-c]PYRROLE, IMIDAZO[4,5-b]QUINOXALINES AND HYDANTOIN DERIVATIVES

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SOME REACTIONS WITH p-ETHOXYPHENYLCYANO-THIOFORAMIDE: SYNTHESIS OF PYRROLE, PYRROLO[2,3-c]PYRROLE, IMIDAZO[4,5-b]QUINOXALINES AND HYDANTOIN DERIVATIVES

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P-Ethoxyphenylcyanothioformamide (**1**) was reacted with α,β-unsaturated ketone (**2**) and N-p-chlorophenylmaleimide (**4**) to furnish pyrrole and pyrrolo[2,3-c]pyrrol-4,6-diones (**3**) and (**5**) respectively. Also, interaction of **1** with anthranilic acid and o-phenylenediamine produced 3-(4'-ethoxyphenyl)-2-thioxoquinazolin-4-one (**6**) and 2-thioxobenzimidazoles (**7**). When, **1** was reacted with iso(thio)cyanates caused cyclization to afford 5-imino-4-thioxoimidazolidinones (**9**). Compound **9** was subjected to some reagents such as hydrazine hydrate, thiosemicarbazide, o-phenylenediamines, hydrogen sulfide and HCl to give 5-hydrazono, 4-thiosemicarbazono, and thiohydantoin derivatives (**10–17**), respectively.

Keywords: pyrrole; Hydantoin derivatives; hydrogen sulfide

INTRODUCTION

The synthesis of cyanothioformamides has attracted considerable attention since these compounds are used as versatile starting materials for the synthesis of a wide variety of fused heterocyclic compounds[1–4]. We have been involved in a program aiming to explore the utility of cyanothioformamides for synthesis of many heterocyclic derivatives[5–8]. As a part of

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this work we report here the results of our investigation on the reactivity of p-ethoxycyanothioformamide (**I**)[9,10], towards a variety of reagents. The work has resulted in the development of several new approaches for the synthesis of pyrrole, pyrrolo[2,3-c]pyrrole, quinazolinone, imidazolidine and imidazoquinoxaline derivatives. The reactivity of **1** towards some activated double bonds was also discussed.

RESULTS AND DISCUSSION

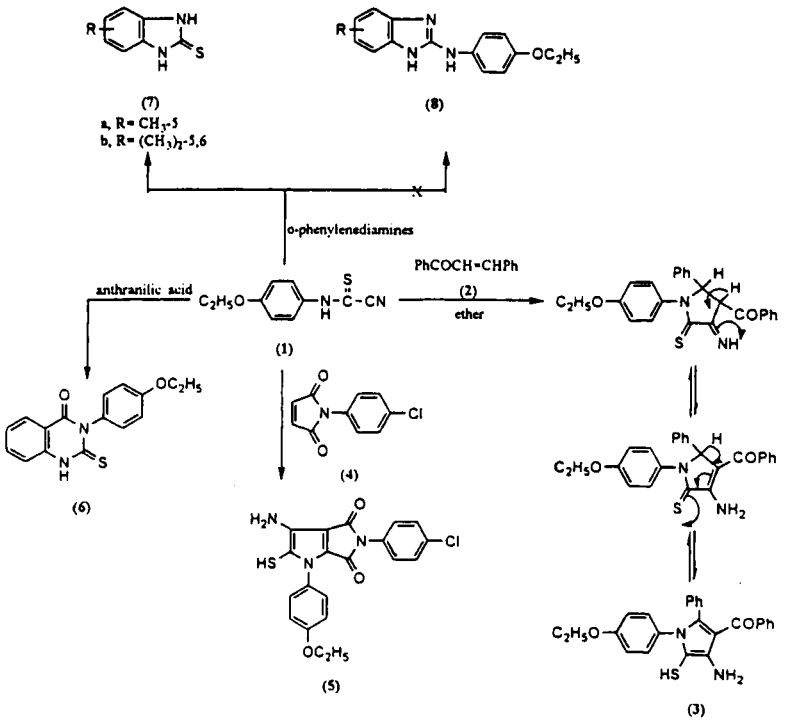
Thus, interaction of **1** with unsaturated ketone (Chalcone) (**2**) at room temperature in the presence of triethylamine effected cyclization to give 4-benzoyl-1-(4'-ethoxyphenyl)-5-phenyl-3-iminopyrrolidine-2-thione, which has the tautomeric structures of pyrroline and pyrrole (**3**) (Scheme 1).

