Synthesis of Some Pyranooxazine, Pyranopyrazolooxazine, Pyrrolothiopyranothiazepine, Triazepine, Thiadiazepine, and Thiadiazocine Derivatives

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The high-yield straightforward synthesis of 1,3-oxazine, pyranopyrazolo[1,3]oxazine, pyrrolothiopyrano[1,4]thiazepine, pyrrolocyclopentanopyridine, pyrrolocyclohexanoazepine, pyrazolinyl-1,2,4-triazepine, and 1,3-thiazepinyl-1,3,7-thiadiazocine is described starting from the intermediates derived from 2-amino-1,1,3-tricyanoprop-1-ene.

β-Enaminonitriles have proved to be valuable for the synthesis of a wide variety of unique heterocyclic systems including pyrazoles [1, 2], imidazoles [3], pyridines [4—6], pyrimidines [7], and thiophenes [8—10].

The scope and applicability of 2-amino-1,1,3-tricyanoprop-1-ene (*I*) as a key precursor for the synthesis of heterocyclic compounds including 1,3-oxazine, pyranopyrazolo[1,3]oxazine, pyrrolothiopyrano[1,4]thiazepine, pyrrolocyclopentanopyridine, pyrrolocyclohexanoazepine, pyrazolinyl-1,2,4-triazepine, and 1,3-thiazepinyl-1,3,7-thiadiazocine is reported. Thus, on refluxing compound *I* [11] along with 2,5-dimethoxytetrahydrofuran in acetic acid 1,1,3-tricyano-2-(pyrrol-1-yl)prop-1-ene (*II*) was obtained (Scheme 1, Tables 1 and 2). Treatment of compound *I* with formaldehyde furnished the corresponding dihydroxymethyl [12] derivative *III* which in turn was converted into the corresponding dichloro derivative *IV* when treated with thionyl chloride. The condensation of compound *I* with two equivalents of *p*-nitrobenzaldehyde afforded 1,1,3-tricyano-3-(*p*-nitrobenzylidene)-2-(*p*-nitrobenzylidenamino)-prop-1-ene (*V*) and 8-cyano-4,5-diimino-2,7-bis(*p*-nitrophenyl)-4,5*H*-1,2-dihydropyrano[4,3-*d*][1,3]oxazine (*VI*). The latter compound underwent intramolecular cyclization on treating with ferric chloride in boiling ethanol to afford the corresponding pyrazolopyrano[1,3]oxazine derivative *VII*. Moreover, the reaction of compound *I* with 2,5-dimethylfuran yielded the corresponding bicyclic compound *VIII*.

Next, the applicability of compound *II* as a precursor for the construction of a variety of fused heterocycles containing a pyrrole ring has been investigated. So, compound *II* was allowed to react with two equivalents of phenyl isothiocyanate in refluxing pyridine to afford the corresponding 1-cyano-4,5-diimino-2,7-bis(phenylimino)-1*H*-pyrrolo[2,1-*c*]thiazepino[4,3-*e*]-thiopyran (*IX*) (Scheme 2). The reaction pathway was assumed to proceed *via* the addition of both H-2 of the pyrryl ring and the methylene group to the two molecules of PhNCS followed by nucleophilic addition of the formed SH groups to the two geminal cyano groups.

The reaction of compound *II* with halo compounds containing active methylene group, namely chloroacetonitrile, phenacyl bromide, chloroacetamide or chloroacetyl chloride in 1:2 mole ratio gave the 3,4-diamino-1,2,5-tricyano- (*Xa*), 3,4-diamino-2,5-dibenzoyl-1-cyano- (*Xb*), 3,4-diamino-2,5-carbamoyl-1-cyano-1*H*-pyrrolo[1,2-*a*]cyclopentadienopyridine (*Xc*) or 4,5-diamino-3,6-dichloro-1-cyano-2,7-dioxo-1*H*-pyrrolo-[1,2-*a*]cyclohexanoazepine (*XI*). The formation of these compounds is believed to proceed *via* the alkylation of both the C-2 of the pyrryl ring and the methylene group followed by intramolecular cyclization through the addition of the two active methylene groups to the geminal cyano groups.

