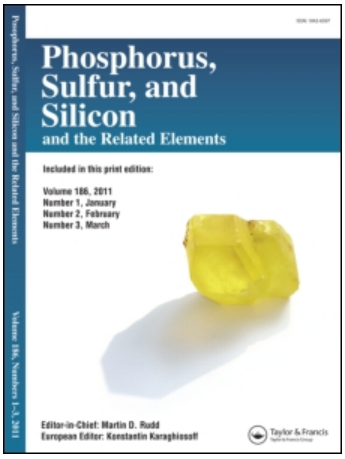

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Condensed Thioxocyclopentapyridine (Isoquinoline)-1,2,4-azines

Kh. M. Hassan[a]; R. A. Ahmed[a]; Sh. H. Abdel-Hafez[a]; M. A. Abdel-Azim[a]
[a] Chemistry Department, Assiut University, Assiut, Egypt

To cite this Article Hassan, Kh. M. , Ahmed, R. A. , Abdel-Hafez, Sh. H. and Abdel-Azim, M. A.(2006) 'Condensed Thioxocyclopentapyridine (Isoquinoline)-1,2,4-azines', Phosphorus, Sulfur, and Silicon and the Related Elements, 181: 3, 481 — 496
To link to this Article: DOI: 10.1080/10426500500263706
URL: http://dx.doi.org/10.1080/10426500500263706

Phosphorus, Sulfur, and Silicon, 181:481–496, 2006

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500500263706

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Condensed Thioxocyclopentapyridine (Isoquinoline)-1,2,4-azines

Kh. M. Hassan
R. A. Ahmed
Sh. H. Abdel-Hafez
M. A. Abdel-Azim
Chemistry Department, Assiut University, Assiut, Egypt

*Pyrido(isoquinolino)-1,2,4-triazepines and pyrido(isoquinolino) pyrazolo-1,2,4-triazepines were obtained from a reaction between o-diaminothioxocyclopentapyridine(isoquinoline), chalcones, diketones, esters, and aldehydes, respectively. It is shown that the more basic 1-NH_2 (pyrido) and/or 2-NH_2 (isoquinolino) group of the starting o-diamines participate in the formation of the azomethine bond of the seven-membered heteroring. Compounds (**3**, **6**, **9**, **12**, **15**, **17**, and **19**) are individual (TLC) and their structures are confirmed by the data from elemental analysis and spectroscopy.*

Keywords Pyrido(isoquinolino)-1,2,4-triazepines; pyrido(isoquinolino)-pyrazolo-1,2,4-triazepines

INTRODUCTION

Several annelated pyridinethiones isolated from natural sources have found a broad spectrum of clinical applications. Members of this class were found to be active in protection against gastric erosions,[1] and useful as a coronary vasodilator and blood pressure heightening agents.[2] Also, they have proved useful as antituberculostatic, antiviral, fungicidal, insecticidal, and pecticidal agents.[3,4] Moreover, they were used for the inhibition of aldose reductase activity and cataract formation in diabetes.[5] On the other hand, condensed heterocyclic-1,2,4-triazepines were found to have salidiuretic and renal vasodilator, antianoxidant, and analgesic and immunomodulating activities.[6–8] These findings promoted our interest to survey the chemistry of the o-diamino compounds (**1**) and its use as raw material for the synthesis of condensed pyrido-1,2,4-triazepines, isoquinolino-1,2,4-triazepines,

Received December 1, 2004; accepted May 1, 2005.
Address correspondence to Kh. M. Hassan, Assiut University, Chemistry Department, Assiut 71516, Egypt. E-mail: Kh_m_hassan@yahoo.com

and isoquinolinopyrazolo-1,2,4-triazepines, with expected biological activity.

RESULTS AND DISCUSSION

Orlov and colleagues[9] have previously described the condition for the synthesis of benzodiazepines on the basis of o-phenylenediamine and chalcones; the reaction was catalyzed by tertiary alkylamines in alcohol.

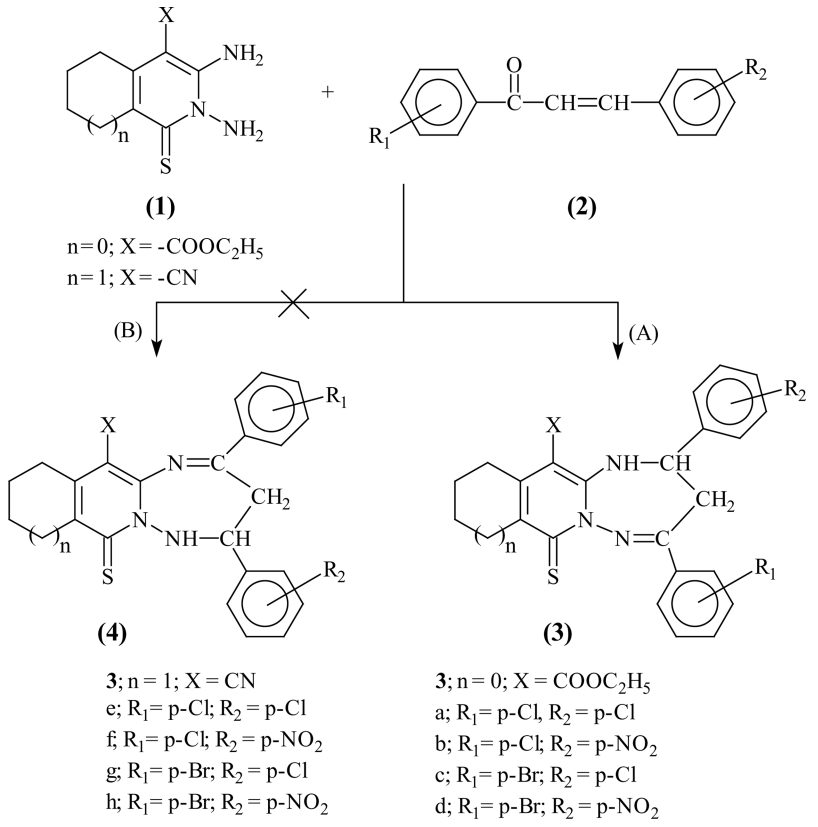
They used the previous method in the synthesis of imidazo[1,2-b]-1,2,4-triazepines on the basis of 1,2-diaminoimidazole and chalcones. They found that the yields of the target triazepines overaged 15–20% lower than in the case of the reaction of o-phenylenediamine and chalcones, probably because of the decreased reactivity of the starting diamine.