Its ^{1}H NMR spectrum showed signals at 1.2–1.6(3H,t,CH_3-ethoxy), 4.1–4.3 (2H, q, CH_2-ethoxy) and its mass spectrum showed a molecular ion peak at m / z 414 (M, 24%), the fragmentation pattern was showed in (scheme 2).

Also, interaction of **1** with N-p-chlorophenylmaleimide (**4**) as other electrophile in the presence of triethylamine, the product 3-amino-5-(4'-chlorophenyl)pyrrolo[2,3-c]pyrrole-4,6-dione (**5**) was precipitated after the reaction was stirred at room temperature for 30 min. The suggested product was elucidated by IR spectrum which showed bands at 3319 (broad; NH), 2990(CH-aliphatic) and 1712 (C=O) and its mass spectrum revealed a molecular ion peak at m / z 416 (M; 2.4%) and 281[M-135 (p-$H_5C_2OC_6H_4$-N); 6.7%]

Furthermore, condensation of **1** with anthranilic acid furnished a product which gave analytical data fitted with 3-(4`-ethoxyphenyl)-2-thioxoquinazolin-4-one (**6**) via elimination of HCN and H_2O. Its ^{1}HNMR spectrum exhibited signals at 1.4–1.7 (3H, q, CH_3-ethopxy), 4.1–4.3 (2H, q, CH_2-ethoxy) and mass spectrum showed a molecular ion peak at m / z 298 (M; 100%), 270 [M-28(C=O); 30.2%].

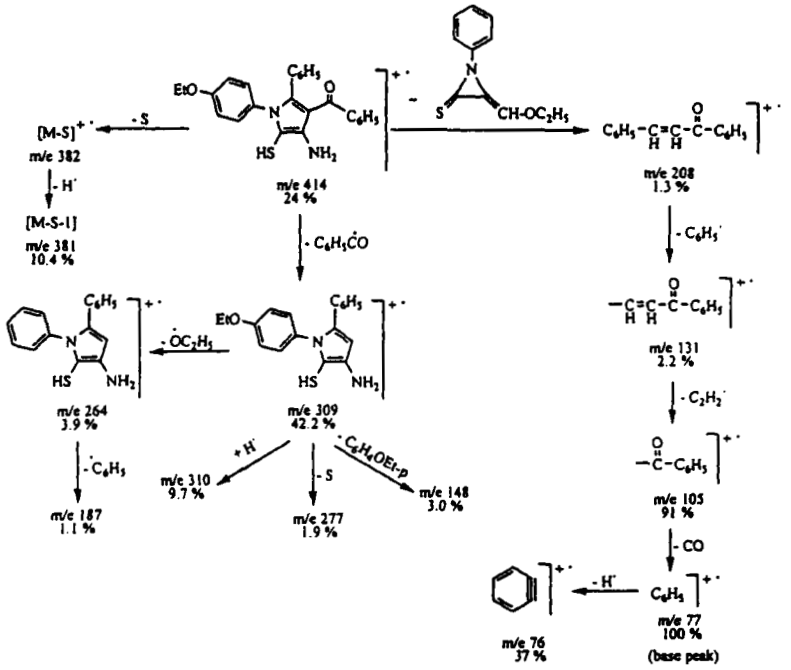
It was reported that cyanothioformamides reacted with o-phenylenediamines to yield 2-substitutedanilinobenzimidazole derivatives (through elimination of HCN and H_2O).



SCHEME 1

In this paper, condensation of **1** with 4-methyl or 4,5-dimethyl-o-phenylenediamines gave products which were expected to have one of the two structure (**7 or 8**). The obtained products were found to be sulfur positive and ^{1}HNMR showed the absence of ethoxy group which favored structure **7** (scheme 3). ^{1}HNMR spectrum of **7b** in DMSO-d_6 showed 2.3(6H,s,2CH_3), also mass spectrum of **7a** exhibited a molecular ion peak at m/z 164(M, 100%) and 132 [M-32(S); 14.3%]. Compounds **7a,b** were also confirmed through their synthesis via the reaction of o-phenylenediamines with CS_2''.

