NOVEL SYNTHESIS OF 4-BROMO-3-OXO-2-PHENYLHYDRAZONO-BUTYRONITRILE AND 4-CYANO-3-OXO-2-PHENYLHYDRAZONO-BUTYRONITRILE: SYNTHESIS OF PYRIDAZINE, THIAZOLE, 1,2,4-TRIAZINE AND PYRIDO[2,3-*e*]-1,2,4-TRIAZINE DERIVATIVES

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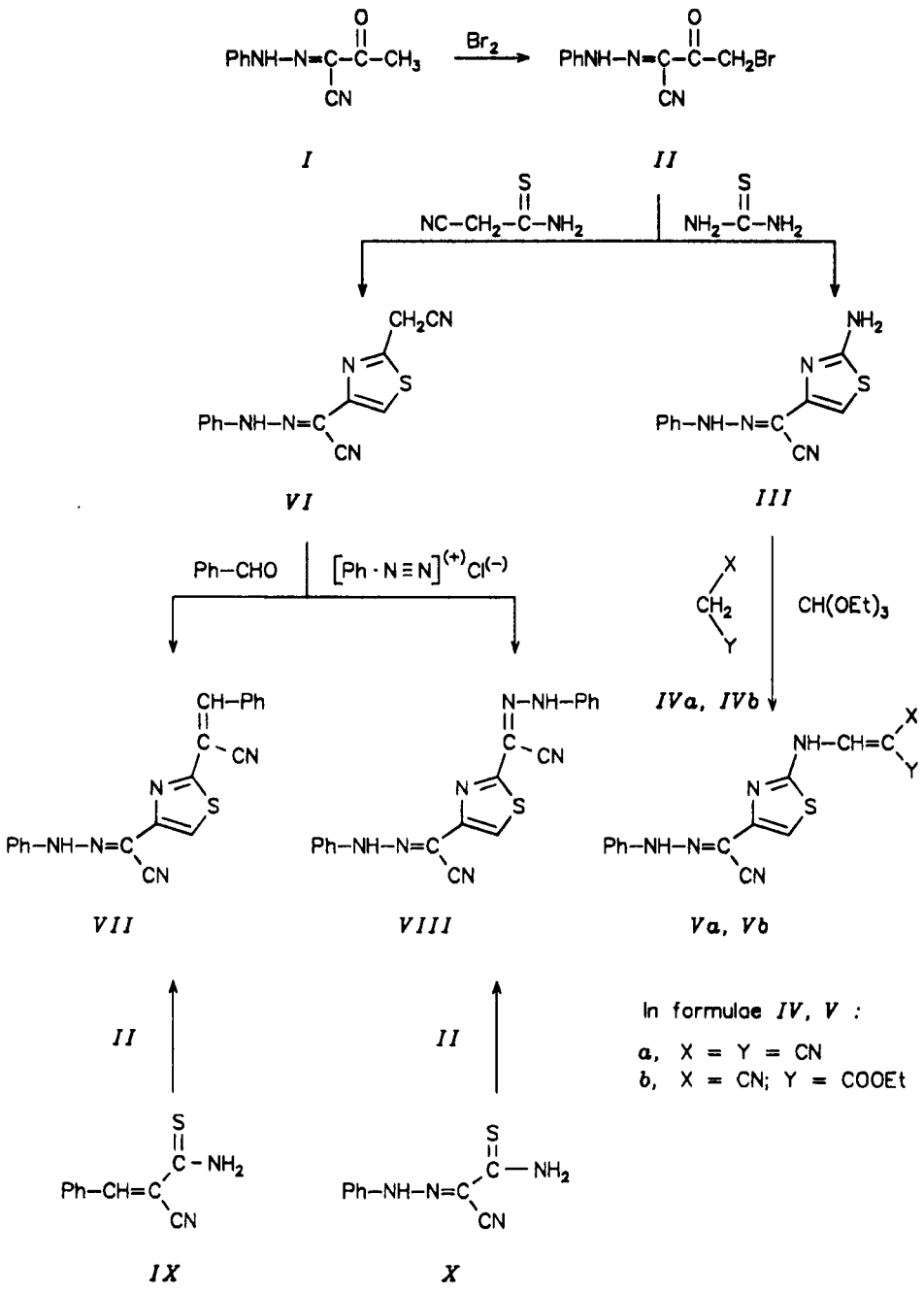
4-Bromo-3-oxo-2-phenylhydrazono-butyronitrile (*II*) reacted with thioamides to afford the thiazole derivatives *III* and *VI*. Compound *II* reacted with nucleophilic reagents to afford *XIIIa* and *XIIIb*. The reactivity of *XIIIa* with some chemical reagents was studied to afford pyridazine, thiazole, 1,2,4-triazine derivatives.

3-Oxoalkanonitrile derivatives are versatile reagents used in heterocyclic synthesis[1-6]. As a continuation of our previous work[7-9] aimed at developing new efficient procedures for the synthesis of such reagents starting from α-bromocarbonyl compounds, we describe in this article a new procedure for synthesis of 4-bromo-3-oxo-2-phenylhydrazono-butyronitrile (*II*) and its use for the synthesis of 4-cyano-3-oxo-2-phenylhydrazono-butyronitrile derivative together with both uses to synthesis pyridazine, thiazole and triazine derivatives which looks interesting as potential agrochemicals[10-12].