Also, compound *IV* is a good starting material for the synthesis of heterocycles. So, treatment of compound *IV* with hydrazine hydrate or thiourea in 1:2 mole ratio in refluxing DMF afforded the corresponding 7-amino-5-(5-amino-3,4-dihydro-2*H*-pyrazol-4-yl)-6-cyano-2,3-dihydro-4*H*-1,2,4-triazepine (*XII*) and 5-amino-4-cyano-3-(4-amino-2-imino-5,6-dihydro-1,3-thiazin-5-yl)-7-imino-2,7*H*-1,2,6-thiadiazepine (*XIII*) (Scheme 3). The reaction pathway was assumed to proceed through the substitution for the two chloro

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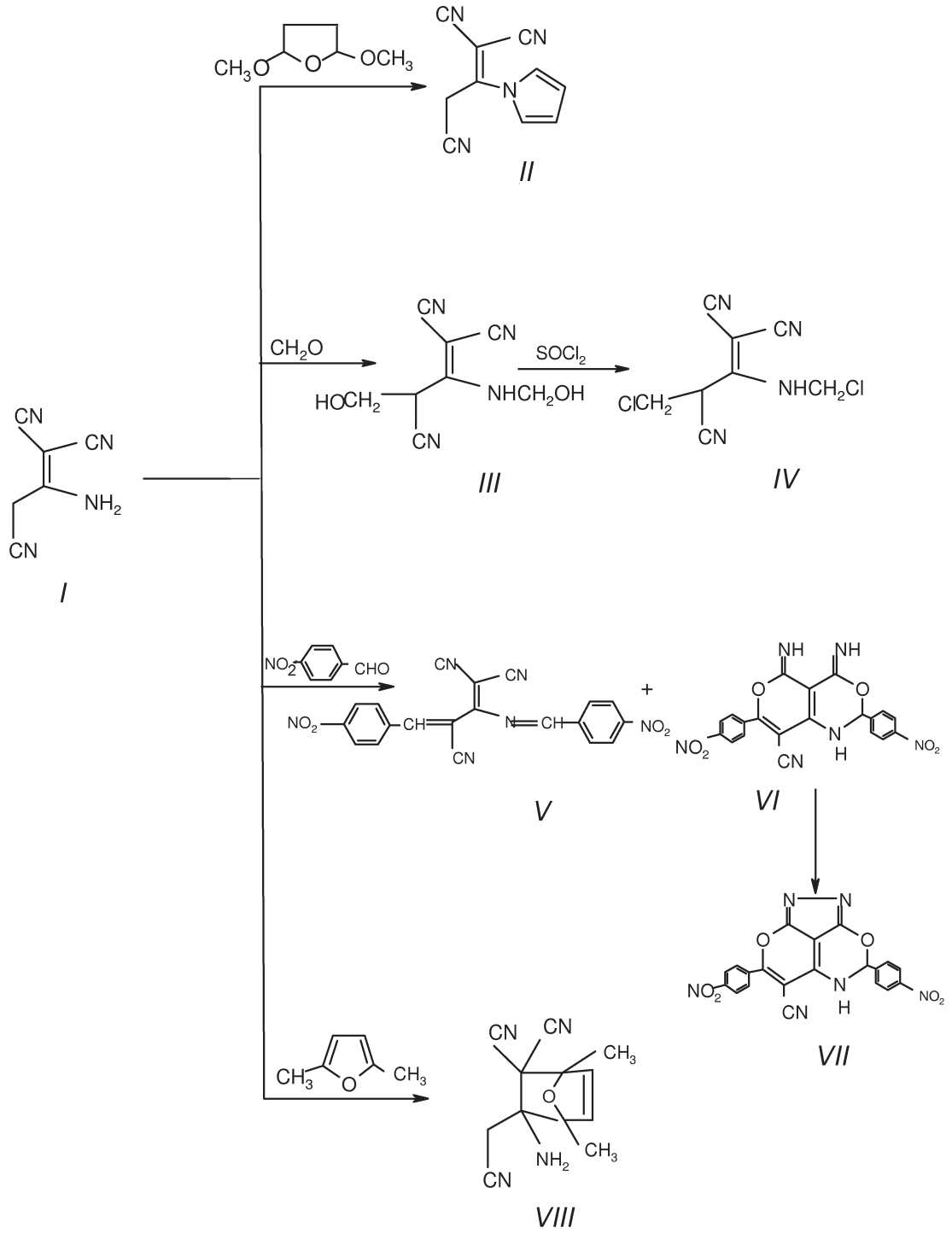


Scheme 1

atoms by either hydrazine hydrate *via* the amino group or thiourea through the thiol group followed by the addition of the amino groups to both the olefinic cyano groups and the aliphatic cyano group.

Moreover, compound *V* was proved to be reactive towards the reagents with two nucleophilic centres. Thus, compound *V* was treated with two equivalents of 2-sulfanylethanol, *o*-aminothiophenol, *o*-phenylenediamine, phenyldithiocarbamate, and *S*,*S*- or *N*,*S*-acetals to yield the corresponding heterocycles {[5-imino-7-(*p*-nitrophenyl)-1,4-thioxepin-6-yl]-[(2-cyano-1,3-thiazolidin-1-yl)methylene]}malonodinitrile (*XIV*), *XV*, 4-[2-imino-6-(*p*-nitrophenyl)-3-phenyl-2-thioxo-1,3-thiazin-5-yl)-5-cyano-6-imino-2-(*p*-nitrophenyl)-7-phenyl-2,3,4,7-tetrahydro-1,3,7-thiadiazocin-8-thione (*XVIa*), 7-cyano-6-[4-imino-6-(*p*-