The reactivity of p-ethoxyphenylcyanothioformamide **1** was extended to cover its behavior towards iso(thio)cyanate for obtaining other type of heterocyclic compounds. Thus, interaction of (**1**) with aryl iso(thio)cyanates in the presence of triethylamine caused cyclization to give 5-amino-4-thi-

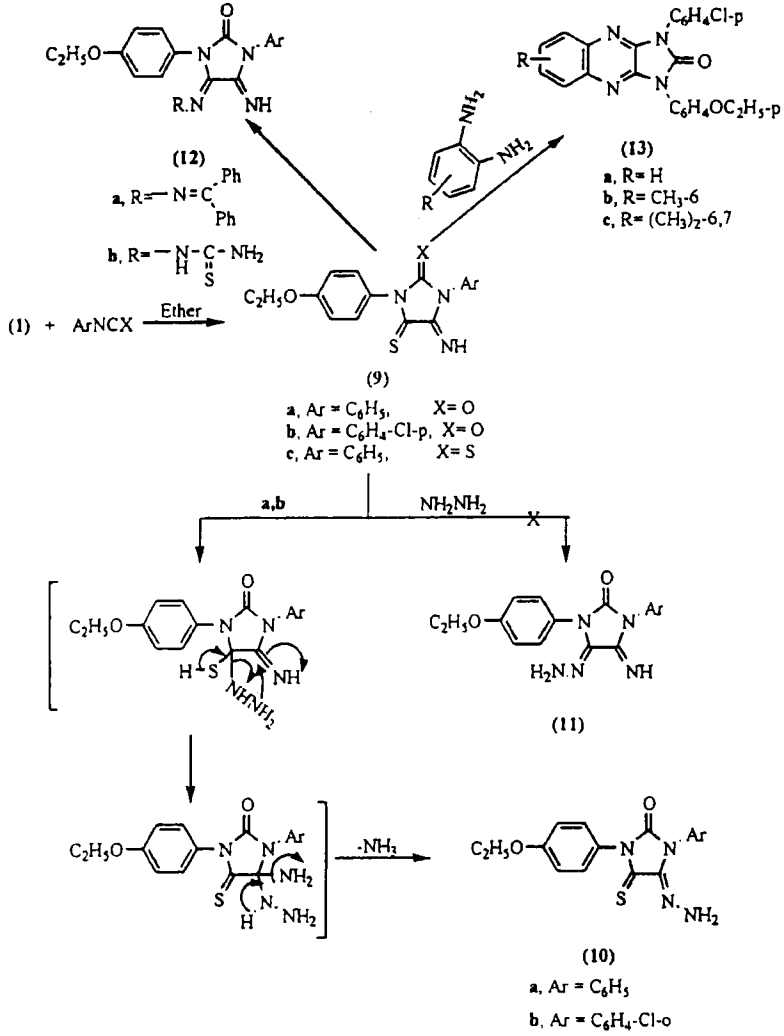


SCHEME 2 Fragmentation pattern of compound (3)

oxoimidazolidin-2-one or 2-thione derivatives (**9a-c**). ^{1}HNMR spectrum of **9b** in DMSO-d_6 revealed signals at 1.3–1.7(3H,t,CH_3-ethoxy), 4.2–4.5(2H,q,CH_2-ethoxy) and 8.8(1H,br,NH).

The imidazolidine derivative (**9**) contain adjacent imino and thione functions in the 5-and 4- positions which appear promising for further chemical transformations. Thus equimolecular amounts of **9b** and hydrazine hydrate gave the monohydrazono derivative for which structure **10 or 11** seemed possible. The positive element test for sulfur and spectral data favored the 5-hydrazono derivative **11**. The formation of **11** may be rationalized as in scheme 4. Mass spectrum of **11b** showed a molecular ion peak at 375 (M, 100%), 377(M+2,37% due to the chlorine isotope), 357[M-16; (NH_2), 25.4%], 347[M-28(CO), 43.7%] and 196[M-179 {$H_5C_2OC_6H_4NCS$), 20%].