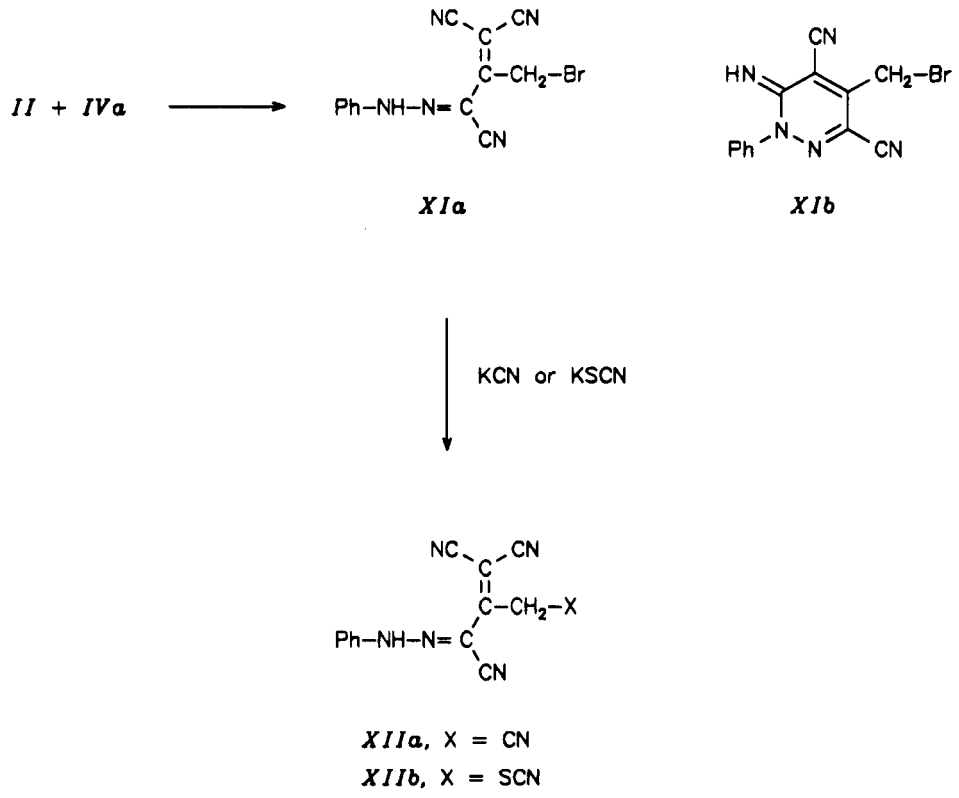
Thus, 2-phenylhydrazono-3-oxobutyronitrile[13] (*I*) reacted with bromine in boiling acetic acid to afford 4-bromo-3-oxo-2-phenylhydrazono-butyronitrile (*II*) (see Scheme 1). The structure of *II* was established on the basis of analytical and spectral data. ^{1}H NMR spectrum of the reaction product revealed the presence of a singlet at δ 3.89 ppm for CH_2, a multiplet at δ 7.32 – 7.36 ppm for C_6H_5 and a broad singlet at δ 8.0 ppm for NH group. Further confirmation of structure *II* was obtained by studying its reactivity towards some chemical reagents. Compound *II* reacted with thioamides to afford thiazole derivatives[14]. Thus, reaction with thiourea afforded 2-aminothiazole derivative *III*. The amino group present in *III* reacted with ethyl orthoformate and active methylene reagents *IVa* and *IVb* to afford 2-aminothiazole derivatives *Va* and *Vb*, respectively. At the other extrem, *II* reacted with cyanothioacetamide[15] to afford the thiazole derivative *VI*. The active methylene group present in *VI* reacted with benzaldehyde in presence of a catalytic amount of piperidine to afford the benzylidene derivative *VII*. On the other hand, *VI* was coupled with benzenediazonium chloride to afford the


PhNH–N=C(CN)–C(=O)–CH3
Br2
PhNH–N=C(CN)–C(=O)–CH2Br
I
II
NC–CH2–C(=S)–NH2
NH2–C(=S)–NH2
Ph–NH–N=C(CN)
CH2CN
NH2
VI
III
Ph–CHO
[Ph · N≡N](+)Cl(-)
CH(OEt)3
IVa, IVb
CH–Ph
N–NH–Ph
NH–CH=C(X)–Y
VII
VIII
Va, Vb
II
II
Ph–CH=C(CN)–C(=S)–NH2
Ph–NH–N=C(CN)–C(=S)–NH2
IX
X
In formulae IV, V :
a, X = Y = CN
b, X = CN; Y = COOEt

SCHEME 1

phenylhydrazone derivative *VIII*. Structures of products *VII* and *VIII* were established on the basis of analytical and spectral data together with their synthesis through other reaction routes. Thus, reaction of *II* with benzalcyanothioacetamide[16] (*IX*) and phenylhydrazono-cyanothioacetamide[17] (*X*) afforded the same products *VII* and *VIII*, respectively.