In the present work, we also studied the reaction of 1,2-diamine thioxocyclopenta(hexa)pyridines (**1**) with chalcones (**2**, **5**, and **8**), unsaturated aldehydes (**11**), diketone (**14**), and esters (**16**, **18**) in basic and acidic medias. It was found that the original components were recovered from the reaction medium unchanged in the case of basic reaction medium. However, the formation of seven-membered triazepines as single products found the best yield being achieved when the reaction is catalyzed by acetic acid in methanol, probably because the high reactivity of the starting o-diamine (Schemes 1–7).

Because o-diamine (**1**) has nonequivalent amino groups at the ortho position, the regioisomeric cyclization products (**3**, **4**, **6**, **7**, **9**, **10**, **12**, **13**, **19**, and **20**) was predicted pathways (A) and (B). However, the formation of single products (**3**, **6**, **9**, **12**, **15**, **17**, and **19**) was observed. Compounds (**3**, **6**, **9**, **12**, **15**, **17**, and **19**) are individual (TLC) and their structures were confirmed by the data from elemental analysis and spectroscopy (Tables I and II).

The choice between pathways (A) and/or (B) can be made on the basis of the following data.

It is known that the basicity of the amine is an important factor that affects the rate of the azomethine condensation and the position of the equilibrium in neutral and weakly basic media.[10] The fact that the amino ($>N\text{-}NH_2$) group in the 1-position of o-diaminothioxocyclopenta(hexa)-pyridine (**1**) has hydrazine character makes it possible to assume that it has higher reactivity in condensation reactions with carbonyl compounds as compared with the 2-amino group, which has the properties of a typical aromatic amine.[11] This conclusion is in good agreement with the data in the literature,[12,13] according to which O-diamino compounds (**1**) react with aldehydes and/or

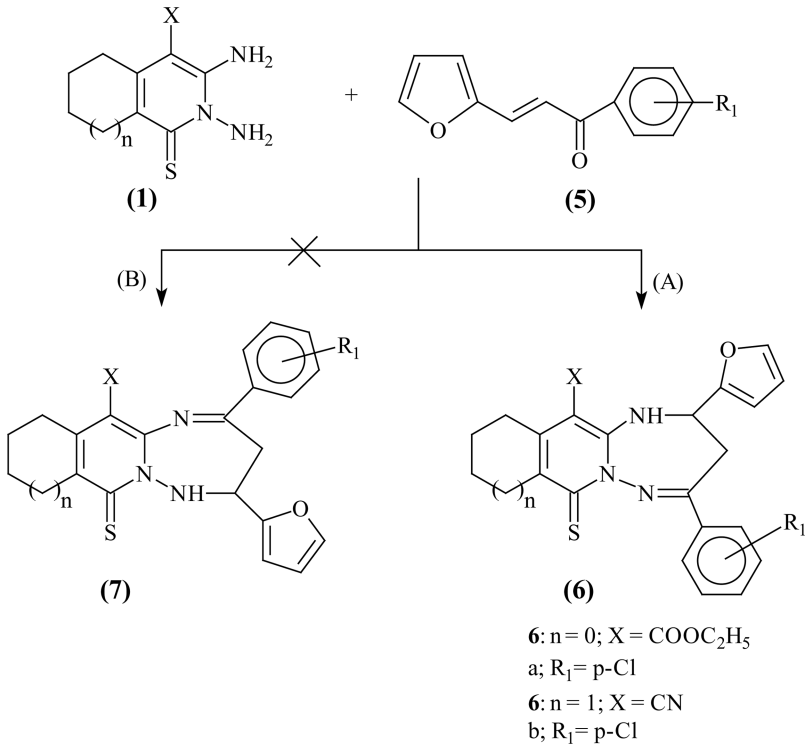


SCHEME 1

ketones in ethanol in the presence of a basic catalyst giving the azomethine exclusively at the >N-NH_2 amino group (Scheme 8).

So in the triazepine formation we assume that in the initial step, the condensation reaction between the carbonyl group of chalcones, unsaturated aldehydes, diketone and esters, and the more nucleophilic (>N-NH_2) amino group in (**1**) takes place.[14–17] In the second step, a Micheal addition of the less nucleophilic amino group in (**1**) to the C=C bond can take place. So, the greater nucleophilicity for the amino group (>N-NH_2) in (**1**) makes it possible to regard pathway (A) as a preferable route in this reaction.

To our satisfaction, a successful attempt was made to prepare isomers (**29–31**) by another route. Condensation of thiopyranethione (**23**) with chalcones, unsaturated aldehyde, diketone and/or esters were carried out in dimethylformamide in the presence of a basic catalyst, leading to the azomethine compounds (**24–28**) (Scheme 9, Tables I and II).

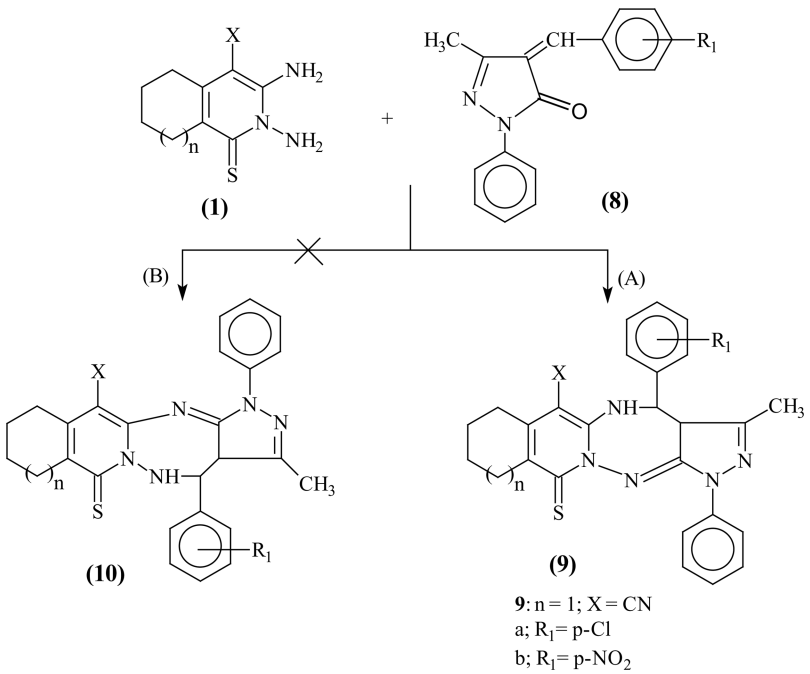


SCHEME 2

A mixture of compounds (**24–28**) and hydrazine hydrate was refluxed in ethanol until the evolution of H_2S gas was ceased. This reaction lead to the formation of isomeric triazepines (**29**, **30**, and **31**) pathway (B).