Table 1. Analytical Data of the New Compounds

Compound	Formula M_r	w_i(calc.)/% w_i/(found)/% C	H	N	S	Yield %	M.p./°C Solvent
II	$C_{10}H_6N_4$	65.93	3.32	30.75	–	80	dec 300
	182.186	66.10	3.40	30.62			
III	$C_8H_8N_4O_2$	50.00	4.20	29.15	–	73	210
	192.179	51.02	4.11	29.06			
IV	$C_8H_6N_4Cl_2$	41.93	2.64	24.45	–	70	dec 300
	229.164	42.09	2.50	24.60			
V	$C_{20}H_{10}N_6O_4$	60.31	2.53	21.10	–	83	265
	398.340	60.25	2.61	21.15			
VI	$C_{20}H_{12}N_6O_6$	55.56	2.80	19.44	–	46	290
	432.355	55.71	2.89	19.33			
VII	$C_{20}H_{10}N_6O_6$	55.82	2.34	19.53	–	60	> 300
	430.339	55.90	2.41	19.45			
VIII	$C_{12}H_{12}N_4O$	63.15	5.30	24.55	–	58	175
	228.256	63.30	5.30	24.48			
IX	$C_{24}H_{16}N_6S_2$	63.70	3.56	18.57	14.20	60	245
	452.563	63.81	3.51	18.60	14.29		Dioxane
Xa	$C_{14}H_8N_6$	64.61	3.10	32.29	–	69	dec > 320
	260.260	64.72	3.00	32.21			Ethanol
Xb	$C_{26}H_{18}N_4O_2$	74.63	4.34	13.39	–	73	> 320
	418.459	74.73	4.28	13.31			Dioxane
Xc	$C_{14}H_{12}N_6O_2$	56.75	4.08	28.36	–	58	> 300
	296.291	56.82	4.17	28.30			Dioxane
XI	$C_{14}H_8N_4O_2Cl_2$	50.16	2.41	16.71	–	67	> 300
	335.246	50.27	2.35	16.65			Dioxane
XII	$C_8H_{12}N_8$	43.63	5.44	50.88	–	78	dec 300
	220.238	43.80	5.39	50.70			Benzene
XIII	$C_9H_{10}N_8S_2$	36.72	3.42	38.07	21.79	71	> 300
	294.362	36.84	3.35	38.18	21.71		Chloroform
XIV	$C_{24}H_{20}N_6S_2O_5$	53.72	3.76	15.66	11.95	59	117
	536.592	53.70	3.85	15.80	11.84		Dioxane
XVa	$C_{32}H_{24}N_8S_2O_4$	59.25	3.73	17.27	9.89	53	240
	648.727	59.41	3.65	17.18	9.78		Xylene
XVb	$C_{32}H_{26}N_{10}O_4$	62.54	4.26	22.79	–	70	218
	614.629	62.56	4.17	22.72			Dioxane
XVIa	$C_{34}H_{24}N_8S_4O_4$	55.42	3.28	15.21	17.41	49	>300
	736.878	55.59	3.19	15.30	17.38		Xylene
XVIb	$C_{34}H_{24}N_8S_4O_4$	55.42	3.28	15.21	17.41	51	212
	736.878	55.51	3.14	15.31	17.38		DMF
XVIIa	$C_{32}H_{26}N_6S_4O_8$	51.19	3.49	11.19	17.08	63	>340
	750.855	51.30	3.38	11.12	17.10		DMF
XVIIb	$C_{36}H_{34}N_6S_4O_{12}$	51.05	4.05	9.92	15.14	57	190
	847.049	51.14	4.00	10.02	15.07		Dioxane
XVIIc	$C_{34}H_{30}N_6S_4O_{10}$	50.36	3.73	10.36	15.82	68	180
	810.908	50.45	3.81	10.28	15.77		Xylene
XVIIIa	$C_{44}H_{36}N_8O_8S_2$	60.82	4.18	12.90	7.38	49	178
	868.955	60.91	4.20	13.00	7.45		DMF
XVIIIb	$C_{48}H_{44}N_8O_{12}S_2$	58.29	4.48	11.33	6.48	52	142
	989.061	58.38	4.56	11.15	6.39		Xylene
XVIIIc	$C_{46}H_{40}N_8O_{10}S_2$	59.47	4.34	12.06	6.90	62	202
	929.007	59.62	4.25	12.00	6.81		Xylene