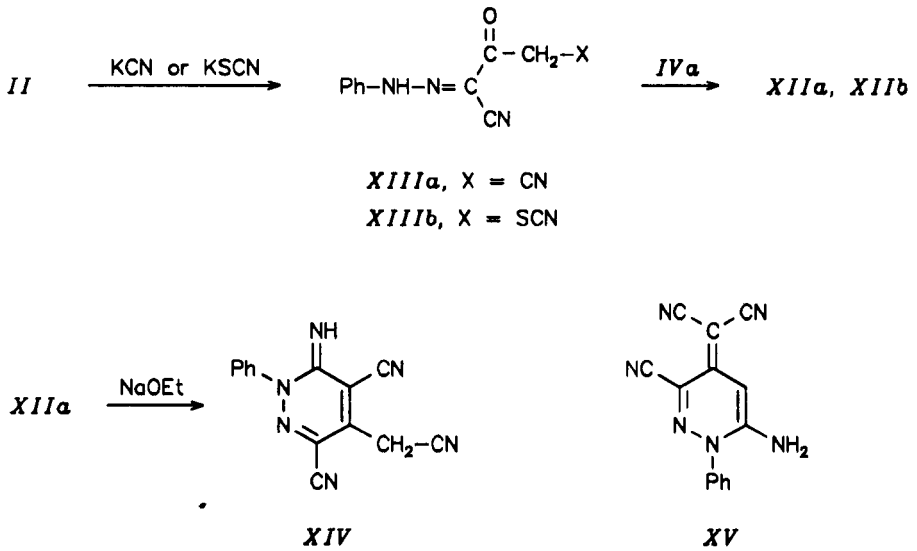
Compound *II* reacted with malononitrile (*IVa*) in N,N-dimethylformamide solution containing a catalytic amount of piperidine to afford a single product with molecular formula $C_{13}H_8N_5Br$. Two isomeric structures *XIa* and *XIb* could be expected for such formula (see Scheme 2). Structure *XIa* was confirmed for the reaction product based on



SCHEME 2

IR spectrum which revealed the presence of three group stretchings at 2 225, 2 220 and 2 215 cm^{-1} . Reaction of *XIa* with nucleophilic reagents like potassium cyanide and potassium thiocyanate afforded the corresponding 1,3-dicarbonitrile derivatives *XIIa*

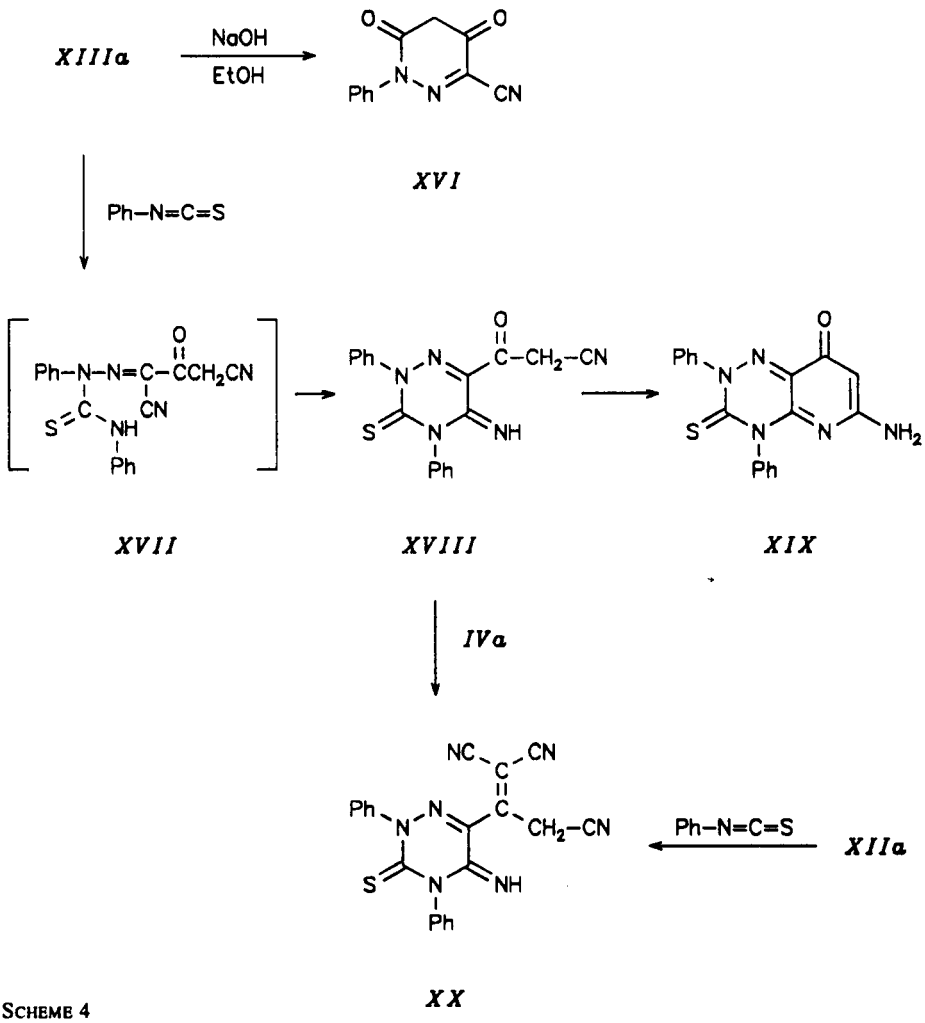
and *XIIb* (see Scheme 3), respectively. The structures of *XIIa* and *XIIb* were established based on the analytical and spectral data together with their synthesis through other reaction routes. Thus, the reaction of *II* with potassium cyanide and potassium thiocyanate afforded the 4-cyano-butyronitrile derivative *XIIIa* and the 4-thiocyano-butyronitrile derivative *XIIIb*, respectively. The structures of *XIIIa* and *XIIIb* were