Thus, we assume that in the foregoing reaction the substitution of the ring sulfur and the Micheal's addition reactions take place spontaneously at the same time, giving the target 1,2,4-triazepines (**29**, **30**, **15**, **17**, and **31**), respectively (Schemes 10 and 11). Also, it should be noted that the azomethines (**26** and **27**) reacted with hydrazine hydrate, giving the same triazepines (**15** and **17**), which were prepared directly from the reaction of O-diamines (**1**) and acetyl acetone and diethyl malonate. The triazepines prepared by the two routes have the same melting points; no depression in the mixed melting points; and the same R_f value, IR spectra, as well as ^{1}HNMR spectra.

The structure of the new triazepines (**29–31**) were confirmed from the data of elemental analysis and spectroscopy (Tables I and II).



SCHEME 3

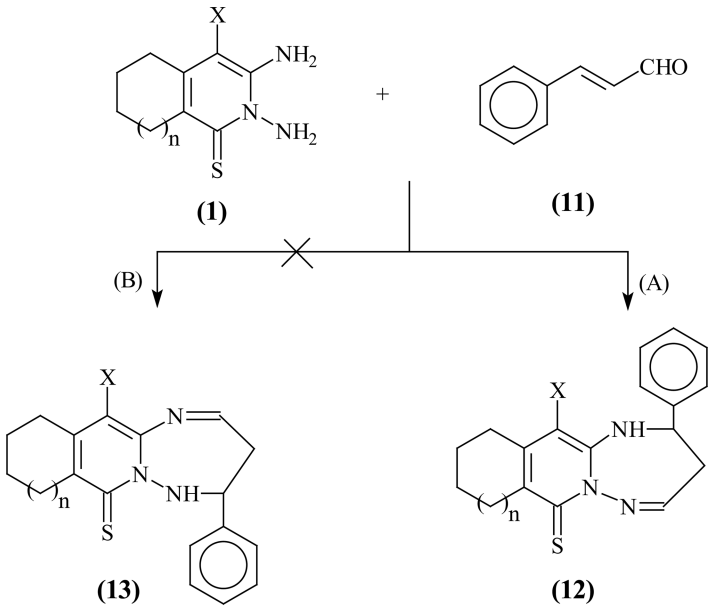
EXPERIMENTAL

All melting points are uncorrected and were determined on a Gallen-Kamp melting point apparatus. IR spectra were taken on Pye-Unicam infrared spectrophotometer using the KBr wafer technique. NMR spectra were recorded by 90 MHz varian NMR spectrometer and NT-200 NMR spectrometer. Mass spectra were determined on Dupont 21-492B mass spectrometer. Elemental analysis was carried out on the Perkin-Elmer 240C microanalyzer.

Compounds **1**, **2**, **5**, **8**, and **23** were prepared according to the literature procedures.[18–21]

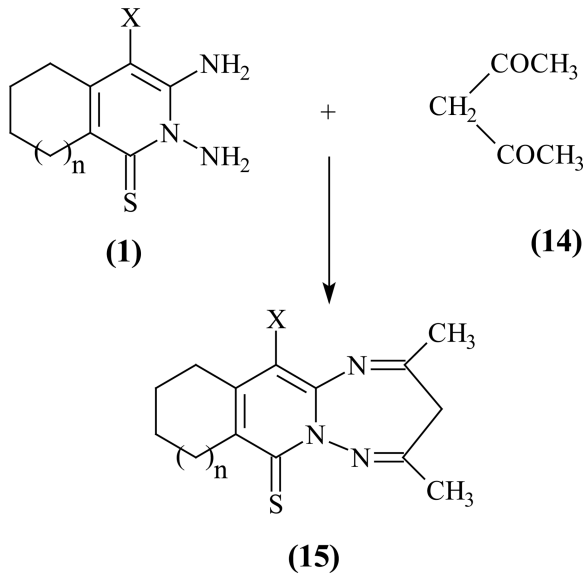
Synthesis of Compounds

Ethyl 2,4-di(4-substituted phenyl)-7-thioxo-2,3,7,8,9,10-hexahydro-1H-cyclopenta[4,5]pyrido[1,2-b][1,2,4]triazepine-11-carboxylate (**3a–d**); 2,4-di(4-substituted phenyl)-7-thioxo-1,2,3,7,8,9,10,11-octahydro [1,2,4] triazepino[2,3-b]isoquinolin-12-yl cyanide (**3e–h**); ethyl 2-(4-chloro-phenyl)-2-furyl-7-thioxo-2,3,7,8,9,10-hexahydro-2H-cyclopenta