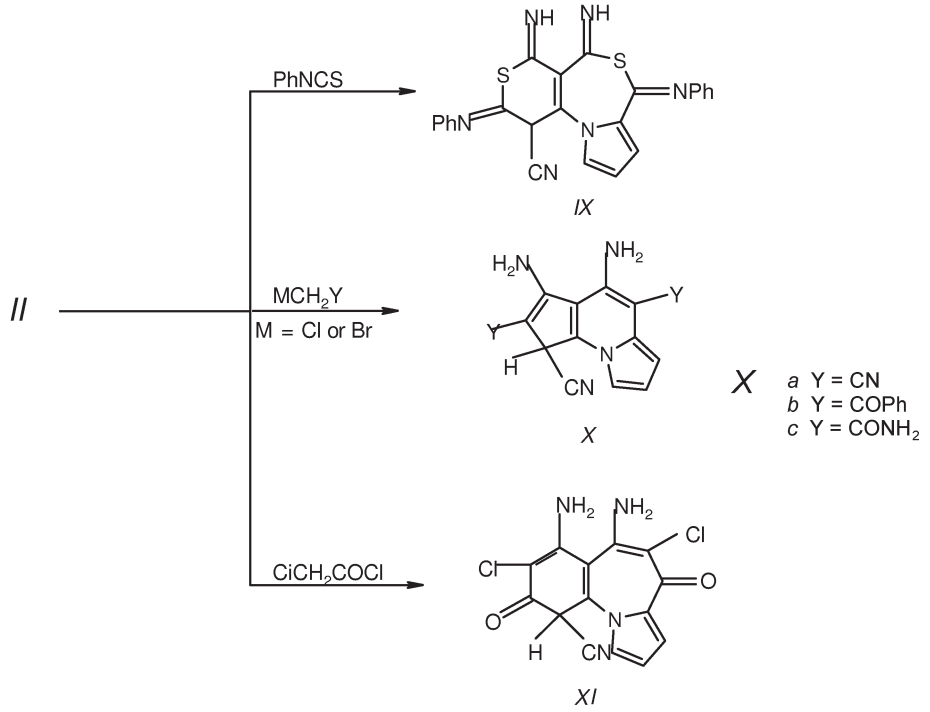
nitrophenyl)-2-phenyl-5,6-dihydro-2-thion-1,3-thiazin-5-yl]-8-imino-4-(*p*-nitrophenyl)-2-phenylimino-4,5-dihydro-1,3,5-dithiazocine (*XVIb*), 7-cyano-2-diacetyl/diethoxycarbonyl/acetyl-ethoxycarbonylmethylene-6-[2-diacetyl/diethoxycarbonyl/acetyl-ethoxycarbonylmethylene-4-imino-6-(*p*-nitrophenyl)-5,6-dihydro-1,3-dithiazin-5-yl]-8-imino-4-(*p*-nitrophenyl)-4,5-dihydro-1,3,5-dithiazocine (*XVIIa*—*XVIIc*) or 8-diacetyl/di-