SCHEME 3

established based on analytical and spectral data. IR spectrum of *XIIIa* revealed the presence of two C≡N group stretchings at 2 220 and 2 215 cm^{-1} and ^1H NMR spectrum revealed the presence of a singlet at δ 4.02 ppm for CH_2 group, a multiplet at δ 7.34 – 7.36 ppm for C_6H_5 and a broad singlet at δ 8.21 ppm for NH group. Reaction of *XIIIa* and *XIIIb* with malononitrile (*IVa*) afforded the Knoevenagel condensation products *XIIa* and *XIIb*, respectively. Boiling of *XIIa* in ethanol/sodium ethoxide solution afforded a product with molecular formula $C_{14}H_8N_6$. Two possible isomeric structures *XIV* and *XV* could be assigned to such formula. The possibility of structure *XV* was ruled out based on IR spectrum of the reaction product which revealed the absence of any NH_2 stretching; instead, an exocyclic C=N streatching appeared at 1 685 cm^{-1}. ^1H NMR spectrum revealed the presence of a singlet at δ 4.02 ppm for CH_2, a multiplet at δ 7.40 – 7.71 ppm for C_6H_5 and a broad singlet at δ 9.32 ppm for NH group. Such data agree with structure *XIV*.

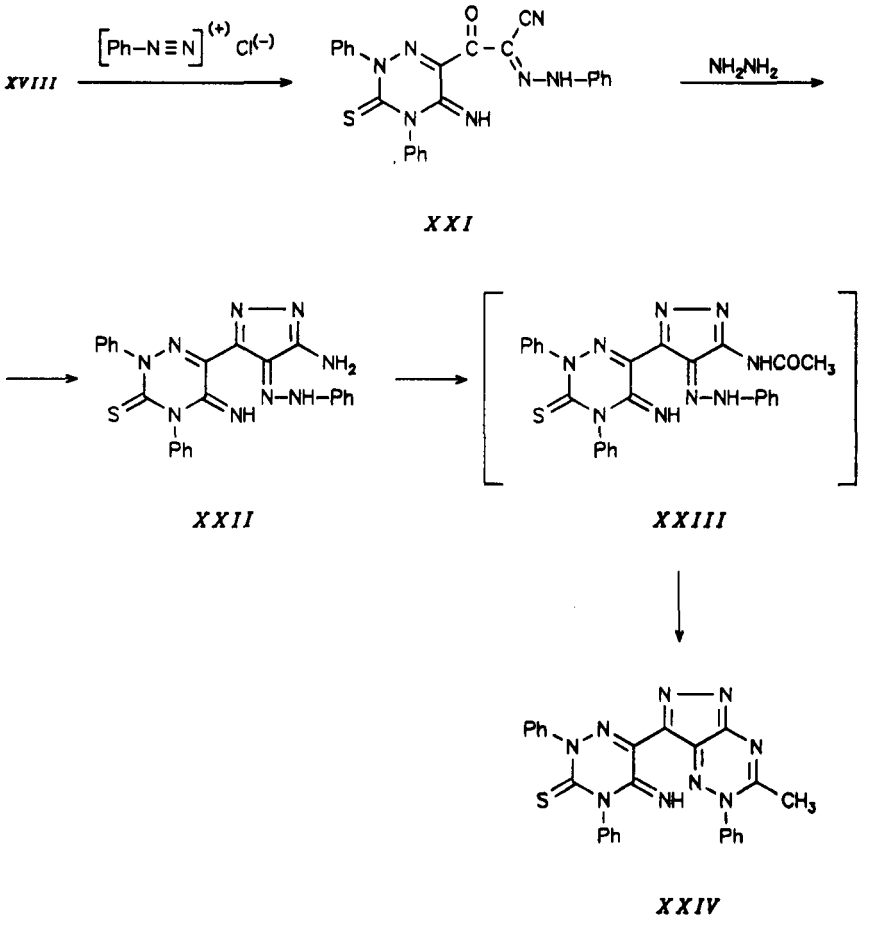
Compound *XIIIa* underwent cyclization in refluxing ethanol/sodium hydroxide solution to afford the pyridazine derivative *XVI* (see Scheme 4). Its formation was explained in terms of cyclization followed by hydrolysis of exocyclic C=NH group[18]. The phenylhydrazono group present in *XIIIa* reacted with phenyl isothiocyanate in basic



SCHEME 4

dioxane solution to afford[19] the 1,2,4-triazine derivative *XVIII* which was formed via the intermediate formation of the expected adduct *XVII*. The triazine derivative *XVIII* underwent further cyclization when heated in ethanol/sodium ethoxide solution to afford the pyrido[2,3-*e*]-1,2,4-triazine derivative *XIX*. The structures of *XVIII* and *XIX* were confirmed based on analytical and spectral data (see Experimental). Reaction of

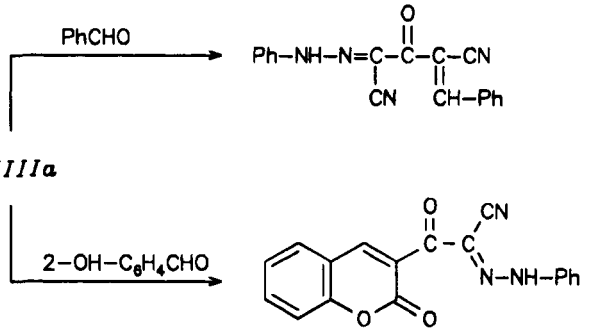
XVIII with malononitrile (*IVa*) in acetic acid/ammonium acetate solution afforded the Knoevenagel condensation product *XX*. This compound was also synthesized through the reaction of *XIIa* with phenyl isothiocyanate. Reaction of *XVIII* with benzenediazonium chloride afforded the phenylhydrazone product *XXI* (see Scheme 5) which



SCHEME 5

reacted with hydrazine hydrate to afford the (pyrazol-3-yl)-1,2,4-triazine derivative *XXII*. Reaction of *XXII* with acetic acid/acetic anhydride mixture afforded the (triazin-6-yl)pyrazolo[3,4-*e*]-1,2,4-triazine derivative *XXIV* which was formed via the intermediate acetyl derivative *XXIII* followed by water elimination.