On the other hand, condensation of **9** with benzalhydrazone or thiosemicarbazide furnished the corresponding 4-azine or thiosemicarbazono



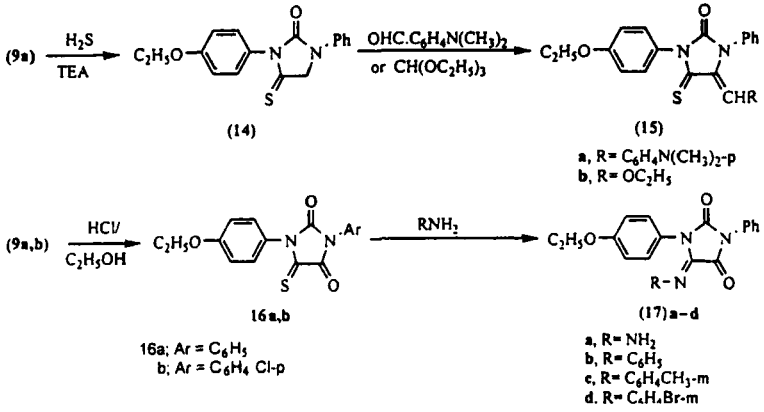
SCHEME 3

derivatives (**12a,b**). Mass spectrum of **12a** showed a molecular ion peak at m/z 492 (M, 100%).

Furthermore, interaction of **9** with o-phenylenediamines, the obtained product gave analytical and spectral data compatible with imiazo[4,5-b]quinoxalines (**13a,b**) via elimination of H_2S and NH_3. ^{1}HNMR

spectrum of **13b** in $CDCl_3$ showed signals at 1.2–1.5 (3H, t, CH_3-ethoxy), 2.6 (6H, s, $2CH_3$), 4,1–4.3 (2H, q,.CH_2-ethoxy).

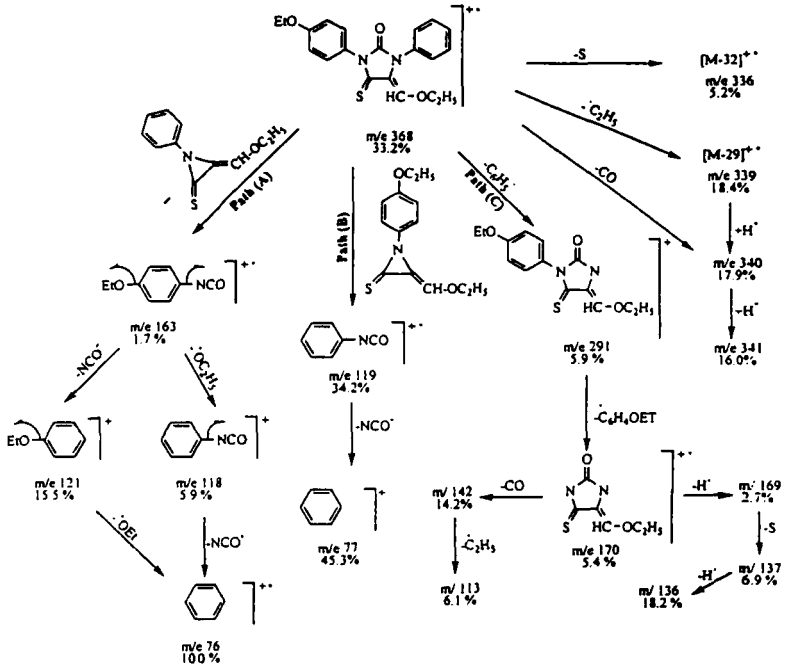
When the iminothione **9a** was subjected to a stream of hydrogen sulfide in presence of triethylamine produced 1-(p-ethoxyphenyl)-3-phenylhydantoin (**14**). Its ^{1}HNMR spectrum in DMSO-d_6 showed signals at 1.3–1.6 (3H, t, CH_3-ethoxy), 4.2–4.5 (2H, q, CH_2-ethoxy) and 5.2 (2H, s, CH_2-methylene).



SCHEME 4

The reactivity of the active methylene in compound **14** was proved through its reaction with p-N,N-dimethylaminobenzaldehyde and triethylorthoformate to give the benzylidene and ethoxymethylene derivatives (**15a,b**). ^{1}HNMR spectrum of **15a** in DMSO-d_6 exhibited signals at 1.3–1.6 (3H,t,CH_3-ethoxy), 3.2 [6H,s, $N(CH_3)_2$], 4.1–4.3 (2H, q, CH_2-ethoxy) and 5.4 (1H, s, CH=). Also, mass spectrum of **15b** showed a molecular ion peak at m/z 368 (M,33.2%), the fragmentation pattern was showed in scheme 5.