Table 2. Spectral Data of the New Compounds

	IR, $\tilde{\nu}/\mathrm{cm}^{-1}$	^{1}H NMR, δ
II	2950 (CN); 2201, 2210 (2CN); 1650 (C═C)	4.10—470 (t, 2H, 2CH); 3.85 (s, 2H, CH_2); 2.85—3.30 (d, 2H, 2CH)
III	3427 (OH); 3250 (NH); 2590, 2880 (CH); 2210, 2160 (3CN); 1650 (C═C)	5.95—6.15 (br, 1H, NH); 4.70—4.95 (d, 2H, CH_2); 4.05—4.45 (t, 1H, CH); 3.80 (s, 2H, 2OH); 2.55 (s, 2H, CH_2)
IV	3270 (NH); 2960 (CH); 2218, 2196 (3CN); 1636 (C═C)	5.85 (s, 1H, NH); 4.90—5.25 (d, 2H, CH_2); 4.15—4.50 (t, 1H, CH); 2.45 (S, 2H, CH_2)
V	3225 (CH); 2950 (CH); 2214 (CN); 1620 (C═N); 1608 (C═C); 1520, 1348 (NO_2)	8.85 (s, 1H, CH═); 8.60 (s, 1H, CH═); 7.65—8.45 (m, 8H$_{arom}$)
VI	3250, 3200 (3NH); 3050 (CH); 2910 (CH); 2206 (CN); 1610 (C═N); 1520, 1333 (NO_2)	9.40—9.70 (br, 2H, 2NH); 8.9 (s, 1H, NH); 7.40—8.15 (m, 8H$_{arom}$); 4.35 (s, 1H, CH)
VII	3250 (NH); 3050 (CH); 2950 (CH); 2200 (CN); 1610, 1600 (C═C) and (C═N)	8.50 (s, 1H, NH); 7.55—8.10 (m, 8H $_{arom}$); 4.25 (s, 1H, CH)
VIII	3350, 3225 (NH_2); 2920 (CH); 2209, 2120 (3CN); 1650 (C═C)	7.7—8.2 (d, 2H, 2CH); 4.2 (s, 2H, NH_2); 3.5 (s, 6H, $2CH_3$); 3.2 (s 2H, CH_2)
IX	3208, 3188 (2NH); 3010 (CH); 2850 (CH); 2179 (CN); 1600 (C═N)	9.10—9.50 (br, 2H, 2NH); 7.25—8.35 (m, 10H$_{arom}$); 6.90—7.15 (d, 1H, CH); 5.15—5.50 (t, 1H, CH); 4.85—5.05 (d, 1H, CH); 3.60 (s, 1H, CH)
Xa	3360, 3245 ($2NH_2$); 2960 (CH); 2210, 2165 (3CN)	6.80—7.05 (d, 1H, CH); 6.25—6.80 (br, 4H, $2NH_2$); 5.10—5.40 (t, 1H, CH); 4.86—5.05 (d, H, CH); 3.60 (s, 1H, CH)
Xb	3322, 3220 ($2NH_2$); 3025, 2960 (CH); 1685 (2CO); 2177 (CN)	7.25—8.15 (m, 10H$_{arom}$); 6.85—7.20 (d, 1H, CH); 6.25—6.55 (br, 4H, $2NH_2$); 5.20—5.55 (t, 1H, CH); 4.7—5.10 (d, 1H, CH); 3.45 (s, 1H, CH)
Xc	3355, 3311, 3250, 3198 ($4NH_2$); 2950 (CH); 2183 (CN); 1654 (2C═O)	6.80—7.10 (d, 1H, CH); 5.75—6.45 (br, 8H, $4NH_2$); 5.45—5.70 (t, 1H, CH); 4.85—5.05 (d, 1H, CH), 3.50 (s, 1H, CH)
XI	3283, 3178 ($2NH_2$); 2910 (CH); 2188 (CN); 1664 (C═O)	6.98—7.20 (d, 1H, CH); 6.20—6.55 (br, 4H, $2NH_2$); 5.45—5.70 (t, 1H, CH); 4.95—5.15 (d, 1H, CH); 3.35 (s, 1H, CH)
XII	3389, 3328, 3310, 3260, 3208 (3NH, $2NH_2$); 2910 (CH); 2210 (CN)	9.45—9.75 (br, 2H, 2NH); 9.10 (s, 1H, NH); 5.05—5.35 (br, 4H, $2NH_2$); 3.25 (s, 2H, CH_2); 2.35 (s, 2H, CH_2)
XIII	3364, 3232 ($2NH_2$, 3NH); 2921 (CH); 2210 (CN); 1650 (C═N)	7.3 (s, 2H, 2NH); 3.8 (s, 2H, CH_2); 2.6—3.5 (br, 5H, $2NH_2$ + NH); 2.2 (s, 1H, CH)
XIV	3354 (NH); 2934 (CH); 2210 (2CN); 1600 (C═N); 1530, 1420 ($2NO_2$)	9.3 (s, 1H, NH); 6.90—8.25 (m, 8H$_{arom}$); 4.75 (s, 1H, CH); 3.75 (s, 1H, CH); 2.95—3.45 (m, 8H, $4CH_2$); 1.65 (s, 1H, CH)
XVa	3356, 3318, 3260, 3205 (NH, $2NH_2$); 3010, 2910 (CH); 2214 (CN); 1540, 1425 ($2NO_2$)	9.45 (s, 1H, NH); 6.75—8.25 (m, 16H$_{arom}$); 6.05—6.35 (br, 4H, $2NH_2$); 4.65 (s, 1H, CH); 2.00—3.25 (d, 1H, CH); 1.60—1.85 (d, 1H, CH)
XVb	3415, 3380, 3325, 3225, 3207 (3NH, $2NH_2$); 3000 (CH); 2910 (CH); 2216 (CN); 1640 (C═N); 1555, 1430 (NO_2)	9.35—9.65 (br, 2H, 2NH); 8.85 (s, 1H, NH); 6.95—8.15 (m, 16H$_{arom}$); 5.85—6.15 (br, 4H, $2NH_2$); 4.55 (s, 1H, CH); 3.05—3.65 (d, 1H, CH); 1.75—1.95 (d, 1H, CH)
XVIa	3361, 3344, 3241 (3NH); 3032 (CH); 2215(CN); 1636 (C═N); 1129, 1124 (2C═S); 1535, 1430 (NO_2)	9.15—9.45 (br, 2H, 2NH); 8.75 (s, 1H, NH); 6.85—8.15 (m,18H$_{arom}$); 4.35 (s, 1H, CH); 3.15—3.35 (d, 1H, CH); 2.15—2.45 (d, 1H, CH)
XVIb	3254, 3137 (3NH); 3050, 2930 (CH); 2213 (CN); 1639 (C═N); 1540, 1320 ($2NO_2$)	9.35—9.70 (br, 2H, 2NH); 8.85 (s, 1H, NH); 6.90—8.25 (m, 18H$_{arom}$); 4.55 (s, 1H, CH); 3.20—3.50 (d, 1H, CH); 2.35—2.60 (d, 1H, CH)
XVIIa	3375, 3210 (3NH); 3110, 2961 (CH); 2217 (CN); 1700 (4C═O); 1610 (C═N); 1545, 1330 ($2NO_2$)	9.15—9.55 (br, 2H, 2NH); 8.95 (s, 1H, NH); 7.25—8.15 (m, 8H$_{arom}$); 4.35 (s, 1H, CH); 3.25—3.55 (d, 1H, CH); 2.85 (s, 12H, $4CH_3$); 2.20—2.45 (d, 1H, CH)
XVIIb	3348, 3210, 3100 (3NH); 2951 (CH); 3213 (CH); 1705 (4C═O); 1540,1338 ($2NO_2$)	9.30—9.65 (br, 2H, 2NH); 8.90 (s, 1H, NH); 7.35—8.25 (m, 8H$_{arom}$); 4.53 (s, 1H, CH); 3.75—4.15 (q, 8H, $4CH_2$); 3.20—3.45 (d, 1H, CH); 2.10—2.35 (d, 1H, CH); 0.90—1.25 (t, 12H, $4CH_3$)
XVIIc	3380, 3200, 3180 (3NH); 3010, 2959 (CH); 2215 (CN); 1715, 1700 (4C═O); 1632 (C═N); 1542, 1330 ($2NO_2$)	9.25—9.50 (br, 2H, 2NH); 8.75 (s, 1H, NH); 7.35—8.25 (m, 8H$_{arom}$); 4.25 (s, 1H, CH); 3.70—4.15 (q, 4H, $2CH_2$); 3.20—3.50 (d, 1H, CH); 2.80 (s, 6H, $2CH_3$); 2.25 (d, 1H, CH); 0.90—1.25 (t, 6H, $2CH_3$)