The active methylene group present in *XIIIa* react with benzaldehyde to afford the benzalidene derivative *XXV* (see Scheme 6). On the other hand, *XIIIa* reacted with salicylaldehyde to give coumarine derivative *XXVI*. Formation of coumarin derivatives from β-oxonitrile derivatives and salicylaldehyde was reported in literature[20 - 22].



XXVI

SCHEME 6

EXPERIMENTAL

All melting points are uncorrected. Infrared spectra were recorded on a Perkin–Elmer SP 177 spectrometer in KBr disc (wavenumbers in cm^{-1}). Proton NMR spectra were taken on a Varian A-300 (300 MHz) instrument at 25 °C in CD_3SOCD_3 with tetramethylsilane as internal standard. Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz.

4-Bromo-3-oxo-2-phenylhydrazonobutyronitrile (*II*)

To a boiled solution of *I* (1.8 g, 0.01 mol) in acetic acid (50 ml), bromine (0.8 g, 0.01 mol) was added dropwise and the reaction mixture was shaken at room temperature for 3 h. The solid product formed upon dilution with water was collected by filtration. Crystallization from ethanol afforded 2.39 g (90%) of compound *II*, m.p. 148 °C. IR spectrum: 3 340 – 3 300 (NH); 3 045 (CH aromatic); 2 870 (CH_2); 2 220 (C≡N); 1 690 (C=O); 1 650 (C=N). ^{1}H NMR spectrum: 3.89 s, 2 H (CH_2); 7.32 – 7.36 m, 5 H (C_6H_5); 8.0 brs, 1 H (NH). For $C_{10}H_9N_3OBr$ (266.2) calculated: 45.07% C, 3.38% H, 15.77% N, 30.05% Br; found: 44.78% C, 3.41% H, 15.89% N, 29.67% Br.

2-Amino-4-(phenylhydrazonocyanomethyl)thiazole (*III*)

To a solution of *II* (2.6 g, 0.01 mol) in absolute ethanol (30 ml), thiourea (0.7 g, 0.01 mol) was added. The reaction mixture was heated under reflux for 2 h and the solid product, that separated from the hot solution, was collected by filtration. Crystallization from dioxane gave product *III*, m.p. 223 – 226 °C; yield 1.9 g (85%). IR spectrum: 3 460 – 3 420 (NH_2, NH); 3 050 (CH aromatic); 2 220 (C≡N); 1 650 (C=N). ^{1}H NMR spectrum: 4.98 s, 2 H (NH_2); 6.87 s, 1 H (thiazole H-5); 7.32 – 7.37 m, 5 H (C_6H_5); 8.04 brs,

1 H (NH). For $C_{11}H_9N_5S$ (243.3) calculated: 54.42% C, 3.69% H, 28.77% N, 13.15% S; found: 54.35% C, 3.39% H, 28.67% N, 12.71% S.

General Procedure for Preparation of 2-Amino-4-(phenylhydrazonocyanomethyl)thiazole Derivatives (*Va* and *Vb*)

Compound *III* (2.4 g, 0.01 mol), ethyl orthoformate (0.9 g, 0.01 mol) and active methylene reagent *IVa* (0.7 g, 0.01 mol) or *IVb* (1.1 g, 0.01 mol) in acetic acid/acetic anhydride (30 ml, 2 : 1) were heated under reflux for 5 h. The solid product was collected by filtration and crystallized from N,N-dimethylformamide.

Compound Va. M.p. 241 – 243 °C, yield 2.0 g (65%). IR spectrum: 3 460 – 3 300 (2 NH); 3 050 (CH aromatic); 2 225, 2 220 – 2 210 (C≡N); 1 655 (C=N). ^{1}H NMR spectrum: 6.02 s, 1 H (CH=C); 6.87 s, 1 H (thiazole H-5); 7.32 – 7.36 m, 5 H (C_6H_5); 7.98, 8.03 2 × brs, 2 H (2 × NH). For $C_{15}H_9N_7S$ (319.3) calculated: 56.37% C, 2.81% H, 30.69% N, 10.02% S; found: 56.22% C, 3.25% H, 30.58% N, 9.94% S.

Compound Vb. M.p. 189 °C, yield 2.5 g (70%). IR spectrum: 3 460 – 3 320 (2 NH), 3 050 (CH aromatic); 2 975, 2 890 (CH_3, CH_2), 2 220 (C≡N); 1 690 (C=O); 1 650 (C=N). ^{1}H NMR spectrum: 1.38 t, 3 H (CH_3); 3.89 q, 2 H (CH_2); 5.79 s, 1 H (CH=C); 6.87 s, 1 H (thiazole H-5); 7.32 – 7.37 m, 5 H (C_6H_5); 7.99, 8.04 2 × s, 2 H (2 × NH). For $C_{17}H_{14}N_6O_2S$ (366.4) calculated: 55.67% C, 3.82% H, 22.92% N, 8.75% S; found: 55.43% C, 3.94% H, 23.28% N, 8.04% S.