Hydrolysis of 5-imino-4-thioxoimidazolidin-2-ones **9a,b** by using ethanolic hydrochloric acid produced the corresponding 4-thioxoimidazolidin-2,5-diones (**16a,b**). Condensation of 16a with hydrazine hydrate or aryl amines took place through the thioxo group via elimination of H_2S and the corresponding 4-hydrazono (**17a**) and 4-substitutedimino derivatives (**17b-d**)were obtained.



SCHEME 5 Fragmentation pattern of compound (15_b)

Experimental

All mps are uncorrected. IR spectra were measured as KBr pellets on a Shimadzu IR 200 spectrophotometer. ^{1}H NMR spectra were recorded in deutrated chloroform at 200 MHz on a Varian Gemini NMR spectrometer using tetramethylsilane as an internal reference. Mass spectra were performed on a Shimadzu GCMS-QP 1000 EX mass spectrometer at 70 eV. Elemental analyses were carried out at the Microanalytical Center of Cairo University.

4-Benzoyl-1-(4-ethoxyphenyl)-5-phenyl-3-iminopyrrolidine-2-thione (3)

To a solution of (**1**, 0.01 mol) in ether (20 ml), the chalcone (**2**, 0.01 mol) and triethylamine (0.5ml) were added. The reaction mixture was stirred at

room temperature for 3 hr and the solid that obtained after filtration was crystallized to furnish (**3**; Table I). Its IR spectrum exhibited 3240, 3307 (NH_2), 2980 (CH-aliphatic), 1640 (C=O) which is lower than the expected value due to the intramolecular hydrogen bond. ^{1}HNMR spectrum in DMSO-d_6 showed signals 1.2–1.6 (3H, t, CH_3-ethoxy), 4.1–4.3(2H,q,CH_2-ethoxy) and 6.8–8.0(16H,m,Ar-H+NH_2).

TABLE I Characteristics of the synthesized compounds

Compd. No.	*M.P.*[a] *[°C]*	*Yield (%)*	*Mol. Formula (Mol. wt)*	*Elemental analyses, % Required/ Found*			
				C	*H*	*N*	*S*
3	155–7[b]	65	$C_{25}H_{22}N_2O_2S$	72.44	5.35	6.76	7.73
			(414.52)	72.30	5.20	6.50	7.60
5	135–6[b]	64	$C_{20}H_{16}N_3O_3SCl$	58.04	3.89	10.15	7.75
			(413.87)	58.10	3.90	10.10	7.80
6	310–12[b]	68	$C_{16}H_{14}N_2O_2S$	64.41	4.73	9.39	10.75
			(298.35)	64.40	4.70	9.40	10.70
7a	275–7[b]	70	$C_8H_8N_2S_3$	58.51	4.91	17.06	19.52
			(164.22)	58.50	4.90	17.00	19.50
7b	300–2[b]	70	$C_9H_{10}N_2S$	60.65	5.65	15.71	17.99
			(178.25)	60.60	5.70	15.80	17.00
9a	125–7[b]	68	$C_{17}H_{15}N_3O_2S$	62.75	4.65	12.91	9.85
			(325.38)	62.70	4.70	12.90	9.80
9b	167–8[b]	71	$C_{17}H_{14}ClN_3O_2S$	65.75	3.92	11.68	8.91
			(359.82)	65.70	3.90	11.60	8.90
9c	135–6[b]	69	$C_{17}H_{15}N_3OS_2$	59.80	4.43	12.31	18.78
			(341.45)	59.90	4.40	12.40	18.70
10a	210[b]	70	$C_{17}H_{16}N_4O_2S$	59.99	4.74	16.46	9.42
			(340.40)	59.90	4.80	16.40	9.50
10b	195[b]	69	$C_{17}H_{15}ClN_4O_2S$	54.47	4.03	14.95	8.55
			(374.84)	54.40	4.10	14.90	8.70
12a	218[b]	65	$C_{30}H_{24}ClN_5O_2$	69.03	4.63	13.42	
			(522.01)	69.00	4.80	13.40	
12b	190[b]	69	$C_{18}H_{18}ClN_6O_2S$	51.86	4.11	20.16	
			(416.88)	51.90	4.10	20.30	
13a	220[b]	64	$C_{23}H_{14}N_4O_2Cl$	66.27	4.11	13.44	