SCHEME 4

[4,5]-pyrido[1,2-b][1,2,4]tirazepine-11-carboxylate (**6a**); 2-(4-chlorophenyl)-4-furo-7-thioxo-3,4,5,7,8,9,10,11-octahydro[1,2,4]triazepino[2,3-b]isoquinolin-12-yl cyanide (**6b**); 4-(4-chloro(nitro)phenyl)-3-methyl-1-phenyl-11-thioxo-3,4,5,7,8,9,10,11-octahydro-1H-pyrazolo[3′,4′:6,7] [1,2,4]triazepino[2,3-b]isoquinolin-6-yl cyanide (**9a**,**b**); ethyl 2-phenyl-7-thioxo-2,3,7,8,9,10-hexahydro-1H-cyclopenta[4,5]pyrido[1,2-b][1,2,4]-triazepine-11-carboxylate (**12a**); 2-phenyl-7-thioxo-1,2,3,7,8,9,10,11-octahydro[1,2,4]triazepino[2,3-b]isoquinoline-12-yl cyanide (**12b**); ethyl 2,4-dimethyl-7-thioxo-7,8,9,10-tetrahydro-3H-cyclopenta[4,5] pyrido-[1,2-b][1,2,4]triazepine-11-carboxylate (**15a**); 2,4-dimethyl-7-thioxo-3,7,8,9,10,11-hexahydro[1,2,4]trizepino[2,3-b]isoquinoline-12-yl cyanide (**15b**); ethyl 2,4-dioxo-7-thioxo-2,3,4,5,7,8,9,10-ocahydro-1H-cyclopenta-[4,5]pyrido[1,2-b][1,2,4]triazepine-11-carboxylate (**17a**); 2,4-dioxo-7-thioxo-1,2,3,4,5,7,8,9,10,11-decahydro[1,2,4]-triazepino[2,3-b]isoquinoline 12-yl cyanide (**17b**); ethyl-4-methyl-2-oxo-7-thioxo-2,3,7,8,9,10-hexahydro-1H-cyclopenta[4,5]pyrido[1,2-b]-triazepine-11-carboxylate (**19a**); 4-methyl-2-oxo-7-thioxo-1,2,3,7,8,9, 10,11-octahydro[1,2,4]-trizepino[2,3-b]isoquinolin-12-yl cyanide (**19b**).



15a: n = 0; X = $COOC_2H_5$
b: n = 1; X = CN

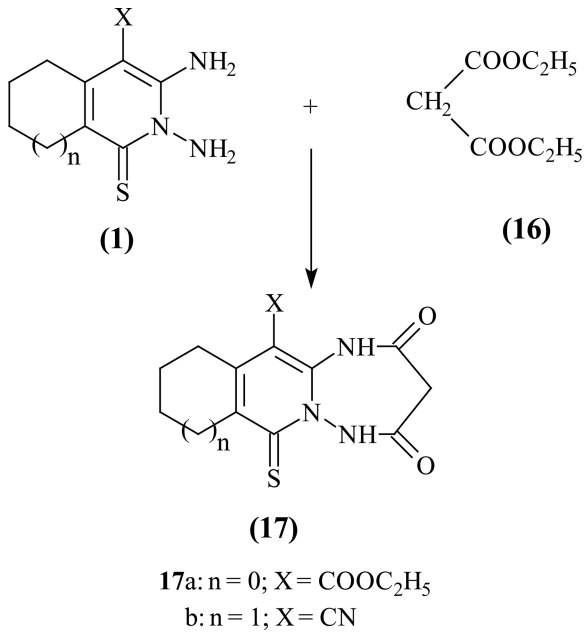
SCHEME 5

General Procedures

A solution of 1,2-diamino compound **1** (n = 0) (5 mmole); 2,3-diamino compound **1** (n = 1) (5 mmole) and (5 mmole) of chalcone **2**; **5** or **8**, and cinnamaldehyde (**11**); aceylacetone (**14**); diethylmalonate (**16**) and ethylacetoacetate (**18**); and 10 mL acetic acid in 30 mL methanol was refluxed for 8 h; the reaction mixture was cooled and the (yellow-brown) precipitate was removed by filtration and crystallized from the proper solvent to give the products (**3**, **6**, **9**, **12**, **15**, **17**, and **19**). The physical and spectral data are listed in Tables I and II.

Synthesis of Compounds (24–28)

3-{[(Z,2Z)-1,3-diphenyl-2-propenylidene]amino}-1-thioxo-5,6,7,8-tetrahydro-1H-4-isothiocromenyl cyanide (**24**), 3-{[(Z,2Z)-3-phenyl-2-propenylidene]amino}-1-thioxo-5,6,7,8-tetrahydro-1H-4-isothiochromenyl cyanide (**25**), 3-{[((E)-1-methyl-3-oxobutylidene]amino}-1-thioxo-5,6,7,8-tetrahydro-1H-4-isothiochromenyl cyanide (**26**), ethyl-3-[(4-cyano-1-thioxo-5,6,7,8-tetrahydro-1H-3-isothiochromenyl)amino]



17a: n = 0; X = $COOC_2H_5$
b: n = 1; X = CN

SCHEME 6

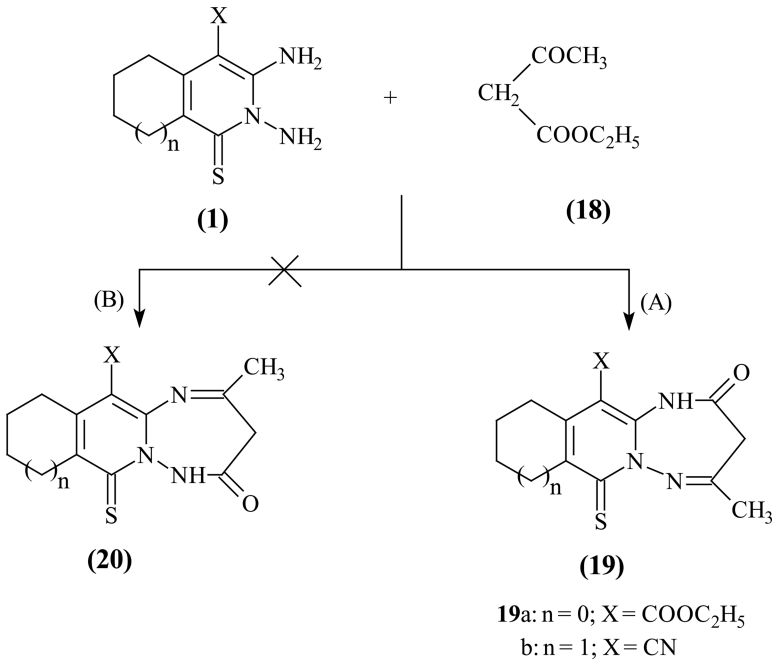
-3-oxopropanoate (**27**); ethyl 3-[(4-cyano-1-thioxo-5,6,7,8-tetrahydro-1H-3-isothiochrom-enyl)imino]butanoate (**28**).