2-Cyanomethyl-4-(phenylhydrazonocyanomethyl)thiazole (*VI*)

To a solution of *II* (2.6 g, 0.01 mol) in ethanol (50 ml) containing triethylamine (0.5 ml), cyanothioacetamide (1.0 g, 0.01 mol) was added. The reaction mixture was heated under reflux for 1 h, then evaporated in vacuo. The remaining product was triturated with ethanol and collected by filtration. Crystallization from dioxane afforded 2.0 g (77%) of compound *VI*, m.p. 165 °C. IR spectrum: 3 460 – 3 350 (NH); 3 050 (CH aromatic); 2 895 (CH_2); 2 225, 2 220 (C≡N); 1 660 (C=N). ^{1}H NMR spectrum: 3.99 s, 2 H (CH_2); 6.87 s, 1 H (thiazole H-5); 7.32 – 7.35 m, 5 H (C_6H_5), 8.07 brs, 1 H (NH). For $C_{13}H_9N_5S$ (267.3) calculated: 58.36% C, 3.36% H, 26.18% N, 11.97% S; found: 58.21% C, 3.03% H, 26.59% N, 11.71% S.

2-Cyanobenzalmethyl-4-(phenylhydrazonocyanomethyl)thiazole (*VII*)

A) A mixture of *VI* (2.6 g, 0.01 mol) in N,N-dimethylformamide (30 ml) containing piperidine (0.5 g) and benzaldehyde (1.1 g, 0.01 mol) was heated under reflux for 6 h. The solid product, formed upon dilution with cold water containing few drops of hydrochloric acid, was collected by filtration. Crystallization from dioxane gave 2.7 g (74%) of compound *VII*, m.p. 278 – 280 °C. IR spectrum: 3 440 – 3 320 (NH); 3 050 (CH aromatic); 2 225, 2 220 (C≡N); 1 660 (C=N). ^{1}H NMR spectrum: 6.21 s, 1 H (ylidene CH); 6.82 s, 1 H (thiazole H-5); 7.33 – 7.36 m, 10 H (2 × C_6H_5); 8.04 brs, 1 H (NH). For $C_{20}H_{13}N_5S$ (355.4) calculated: 67.52% C, 3.65% H, 19.70% N, 9.01% S; found: 67.42% C, 3.95% H, 19.30% N, 8.62% S.

B) To a solution of *II* (2.6 g, 0.01 mol) in ethanolic sodium ethoxide solution (prepared from sodium metal (0.3 g, 0.01 mol) and absolute ethanol (40 ml)), compound *XIX* (3.4 g, 0.01 mol) was added. The reaction mixture was heated on a boiling water bath for 15 h, then poured into ice/water mixture containing hydrochloric acid (till pH 6) and the solid product was collected by filtration. Crystallization from dioxane afforded 1.8 g (52%) of compound *VII* identical with product prepared by procedure *A*).

2,4-Bis(phenylhydrazonocyanomethyl)thiazole (*VIII*)

A) To a cold solution of *VI* (2.6 g, 0.01 mol) in ethanol (80 ml) containing sodium hydroxide (10 ml, 10%), benzenediazonium chloride (prepared by adding concentrated hydrochloric acid (3 ml) to aniline (0.9 g, 0.01 ml) at 0 – 5 °C then treating the resulting hydrochloride with a cold solution of sodium nitrite

(0.7 g, 0.01 mol) in water (6 ml)) was added with stirring at 0 – 5 °C. The reaction mixture was stirred at room temperature for 3 h. The precipitated crude product was collected by filtration and crystallized from dioxane. Yield 3.2 g (88%), m.p. 266 – 269 °C. IR spectrum: 3 450 – 3 320 (NH); 3 050 (CH aromatic); 2 225, 2 220 (C≡N); 1 655 (C=N). ^{1}H NMR spectrum: 6.82 s, 1 H (thiazole H-5); 7.33 – 7.37 m, 10 H (2 × C_6H_5); 8.04, 8.32 2 × brs, 2 H (2 × NH). For $C_{19}H_{13}N_7S$ (371.4) calculated: 61.38% C, 3.50% H, 26.38% N, 8.61% S; found: 61.28% C, 3.16% H, 26.72% N, 8.32% S.

B) To a solution of *II* (2.6 g, 0.01 mol) in dimethylformamide (40 ml) contains triethylamine (0.5 ml), *X* (2.0 g, 0.01 mol) was added. The reaction mixture was heated under reflux for 8 h and poured into ice/water mixture. The solid product was collected by filtration. Crystallization from dioxane gave 2.5 g (69%) of title compound identical with product prepared of procedure *A*).

4-Bromo-3-dicyanomethylene-2-phenylhydrazonobutyronitrile (*XIa*)

To a solution of *II* (2.6 g, 0.01 mol) in N,N-dimethylformamide (30 ml) containing piperidine (0.5 ml), malononitrile (0.66 g, 0.01 mol) was added. The reaction mixture was heated under reflux for 3 h and poured into ice/water mixture. The solid product, formed upon standing for 5 h, was collected by filtration and crystallized from dioxane. M.p. 215 – 219 °C, yield 3.4 g (90%). IR spectrum: 3 420 – 3 300 (NH); 2 225, 2 220, 2 215 (C≡N); 1 660 (C=N). ^{1}H NMR spectrum: 3.93 s, 2 H (CH_2); 7.34 – 7.36 m, 5 H (C_6H_5); 8.32 brs, 1 H (NH). For $C_{13}H_8N_5Br$ (314.2) calculated: 49.64% C, 2.54% H, 22.27% N, 25.46% Br; found: 49.37% C, 3.07% H, 22.04% N, 25.11% Br.