Compd. No.	M.P.[a] [°C]	Yield (%)	Mol. Formula (Mol. wt)	Elemental analyses, % Required/ Found			
				C	H	N	S
			(416.87)	66.30	4.20	13.60	
13b	200[b]	68	$C_{24}H_{19}N_4O_2Cl$	66.90	4.44	13.00	
			(430.89)	66.80	4.60	13.20	
13c	270[b]	70	$C_{25}H_{21}N_4O_2Cl$	67.49	4.76	12.59	
			(444.92)	67.40	4.90	12.80	
14	175[c]	67	$C_{17}H_{16}N_2O_2S$	65.37	5.16	8.97	10.26
			(312.38)	65.50	5.00	8.80	10.10
15a	155[b]	63	$C_{26}H_{25}N_3O_2S$	70.41	5.68	9.47	7.23
			(443.55)	70.60	5.80	9.30	7.40
15b	168[b]	40	$C_{20}H_{20}N_2O_3S$	65.20	5.47	7.60	8.69
			(368.44)	65.30	5.60	7.80	8.50
16a	140[b]	70	$C_{17}H_{14}N_2O_3S$	62.57	4.32	8.58	9.82
			(326.36)	62.70	4.30	8.40	9.90
16b	150–2[d]	68	$C_{17}H_{13}N_2O_3SCl$	56.59	3.63	7.76	8.88
			(360.80)	56.70	3.80	7.60	8.70
17a	210[d]	66	$C_{17}H_{16}N_4O_3$	62.96	4.97	17.28	
			(324.34)	62.70	5.00	17.40	
17b	220[b]	66	$C_{23}H_{19}N_3O_3$	71.68	4.97	10.90	
			(385.42)	71.80	4.70	10.70	
17c	215[b]	69	$C_{24}H_{21}N_3O_3$	72.17	5.29	10.52	
			(399.45)	72.30	5.40	10.60	
17d	240[b]	71	$C_{23}H_{18}N_3O_3Br$	59.49	3.91	9.05	
			(464.31)	59.60	3.80	9.20	

a. Solvent cryst.
b. from ethanol
c. from chloroform
d. from benzene

3-Amino-5-(4'-chlorophenyl)-1-(4'-ethoxyphenyl)-2-mercaptopyrrolo [2,3-c]pyrrol-4,6-dione (5)

A mixture of (1, 0.01 mol), N-p-chlorophenylmaleimide (4, 0.01mol) and triethylamine (0.5 ml) in ether (20ml) was stirred at room temperature for 3 hr. The obtained product after treatment with pet-ether (40–60) and fil-

tration was crystallized to give (**5**; Table I). IR spectrum showed a broad band around 3319(NH_2), 2930(CH-aliphatic) and 1712 (C=O). Also its mass spectrum showed m/z 416 (2.4%) with a base peak at m/z =86 and other significant peaks 344 (2.0%), 307 (5.6%), 274 (6.7%), 226 (7.7%), 191 (5.0%), 180 (12.3%), 148 (12.1%), 129 (16.5%) and 127 (46.2%).

3-(4'-ethoxyphenyl)-2-thioxoquinazolin-4-one (6)

A solution of (**1**, 0.01mol) in DMF (15ml) was treated with anthranilic acid (0.01mol) and piperidine (0.5ml) then refluxed for 3hr. The solid that obtained after cooling and filtration was crystallized to afford (**6**; Table I). Its ^{1}HNMR spectrum in DMSO-d_6 showed signals at 1.4–1.7(3H,t,CH_3-etoxy), 4.1–4.3(2H,q,CH_2-ethoxy) and 7.2–8.3 (9H, m, Ar-H+NH) and mass spectrum exhibited m/z 299 (M + 1,14.1%), 298 (M^+, 100%), 270 (30.2%), 237 (4.7%), 211 (10.7%), 163 (35.7%), 135 (24.4%), 119 (17.7%), 90 (10.0%) and 77(20.0).