Table 2. (continued)

	IR, $\tilde{\nu}/cm^{-1}$	^1H NMR, δ
XVIIIa	3320, 3275, 3190 (3NH); 3030, 2963 (CH); 2214 (CN); 1700 (4C=O); 1610 (C=N); 1540, 1335 ($2NO_2$)	9.70—9.85 (br, 2H, 2NH); 8.85 (s, 1H, NH); 7.25—8.30 (m, $18H_{arom}$); 4.40 (s, 1H, CH); 3.25—3.60 (d, 1H, CH); 2.80 (s, 12H, $4CH_3$); 2.15—4.40 (d, 1H, CH)
XVIIIb	3342, 3312, 3293 (3NH); 3025, 2964 (CH); 2216 (CN); 1720 (4C=O); 1637 (C=N); 1555, 1416 ($2NO_2$)	9.55—9.75 (br, 2H, 2NH); 8.85 (s, 1H, NH); 7.15—8.20 (m, $18H_{arom}$); 4.35 (s, 1H, CH); 3.15—3.65 (q, 8H, $4CH_2$); 3.15—3.50 (d, 1H, CH); 2.10—2.30 (d, 1H, CH); 0.90—1.30 (t, 12H, $4CH_3$)
XVIIIc	3339, 3295, 3270 (3NH); 3020, 2950 (CH); 2217 (CN); 1700 (4C=O); 1638 (C=N); 1560, 1415 ($2NO_2$)	9.40—9.65 (br, 2H, 2NH); 8.75 (s, 1H, NH); 7.20—8.10 (m, $18H_{arom}$); 4.30 (s, 1H, CH); 3.75—4.15 (q, 4H, $2CH_2$); 3.15—3.55 (d, 1H, CH); 2.85 (s, 6H, $2CH_3$); 2.05—2.30 (d, 1H, CH); 0.85—1.20 (t, 6H, $2CH_3$)



Scheme 2

ethoxycarbonyl/acetyl-ethoxycarbonylmethylene-6-[2-diacetyl/diethoxycarbonyl/acetyl-ethoxycarbonyl-methylene-4-imino-6-(*p*-nitrophenyl)-3-phenyl-5,6-dihydro-1,3-dithiazin-5-yl]-5-cyano-6-imino-2-(*p*-nitrophenyl)-7-phenyl-1,3,7-thiadiazocine (*XVIIIa*—*XVIIIc*).