General Procedure for Reaction of Compounds *II* and *XIa* with Potassium Cyanide and Potassium Thiocyanate

A solution of potassium cyanide (3.0 g, 0.05 mol) or potassium thiocyanate (4.0 g, 0.05 mol) in water (20 ml) was added dropwise under stirring at 70 °C to a solution of *XIa* (3.1 g, 0.01 mol) or *II* (2.6 g, 0.01 mol) in ethanol (50 ml). The reaction mixture was kept at 70 °C for 0.5 h and the solid product formed upon addition of water containing few drops of hydrochloric acid (till pH 6) was collected by filtration and crystallized from N,N-dimethylformamide (compounds *XIIa* and *XIIb*) or from ethanol (compounds *XIIIa* and *XIIIb*).

4-Cyano-3-dicyanomethylene-2-phenylhydrazonobutyronitrile (XIIa), m.p. 199 – 202 °C, yield 2.1 g (80%). IR spectrum: 3 450 – 3 320 (NH); 3 050 (CH aromatic); 2 225, 2 220 – 2 210 (C≡N); 1 660 (C=N). ^{1}H NMR spectrum: 4.21 s, 2 H (CH_2); 7.32 – 7.36 m, 5 H (C_6H_5); 8.03 brs, 1 H (NH). For $C_{14}H_8N_6$ (260.3) calculated: 64.54% C, 3.07% H, 32.27% N; found: 64.42% C, 3.39% H, 32.04% N.

3-Dicyanomethylene-2-phenylhydrazono-4-thiocyanobutyronitrile (*XIIb*), m.p. 240 – 244 °C, yield 2.1 g (72%). IR spectrum: 3 420 – 3 320 (NH); 3 050 (CH aromatic); 2 890 (CH_2); 2 225, 2 220 – 2 210 (C≡N); 1 655 (C=N). ^{1}H NMR spectrum: 4.32 s, 2 H (CH_2); 7.34 – 7.36 m, 5 H (C_6H_5); 8.06 brs, 1 H (NH). For $C_{14}H_8N_6S$ (292.3) calculated: 57.47% C, 2.73% H, 28.73% N, 10.94% S; found: 57.42% C, 2.41% H, 28.79% N, 10.72% S.

4-Cyano-3-oxo-2-phenylhydrazonobutyronitrile (XIIIa), m.p. 208 – 211 °C, yield 1.9 g (90%). IR spectrum: 3 420 – 3 320 (NH); 3 050 (CH aromatic); 2 870 (CH_2); 2 220, 2 215 (C≡N); 1 685 (C=O); 1 660 (C=N). ^{1}H NMR spectrum: 4.02 s, 2 H (CH_2); 7.34 – 7.36 m, 5 H (C_6H_5); 8.21 brs, 1 H (NH). For $C_{11}H_8N_4O$ (212.2) calculated: 62.20% C, 3.77% H, 26.39% N; found: 62.06% C, 3.58% H, 26.33% N.

3-Oxo-2-phenylhydrazono-4-thiocyanobutyronitrile (XIIIb), crystallized from ethanol, m.p. 170 – 172 °C, yield 2.1 g (88%). IR spectrum: 3 430 – 3 320 (NH); 3 050 (CH aromatic); 2 220, 2 210 (2 C≡N); 1 690 (C=O); 1 655 (C=N). ^{1}H NMR spectrum: 4.32 s, 2 H (CH_2); 7.29 – 7.36 m, 5 H (C_6H_5); 8.21 brs, 1 H (NH). For $C_{11}H_8N_4OS$ (244.3) calculated: 54.03% C, 3.27% H, 22.92% N, 13.09% S; found: 45.42% C, 3.07% H, 23.48% N, 13.64% S.

Conversion of *XIIIa* and *XIIIb* into *XIIa* and *XIIb*

To a solution of *XIIIa* (2.1 g, 0.01 mol) or *XIIIb* (2.4 g, 0.01 mol) in benzene (50 ml) and glacial acetic acid (10 ml) containing ammonium acetate (2 g), malononitrile (*IVa*, 0.6 g, 0.01 mol) was added. The reaction mixture was heated under reflux for 8 h then evaporated in vacuo. The remaining product was triturated with ether (50 ml), then collected by filtration.

Compound XIIa: Crystallization from N,N-dimethylformamide afforded 1.8 g (70%) of *XIIa* identical in all respects (m.p., mixed m.p., spectral and elemental data) with an authentic sample prepared above.

Compound XIIb: Crystallization from N,N-dimethylformamide gave yield 1.9 g (66%) of *XIIb* identical in all respects (m.p., mixed m.p., spectral and elemental data) with an authentic sample prepared above.