2-Thioxobenzimidazoles (7a,b)

a - A mixture of (**1**, 0.01mol), o-phenylenediamines (0.01mol) and piperidine (0.5ml) in DMF (15ml) was heated under reflux for 3hr. Cooling, filtered and the obtained product was crystallized to give (**7a,b**; Table I). ^{1}HNMR spectrum of **7a** in DMSO-d_6 showed signals at 2.3(3H,s,CH_3), 7.2–7.7(5H,m,Ar+NH) and ^{1}HNMR of **7b** in DMSO-$d_6$2.3(6H,s,2CH_3) and 7.2(2H,s,Ar-H). Mass spectrum of **7a** showed m/z 164 (M^+, 100%), 132[M-32(S), 14.3%], 106(24.5%) and 77(15.6%).

b - Compound **7a,b** were prepared according to the reported method[11].

5-Imino-4-thioxoimidazolidin-2-ones and –2,4-dithione (9a-c)

To a solution of (**1**, 0.01mol) in ether (20ml), iso(thio)cyanates (0.01mol) and triethylamine (0.5 ml) were added, the reaction mixture was stirred at room temperature for 2 hr. The obtained products were crystallized from the proper solvent to afford (**9a-c**; Table I). IR of **9a** showed bands at 3240 (NH), 2980 (CH-aliphatic) and 1740 (C=O). While IR spectrum of **9c** showed the absence of CO group. ^{1}HNMR spectrum of **9a** in DMSO-d_6 1.3–1.6 (3H, t, CH_3-ethoxy), 4.2–4.5 (2H, q, CH_2) and 7.3–8.0 (10H, m,

Ar-H+ NH) and ^{1}HNMR spectrum of **9b** in DMSO-d_6 1.3–1.7 (3H, t, CH_3), 4.2–4.5 (2H, q, CH_2), 7.8–8.6 (8H, m, Ar-H) and 8.8 (1H, br, NH; cancelled with D_2O).

3-(4'-Ethoxyphenyl)-5-hydrazono-1-substitutedphenyl-4-thioxoimidazolidin-2-ones (10a,b)

A mixture of (**9a or b**, 0.01mol) and hydrazine hydrate (0.012mol) in ethanol (20 ml) was stirred at room temperature for one hr. The obtained product after filtration was crystallized to give (**10a,b**; Table I). IR spectrum of **10a** showed bands at 3430, 3366 (NH_2), 2993 (CH-aliphatic) and 1734(C=O). Also mass spectrum of **10b** showed 377 (M+2, 37.0% chlorine isotope), 375 (M^+, 100%), 359 (M-16; NH_2; 25.4%), 347(M-28; C=O; 43.7), 317 (12.2%), 284 (4.0%), 248 (4.9%), 196 (7.0%), 179 (20%), 149 (48.7%), 135 (84.9%), 121 (50%) and 107 (52.7%).

Interaction of (9b) with diphenylhydrazone or thiosemicarbazide

To a solution of (**9b**, 0.01mol) in ethanol (20ml), diphenylhydrazone or thiosemicarbazide (0.01mol) was added and the reaction mixture was refluxed for 3hr. The obtained product was filtered, washed with ethanol and crystallized to furnish (**12a,b**; Table I). IR spectrum of **12b** showed bands at 3263, 3163 (NH_2,NH) and 1763 (C=O) and mass spectrum of **12a** exhibited m/z 523 (M+1, 1.1%), 522 (M^+, 1.6%), 492 (100%), 444 (23.3%), 416 (3.9%), 362 (4.0), 358 (13.3%), 357 (37.8), 330 (4.8%), 292 (50.2%), 281 (4.1%), 264 (2.7%), 232 (5.6%), 182 (12.8%), 180 (58.9%), 153 (12.3%), 135 (12.2%), 125 (10.5%), 104 (13.6%), 77 (78.0%).