General Procedure

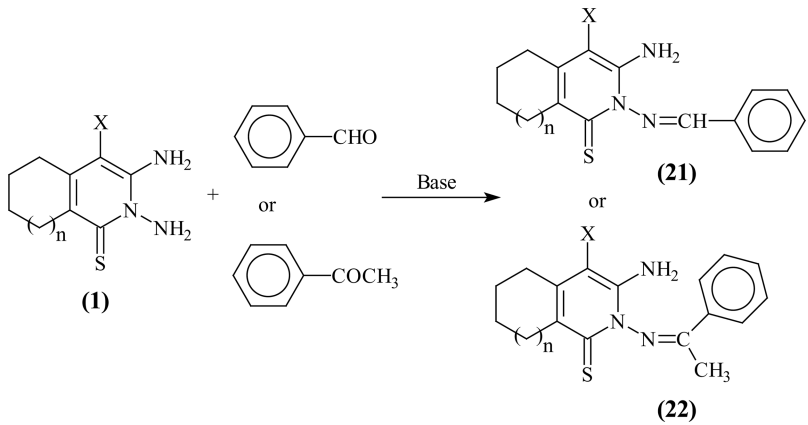
A solution of thiopyranethione (**23**) (5 mmole) and chalcone (**2a**) (5 mmole); cinnamaldehyde (**11**); acetylacetone (**14**); diethylmalonate (**16**) and ethyl acetoacetate (**18**) in 30 mL methanol; and 5 mL of triethylamine was refluxed for 8 h; after cooling the precipitate was collected by filteration and crystallized from the proper solvent to give the products (**24–28**).

Synthesis of Compounds (29–31)

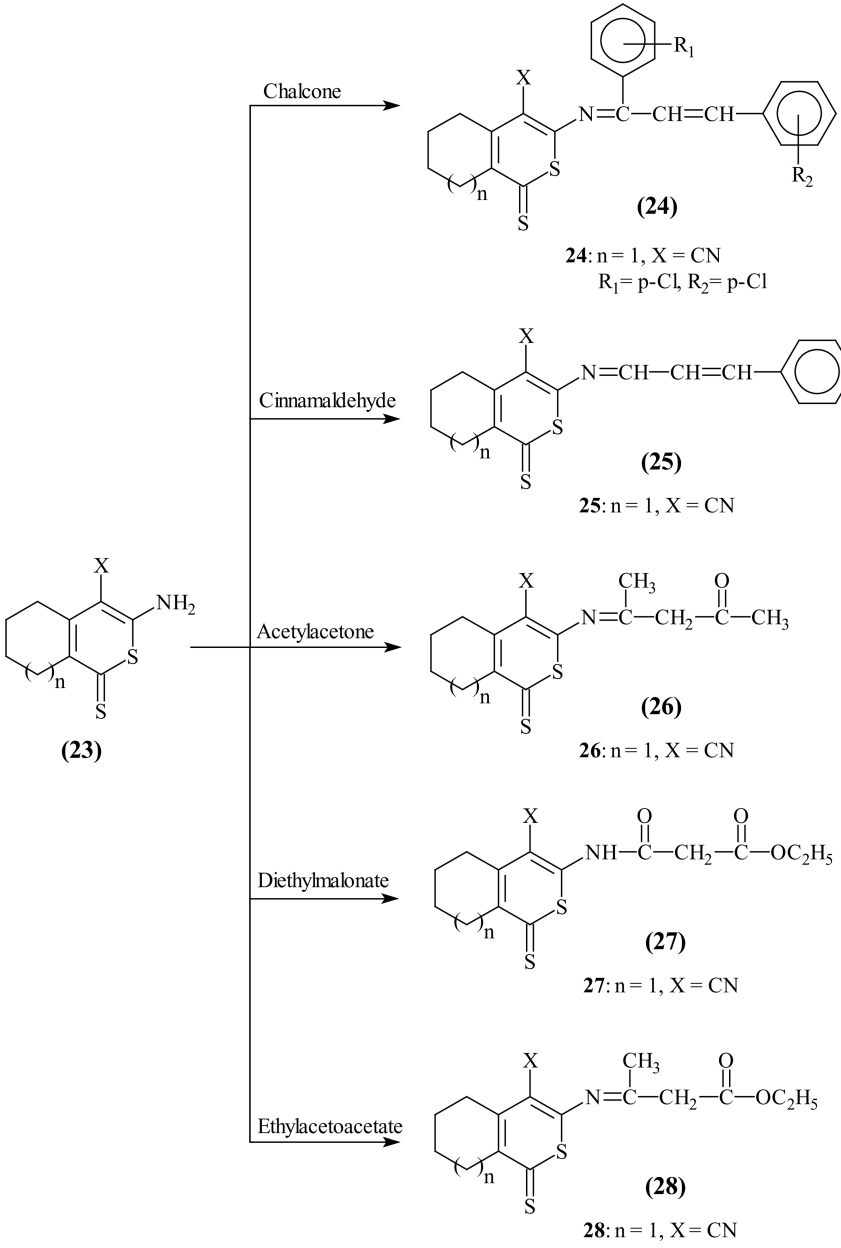
2,4-di(4-chlorophenyl)-7-thioxo-3,4,5,7,8,9,10,11-octahydro[1,2,4]-triazepino[2,3-b]isoquinolin-12-yl-cyanide (**29**);4-phenyl-7-thioxo-3,4,5,7,8,9,10,11-octahydro[1,2,4]triazepino[2,3-b]isoquinolin-12-yl-cyanide (**30**); 2-methyl-4-oxo-7-thioxo-3,4,5,7,8,9,10,11-octahydro[1,2,4]-triazepino [2,3-b]isoquinolin-12-yl cyanide (**31**).