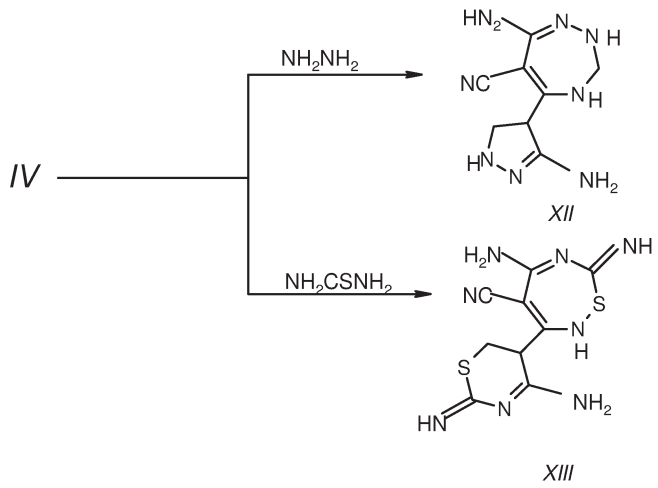
The reaction mechanism is believed to proceed *via* the addition of the —SH or $—NH_2$ groups to both C=C and N=C followed by cycloaddition of the $—NH_2$, —OH, —NH or —SH groups to both the olefinic cyano groups and the aliphatic cyano group.

EXPERIMENTAL

Melting points were determined on Kofler apparatus. IR spectra were obtained (KBr disc) on Nicolet FT-IR 710 spectrophotometer. ^1H NMR spectra were recorded at 60 MHz on Varian EM 360 L, spectrometer TMS was used as internal reference and DMSO-d_6 as solvent. Elemental analyses were carried out on an elemental analyzer 240 C. Most of the chemicals used are produced by Aldrich Chemical Company.

Compound *II*

To a solution of compound *I* (0.001 mol) in acetic acid (20 cm^3) 2,5-dimethoxytetrahydrofuran (0.001 mol) was added. The reaction mixture was refluxed for 2 h, poured into ice-cold water (200 cm^3) and the separated solid was collected by filtration and crystallized from dioxane.



Scheme 3

Compound *IV*

Compound *III* (0.001 mol) was dissolved in thionyl chloride (20 cm^3). The reaction mixture was left for 24 h at room temperature. The solvent was evaporated *in vacuo*. The residual solid was washed with petroleum ether (40—60 °C) and crystallized from xylene.

Compound *VI*

A mixture of compound *I* (0.001 mol), dioxane (30 cm^3), and *p*-nitrobenzaldehyde (0.002 mol) was treated with two drops of piperidine, refluxed for 2 h, concentrated and cooled. The precipitated solid was filtered off and crystallized from acetic acid whereby compound *VI* was obtained. The filtrate was evaporated *in vacuo* and the residual solid was crystallized from ethanol whereby compound *V* was obtained.

Compound *VII*

To a solution of compound *VI* (0.01 mol) in ethanol (20 cm^3) a solution of $FeCl_3$ (0.01 mol) in 10 cm^3 of H_2O and 2 cm^3 of diluted HCl was added. The reaction mixture was refluxed for 5 h, then it was concentrated and the solid product was washed with water, filtered off and recrystallized from acetic acid.

Compound *VIII*

To a solution of compound *I* (0.005 mol) in xylene (20 cm^3) 2,5-dimethylfuran (0.005 mol) and few crystals of hydroquinone were added. The reaction mixture was refluxed for 13 h, concentrated and cooled. The precipitated solid was filtered off and crystallized from dioxane.

Compounds *IX*, *Xa*—*Xc*, and *XI*

To a solution of compound *II* (0.02 mol) in pyridine (20 cm^3) 0.04 mol of phenylisothiocyanate, chloroacetonitrile, phenacyl bromide, chloroacetamide or chloroacetyl chloride was added. The reaction mixture was refluxed for 3 h and poured into ice-cold water (300 cm^3) with few drops of HCl. The precipitate was collected by filtration and crystallized from the proper solvent.