Imidaz[4,5-b]quinoxalines (13a-c)

A solution of (**9b**, 0.01mol) in ethanol (20 ml) was treated with o-phenylenedi amines (0.01mol) and triethylamine (0.5 ml). The reaction mixture was refluxed for 3hr and the solid that obtained after filtration was crystallized to give (**13a-c**, Table I). IR spectrum of **13a** showed 2997 (CH-aliphatic), 1748 (C=O) and 1604 (C=N), ^{1}H NMR spectrum of **13c** in DMSO-d_6 exhibited signals at 1.2–1.5 (3H, t, CH_3-ethoxy), 2.6 (6H, s, $2CH_3$), 4.1–4.3 (2H, q, CH_2-ethoxy) 7 7.2–8.8 (10H, m, Ar-H) and mass

spectrum of **13a** showed m/z 417 (M^+, 100%), 389 (67.5%), 360 (3.0%), 324 (2.9%), 277 (10.2%), 235 (16.2%), 206 (32.7%), 180 (4.6%), 148 (1.3%). 107 (2.7%) and 90 (10.4%).

1-(4'-Ethoxyphenyl)-3-phenylthiohydantoin (14)

A solution of (**9a**, 0.01mol) in ethanol (20 ml) was treated with triethylamine (1 ml) and subjected to a stream of hydrogen sulfide for half an hour at room temperature. The obtained solid after filtration and washed with ethanol was crystallized to afford (**14**; Table I). ^{1}HNMR spectrum in DMSO-d_6 showed signals 1.3–1.6 (3H, t, CH_3-ethoxy), 4.2–4.5 (2H, q, CH_2-ethoxy), 5.2 (2H, s, CH_2-methylene) and 7.3–8.1(9H,m,Ar-H).

1-(4'-Ethoxyphenyl)-4-(4'-N,N-dimethylaminophenylmethylene)-3-phenylthiohydantoin (15a)

A mixture of (**14**, 0.01 mol), p-N,N-dimethylaminobenzaldehyde (0.01 mol) and triethylamine (0.5 ml) in ethanol (20 ml) was refluxed for 3hr. The solid that obtained after cooling and filtration was crystallized to give (**15a**; Table I). ^{1}Hnmr spectrum in DMSO-d_6 showed signals at 1.3–1.6 (3H, t, CH_3-ethoxy), 3.2 [6H, s, $N(CH_3)_2$], 4.1–4.3 (2H, q, CH_2-ethoxy), 6.1 (1H, s, CH=) and 7.0.8.2 (13H, m, Ar-H).

1-(4'-Ethoxyphenyl)-4-ethoxymethylene-1-phenylthiohydantoin (15b)

Compound (**14**, 0.01 mol) was added to a mixture of acetic anhydride and triethylorthoformate (1:1; 10 ml) and was refluxed for 4hr. The product that obtained after cooling and filtration was refluxed to afford (**15b**; Table I). Mass spectrum displayed m/z 368 (M^+, 33.2%), 352 (17.4%), 326 (100%), 309 (17.4%), 288 (7.1%), 224 (11.4%), 193 (12.8%), 177 (26.5%), 150 (54.2%), 119 (34.2%), 104 (15.0%) and 77 (45.0%).

3-(4'-Ethoxyphenyl)-1-(phenyl or 4'-chlorophenyl)-4 thioxoimidazolidine-2,5-dione (16a,b)

To a solution of (**9a,b**, 0.01mol) in ethanol (20ml), Conc.HCl (5ml) was added with stirring at room temperature for 1/2 hr. The solid that precipi-

tated was filtered, washed with ethanol and crystallized to yield (**16a,b**; Table I). IR spectrum showed the complete disappearance of NH band already present in the parent compound.

3-(4'-Ethoxyphenyl)-4-hydrazono-1-phenylimidazolidine-2,5-dione (17a)

To a solution of (**16**, 0.01mol) in ethanol (20ml), hydrazine hydrate (0.012mol) was added and the solution was stirred at room temperature for 2hr. The solid that obtained was crystallized to give (**17a**; Table I). Its IR spectrum showed bands 3230, 3310 (NH_2), 2970 (CH-aliphatic) and 1750, 1710 (2C=O).

3-(4'-Ethoxyphenyl)-1-phenyl-4-substitutediminoimidazolidine-2,5-dione (17b-c)

A mixture of (**16**, 0.01mol) and the requisite amine (0.01mol) in ethanol (20ml) was refluxed for 3hr. The obtained product after cooling and filtration was crystallized to afford (**17b-c**; Table I). Mass spectrum of **17b** showed m/z 385(M^+, 5.7%), 238 (2.8%), 209 (2.6%), 163 (3.6%), 135 (4.2%), 119 (15.2%), 93 (100%) and 77 (14.3%).

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