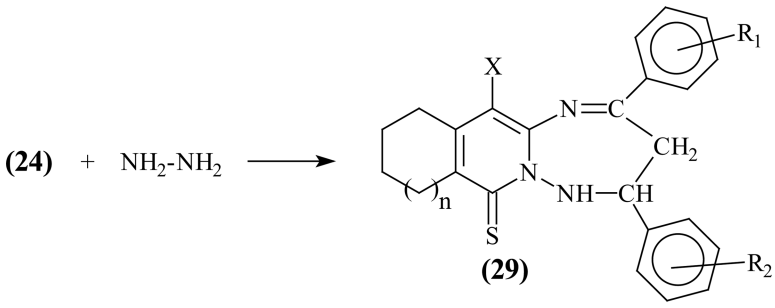
SCHEME 7



SCHEME 8

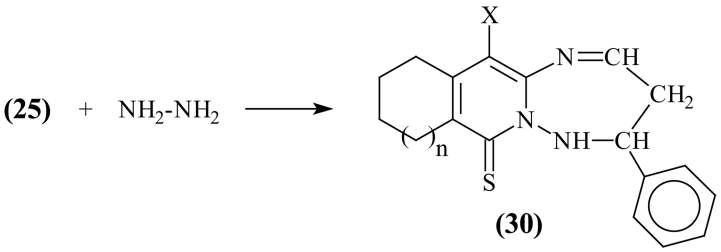


SCHEME 9



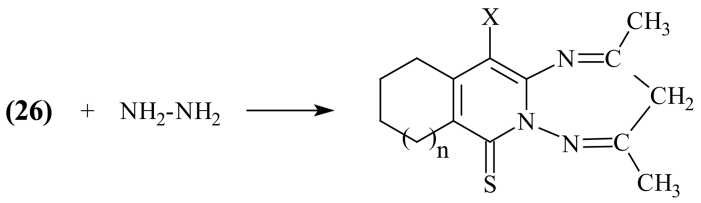
(29)

29: n = 1; X = CN
R_1= p-Cl, R_2= p-Cl



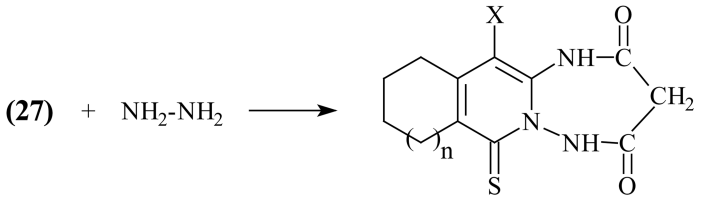
(30)

30: n = 1; X = CN



(15b)

15b: n = 1, x = CN



(17b)

17b: n = 1, x = CN

SCHEME 10

TABLE I Analytical Data of the Synthesized Compounds

Compd. no.	N	X	R_1	R_2	M.p.	Yield %	Found				Calculated			
							C	H	N	S	C	H	N	S
3a	0	$COOC_2H_5$	p-Cl	p-Cl	142–144	85	60.90	4.40	8.10	6.12	60.93	4.49	8.20	6.25
3b	0	$COOC_2H_5$	p-Cl	p-NO_2	147–149	88	59.62	4.30	10.61	6.05	59.71	4.40	10.71	6.12
3c	0	$COOC_2H_5$	p-Br	p-Cl	158–160	86	56.01	3.91	7.42	5.60	56.06	4.13	7.54	5.75
3d	0	$COOC_2H_5$	p-Br	p-NO_2	139–141	92	55.00	3.95	9.73	5.51	55.02	4.05	9.87	5.64
3e	1	CN	p-Cl	p-Cl	122–124	90	62.60	3.98	11.61	6.52	62.63	4.17	11.69	6.68
3f	1	CN	p-Cl	p-NO_2	168–170	91	61.20	3.95	14.21	6.43	61.28	4.08	14.30	6.53
3g	1	CN	p-Br	p-Cl	173–174	87	57.20	3.72	10.63	5.91	57.30	3.82	10.69	6.11
3h	1	CN	p-Br	p-NO_2	156–158	91	56.00	3.61	12.61	5.82	56.17	3.74	13.10	5.99
6a	0	$COOC_2H_5$	p-Cl	—	232–234	82	61.50	4.63	8.81	6.72	61.60	4.70	8.98	6.84
6b	1	CN	p-Cl-	—	192–194	78	63.42	4.21	12.81	7.23	63.52	4.37	12.88	7.36
9a	1	CN	p-Cl	—	160–162	73	64.90	4.56	16.73	6.31	64.99	4.61	16.85	6.41
9b	1	CN	p-NO_2	—	170–172	80	63.51	4.42	19.10	6.13	63.65	4.51	19.25	6.28
12a	0	$COOC_2H_5$	—	—	176–178	85	65.21	5.62	11.30	8.61	65.39	5.72	11.44	8.71
12b	1	CN	—	—	145–147	78	68.10	5.21	16.61	9.42	68.26	5.38	16.76	9.58
15a	0	$COOC_2H_5$	—	—	254–256	62	60.41	5.82	13.10	9.81	60.56	5.99	13.24	10.09
15b	1	CN	—	—	180–182	55	63.21	5.50	19.62	11.10	63.38	5.63	19.71	11.26
17a	0	$COOC_2H_5$	—	—	244–246	63	52.21	4.52	13.00	9.83	52.33	4.67	13.08	9.96
17b	1	CN	—	—	Over 300	61	53.91	4.01	19.31	10.94	54.16	4.16	19.44	11.11
19a	0	$COOC_2H_5$	—	—	238–240	67	56.30	5.21	12.98	9.84	56.42	5.32	13.16	10.03
19b	1	CN	—	—	216–218	61	58.62	4.74	19.4	10.98	58.74	4.89	19.58	11.18
24	1	CN	p-Cl	p-Cl	126–128	77	62.04	3.62	5.71	13.20	62.37	3.74	5.82	13.30
25	1	CN	—	—	162–164	87	67.7o	4.61	8.20	18.95	67.85	4.76	8.33	19.04
26	1	CN	—	—	236–238	89	59.11	5.10	9.10	20.96	59.21	5.26	9.21	21.05
27	1	CN	—	—	156–158	85	53.43	4.61	7.83	18.97	53.57	4.76	8.33	19.04
28	1	CN	—	—	206–208	90	57.32	5.20	8.21	18.89	57.48	5.38	8.38	19.16
29	1	CN	p-Cl	p-Cl	180–182	86	62.50	3.96	11.36	6.45	62.63	4.17	11.69	6.68
30	1	CN	—	—	238–240	78	68.01	5.12	16.36	9.24	68.26	5.38	16.76	9.58
31	1	CN	—	—	256–258	83	58.60	4.72	19.44	10.89	58.74	4.89	19.58	11.18