Compounds *XII* and *XIII*

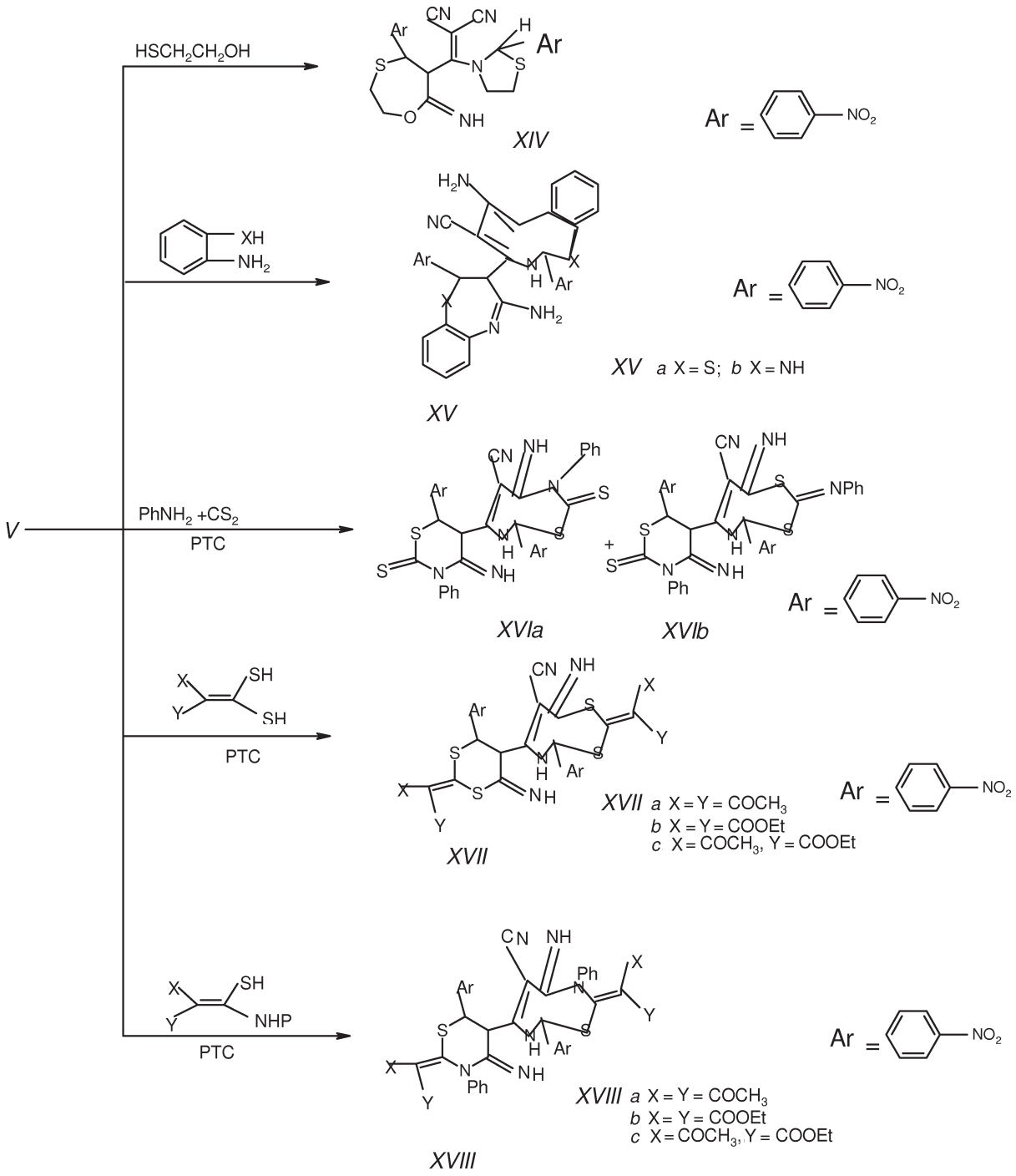
A solution of compound *IV* (0.01 mol) in DMF (30 cm^3) was treated with hydrazine hydrate or thiourea (0.02 mol) and refluxed for 3 h. The reaction mixture was poured into ice-cold water (300 cm^3) in the presence of few drops of HCl. The precipitate was filtered off and crystallized from the proper solvent.

Compounds *XIV* and *XVa*, *XVb*

A mixture of compound *V* (0.01 mol) in dioxane (50 cm^3) and 0.02 mol of 2-sulfanylethanol, 2-aminothiophenol or *o*-phenylenediamine was treated with two drops of piperidine and refluxed for 7 h. The reaction mixture was concentrated and cooled. The separated solid was collected by filtration and crystallized from the proper solvent.

Compounds *XVIa*, *XVIb*

A mixture of aniline (0.02 mol) and CS_2 (0.02 mol), anhydrous potassium carbonate (4 g), catalytic amount of tetrabutylammonium bromide (TBAB), and dry dioxane (30 cm^3) was stirred for 30 min at 60 °C. To the reaction mixture compound *V* (0.01



Scheme 4

mol) was added. The reaction mixture was stirred for 5 h and filtered off. The filtrate was evaporated *in vacuo*. The residue was treated with petroleum ether to give a solid product *XVIa* which was crystallized from ethanol. The solid potassium carbonate was dissolved in distilled water (50 cm^3) and acidified with diluted HCl, the separated solid was collected by filtration and crystallized from dioxane to give compound *XVIb*.

Compounds *XVIIa*—*XVIIc* and *XVIIIa*—*XVIIIc*

A mixture of the proper active methylene, namely acetyl acetone, diethyl malonate or ethylacetoacetate (0.02 mol), CS_2 (0.02 mol) or phenyl isothiocyanate (0.02 mol), anhydrous potassium carbonate (4 g), catalytic amount of TBAB, and dry dioxane (30 cm^3) was stirred for 30 min at 60 °C. The procedure was per-

formed as before. The solid material was filtered off and the filtrate was evaporated *in vacuo*. The residual solid was treated with petroleum ether and crystallized from the suitable solvent.

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