TABLE II Spectral Data of the Synthesized Compounds

Compd. no.	I.R. (KBr, ν_{max} cm^{-1})	^{1}H-NMR (DMSO-d_6/TMS) (δ/ppm)
3a	3400 (NH); 1660 (C=O); 1630 (C=N)	1.4 (t, 3H, CH_3), 4.1 (q, 2H, CH_2) ; 1.8 (m, 2H, CH_2); 2.6 (t, 2H, CH_2), 3.1(t, 2H, CH_2); 2.3 (d, 2H, CH_2-triazepine), 3.6 (t, 1H, CH-triazepine), 6.7 (s, 1H, NH-triazepine); 7.7–8.1 (m, 8H, Ar-H).
3b	3400 (NH); 1660(C=O); 1630 (C=N)	1.2 (t, 3H, CH_3), 4.2 (q, 2H, CH_2); 1.9 (m, 2H, CH_2), 2.5 (t, 2H, CH_2), 3.4 (t, 2H, CH_2); 2.5 (d, 2H, CH_2-triazepine), 3.3 (t, 1H, CH-triazepine), 6.7 (s, 1H, NH-triazepine); 7.2–7.8 (m, 8H, Ar-H).
3c	3300 (NH); 1660 (C=O); 1640 (C=N)	1.3 (t, 3H, CH_3), 4.1 (q, 2H, CH_2); 1.7 (m, 2H, CH_2); 2.5 (t, 2H, CH_2), 3.2 (t, 2H, CH_2); 2.3 (d, 2H, CH_2-triazepine), 3.3 (t, 1H, CH-triazepine), 6.6 (s, 1H, NH-triazepine); 7.2–7.8 (m, 8H, Ar-H).
3d	3300 (NH); 1660 (C=O); 1640 (C=N)	1.2 (t, 3H, CH_3), 4.2 (q, 2H, CH_2); 1.8 (m, 2H, CH_2); 2.4 (t, 2H, CH_2), 3.1 (t, 2H, CH_2); 2.2 (d, 2H, CH_2-triazepine), 3.2 (t, 1H, CH-triazepine); 6.8 (s, 1H, NH-triazepine); 7.3–8.1 (m, 8H, Ar-H).
3e	3500 (NH); 2200 (C≡N); 1630 (C=N)	1.2 (m, 4H, $2CH_2$), 2.3 (m, 4H, $2CH_2$); 2.1 (d, 2H, CH_2-triazepine), 3.1 (t, 1H, CH-triazepine), 6.8 (s, 1H, NH-triazepine); 7.9–8.2 (m, 8H, Ar-H).
3f	3400 (NH); 2200 (C≡N); 1630 (C=N)	1.3 (m, 4H, $2CH_2$), 2.4 (m, 4H, $2CH_2$); 2.2 (d, 2H, CH_2-triazepine), 3.3 (t, 1H, CH-triazepine), 6.8 (s, 1H, NH-triazepine); 7.9–8.3 (m, 8H, Ar-H).
3g	3300 (NH); 2200 (C≡N); 1650 (C=N)	1.3 (m, 4H, $2CH_2$), 2.2 (m, 4H, $2CH_2$); 2.8 (d, 2H, CH_2-triazepine), 3.6 (t, 1H, CH-triazepine), 6.6 (s, 1H, NH-triazepine); 7.3–7.9 (m, 8H, Ar-H).
3h	3400 (NH); 2200 (C≡N); 1630 (C=N)	1.3 (m, 4H, $2CH_2$), 2.4 (m, 4H, $2CH_2$); 2.6 (d, 2H, CH_2-triazepine), 3.1 (t, 1H, CH-triazepine), 6.7 (s, 1H, NH-triazepine); 7.8–8.2 (m, 8H, Ar-H).
6a	3300 (NH); 1630 (C=N)	1.3 (t, 3H, CH_3), 4.2 (q, 2H, CH_2); 2.1 (m, 2H, CH_2); 2.7 (t, 2H, CH_2), 3.1 (t, 2H, CH_2); 3.8 (d, 2H, CH_2-triazepine), 4.2 (t, 1H, CH-triazepine),9.4 (s, 1H, NH-triazepine); 7.4–7.7 (m, 7H, Ar-H).
6b	3300 (NH); 2200 (C≡N); 1650 (C=N)	1.2 (m, 4H, $2CH_2$), 1.7 (m, 4H, $2CH_2$); 3.6 (d, 2H, CH_2-triazepine), 4.1 (t, 1H, CH-triazepine), 7.8 (s, 1H, NH-triazepine; 7.2–7.8 (m, 7H, Ar-H).
9a	3400 (NH); 2200 (C≡N); 1620 (C=N)	1.2 (m, 4H, $2CH_2$), 1.9 (m, 4H, $2CH_2$); 2.4 (d, 1H, CH-triazepine), 2.7 (d, 1H, CH-triazepine), 6.8 (s, 1H, NH-triazepine); 2.2 (s, 3H, CH_3); 7.2–7.8 (m, 9H, Ar-H).
9b	3300 (NH); 2200 (C≡N); 1620 (C=N)	1.2 (m, 4H, $2CH_2$), 1.9 (m, 4H, $2CH_2$); 2.2 (d, 1H, CH-triazepine), 2.6 (d, 1H, CH-triazepine), 5.2 (s, 1H, NH-triazepine); 2.4 (s, 3H, CH_3); 7.1–7.9 (m, 9H, Ar-H).

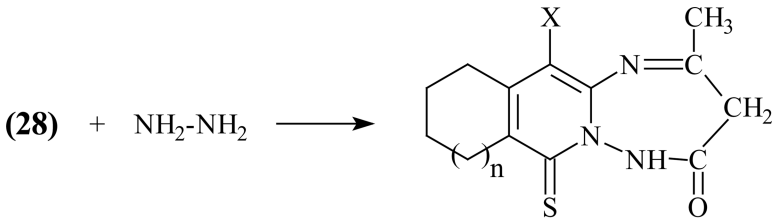
(Continued on next page)

TABLE II Spectral Data of the Synthesized Compounds *(Continued)*

Compd. no.	I.R. (KBr, ν_{max} cm^{-1})	^{1}H-NMR (DMSO-d_6/TMS) (δ/ppm)
12a	3300 (NH); 1670(C═O); 1590 (C═N)	1.2 (t, 3H, CH_3), 4.2 (q, 2H, CH_2); 1.9 (m, 2H, CH_2), 2.8 (t, 2H, CH_2), 3.1 (t, 2H, CH_2); 2.4 (t, 1H, CH-triazepine), 2.8 (t, 2H, CH_2-triazepine), 3.6 (t, 1H, CH-triazepine), 6.7 (s, 1H, NH-triazepine); 7.2–7.4 (m, 5H, Ar-H).
12b	3400 (NH); 2200 (C≡N)	1.2 (m, 4H, $2CH_2$), 2.1 (m, 4H, $2CH_2$); 2.5 (t, 1H, CH-triazepine), 2.6 (t, 2H, CH_2-triazepine), 2.9 (t, 1H, CH-triazepine), 6.7 (s, 1H, NH-triazepine); 7.2–7.5 (m, 5H, Ar-H).
15a	1680 (C═O); 1630 (C═N)	1.2 (t, 3H, CH_3), 4.2 (q, 2H, CH_2) ; 1.9 (m, 2H, CH_2), 2.8 (t, 2H, CH_2), 3.1 (t, 2H, CH_2); 2.6 (s, 2H, CH_2-triazepine), 2.0 (s, 3H, CH_3); 2.2 (s, 3H, CH_3).
15b	2200 (C≡N); 1620(C═N)	1.3 (m, 4H, $2CH_2$), 2.5 (m, 4H, $2CH_2$); 3.3 (s, 2H, CH_2-triazepine); 2.1 (s, 3H, CH_3); 2.3 (s, 3H, CH_3).
17a	3500 (NH); 1670(C═O); 1620(C═N)	1.2 (t, 3H, CH_3), 4.6 (q, 2H, CH_2) ; 1.8 (m, 2H, CH_2), 2.4 (t, 2H, CH_2), 4.1 (t, 2H, CH_2); 3.2 (s, 2H, CH_2-triazepine), 3.4 (s, 1H, NH-triazepine), 3.9 (s, 1H, NH-triazepine).
17b	3500 (NH); 2200 (C≡N); 1610 (C═O)	1.4 (m, 4H, $2CH_2$), 2.2 (m, 4H, $2CH_2$); 3.1 (s, 2H, CH_2-triazepine), 3.6 (s, 1H, NH-triazepine), 4.1 (s, 1H, NH-triazepine).
19a	3400 (NH); 1660 (C═O); 1620 (C═N)	1.2 (t, 3H, CH_3), 4.1 (q, 2H, CH_2); 1.8 (m, 2H, CH_2), 2.3 (t, 2H, CH_2), 3.5 (t, 2H, CH_2); 3.1 (s, 2H, CH_2-triazepine), 3.3 (s, 1H, NH-triazepine); 2.5 (s, 3H, CH_3).
19b	3400 (NH); 2200 (C≡N); 1680 (C═O); 1620 (C═N)	1.2 (m, 4H, $2CH_2$), 1.9 (m, 4H, $2CH_2$); 3.7 (s, 2H, CH_2-triazepine), 3.9 (s, 1H, NH-triazepine); 2.3 (t, 3H, CH_3).
24	2200 (C≡N); 1620 (C═N)	1.2 (m, 4H, $2CH_2$), 1.9 (m, 4H, $2CH_2$); 4.1 (d, 1H, CH), 4.3 (d, 1H, CH); 7.2–7.8 (m, 8H, Ar-H).
25	2200 (C≡N); 1620 (C═N)	1.3 (m, 4H, $2CH_2$), 2.1 (m, 4H, $2CH_2$); 4.3 (d, 1H, CH), 6.1 (d, 1H, N═CH), 4.5 (t, 1H, CH); 7.2 (m, 5H, Ar-H).
26	2200 (C≡N); 1700 (C═O); 1650 (C═N)	1.2 (m, 4H, $2CH_2$), 1.9 (m, 4H, $2CH_2$); 2.8 (s, 3H, CH_3); 3.1 (s, 3H, CH_3); 3.4 (s, 2H, CH_2).
27	3400 (NH); 2200 (C≡N); 1680 (C═O)	1.5 (m, 4H, $2CH_2$), 2.2 (m, 4H, $2CH_2$); 1.3 (t, 3H, CH_3); 4.3 (q, 2H, CH_2); 3.9 (s, 2H, CH_2); 8.9 (s, 1H, NH).
28	2200 (C≡N); 1670 (C═O); 1620(C═N)	1.5 (m, 4H, $2CH_2$), 1.9 (m, 4H, $2CH_2$); 2.6 (s, 3H, CH_3); 1.3 (t, 3H, CH_3); 3.4 (s, 2H, CH_2); 4.1 (q, 2H, CH_2).

TABLE II Spectral Data of the Synthesized Compounds *(Continued)*

Compd. no.	I.R. (KBr, ν_{max} cm^{-1})	^{1}H-NMR (DMSO-d_6/TMS) (δ/ppm)
29	3500 (NH); 2200 (C≡N); 1620 (C=N)	1.3 (m, 4H, $2CH_2$), 1.8 (m, 4H, $2CH_2$); 3.1 (d, 2H, CH_2-triazepine), 3.6 (t, 1H, CH-triazepine), 6.5 (s, 1H, NH-triazepine); 7.2–7.8 (m, 8H, Ar-H.)
30	3400 (NH); 2200 (C≡N); 1630(C=N)	1.2 (m, 4H, $2CH_2$), 1.9 (m, 4H, $2CH_2$); 2.8 (t, 1H, CH-triazepine), 3.6 (t, 2H, CH_2-triazepine), 4.2 (t, 1H, CH-triazepine); 7.0–7.4 (m, 5H, Ar-H).
31	3300 (NH); 2200 (C≡N); 1670 (C=O); 1620(C=N)	1.3 (m, 4H, $2CH_2$), 1.8 (m, 4H, $2CH_2$); 3.5 (s, 2H, CH_2-triazepine), 6.5 (s, 1H, NH-triazepine); 2.9 (s, 3H, CH_3).



(31)

31: n = 1; X = CN

SCHEME 11

General Procedure

Five mmole of the azomethines (**24–28**) in 30 mL methanol and 1 mL of hydrazine hydrate was refluxed for 10 h until the evolution of H_2S was ceased. The precipitated products were collected and crystallized from the proper solvent to give products (**29–31**).

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