4-Cyanomethyl-3,5-dicyano-6-imino-1-phenylpyridazine (*XIV*)

A suspension of *XIIa* (2.6 g, 0.01 mol) in ethanolic sodium ethoxide (prepared from sodium metal (0.23 g, 0.01 mol) and absolute ethanol (50 ml)), was heated under reflux for 6 h and poured into ice/water. The solid product, formed upon addition of hydrochloric acid (till pH 6) was collected by filtration. Crystallization from dioxane afforded 2.0 g (77%) of title compound, m.p. > 300 °C. IR spectrum: 3 420 – 3 310 (NH); 3 050 (CH aromatic); 2 225, 2 220 – 2 210 (C≡N); 1 685 (exocyclic C=N). ^{1}H NMR spectrum: 4.02 s, 2 H (CH_2); 7.40 – 7.71 m, 5 H (C_6H_5); 9.32 brs, 1 H (NH). For $C_{14}H_8N_6$ (260.3) calculated: 64.41% C, 3.07% H, 32.27% N; found: 64.22% C, 2.63% H, 32.59% N.

3-Cyano-4,6-dioxo-1-phenylpyridazine (*XVI*)

A solution of *XIIIa* (2.1 g, 0.01 mol) in ethanol (50 ml) containing sodium hydroxide (0.5 ml) was heated under reflux for 5 h. The solid product, formed upon dilution with water containing hydrochloric acid (till pH 6) was collected by filtration and crystallized from ethanol. Yield 1.4 g (69%) of title compound, m.p. 233 – 237 °C. IR spectrum: 3 050 (CH aromatic); 2 220 (C≡N); 1 690, 1 680 (C=O); 1 660 (C=N). ^{1}H NMR spectrum: 5.61 s, 2 H (CH_2); 7.32 – 7.35 m, 5 H (C_6H_5). For $C_{11}H_7N_3O_2$ (213.2) calculated: 61.91% C, 3.28% H, 19.69% N; found: 61.62% C, 3.56% H, 19.93% N.

6-Cyanoacetyl-2,4-diphenyl-5-imino-1,2,4-triazin-3-thione (*XVIII*)

To a solution of *XIIIa* (2.1 g, 0.01 mol) in dioxane (30 ml) containing triethylamine (0.7 g, 0.01 mol), phenyl isothiocyanate (1.3 g, 0.01 mol) was added. The reaction mixture was heated under reflux for 5 h, then evaporated in vacuo. The remaining product was triturated with ethanol and collected by filtration. Crystallization from ethanol afforded 2.3 g (70%) of compound *XVIII*, m.p. 178 °C. IR spectrum: 3 420 – 3 340 (NH); 3 050 (CH aromatic); 2 890 (CH_2); 1 690 (C=O); 1 655 (C=N); 1 210 (C=S). ^{1}H NMR spectrum: 3.98 s, 2 H (CH_2); 7.34 – 7.38 m, 10 H (2 × C_6H_5); 10.21 s, 1 H (NH). For $C_{18}H_{13}N_5OS$ (347.4) calculated: 62.17% C, 3.74% H, 20.15% N, 9.21% S; found: 62.02% C, 3.33% H, 20.21% N, 8.95% S.

6-Amino-2,4-diphenyl-8-oxopyrido[2,3-*e*]-1,2,4-triazin-3-thione (*XIX*)

Preparation of title compound was carried out from *XVIII* (3.5 g, 0.01 mol) by the same procedure as described for preparation of *XVI* from *XIIIa*. Crystallization from N,N-dimethylformamide afforded 2.0 g (60%) of *XIX*, m.p. > 300 °C. IR spectrum: 3 460 – 3 340 (NH_2); 3 050 (CH aromatic); 1 700 (C=O); 1 200 – 1 190 (C=S). ^{1}H NMR spectrum: 5.21 s, 2 H (NH_2); 7.0 s, 1 H (pyridine H-3); 7.33 – 7.36 m, 10 H (2 × C_6H_5). For $C_{18}H_{13}N_5OS$ (347.4) calculated: 62.17% C, 3.74% H, 20.15% N, 9.21% S; found: 62.48% C, 3.41% H, 20.16% N, 8.92% S.

6-(2,4-Dicyano-2-butenonitrilo-3-yl)-2,4-diphenyl-5-imino-1,2,4-triazin-3-thione (*XX*)

A) To a solution of *XVIII* (3.4 g, 0.01 mol) in acetic acid (50 ml) containing ammonium acetate (2 g), malononitrile (0.7 g, 0.01 mol) was added. The reaction mixture was heated under reflux for 8 h and then poured into ice/water mixture. The precipitated solid product was collected by filtration. Crystallization from dioxane gave 2.7 g (70%) of title compound, m.p. 227 – 230 °C. IR spectrum: 3 420 – 3 380 (NH); 3 045 (CH aromatic); 2 225, 2 220 – 2 210 (C≡N); 1 690 (exocyclic C=NH); 1 200 – 1 190 (C=S). ^{1}H NMR spectrum: 4.02 s, 2 H (CH_2); 7.31 – 7.37 m, 10 H (2 × C_6H_5); 10.23 s, 1 H (NH). For $C_{21}H_{13}N_7S$ (395.4) calculated: 63.73% C, 3.28% H, 24.78% N, 8.09% S; found: 63.41% C, 3.48% H, 24.81% N, 8.08% S.

B) Preparation of title compound was carried out from *XIIa* (2.6 g, 0.01 mol) by the same procedure as preparation of *XVIII* from *XIIIa*. Yield 2.5 g (66%) of *XX* identical with product prepared by procedure *A*).

2,4-Diphenyl-5-imino-6-(phenylhydrazonocyanoacetyl)-1,2,4-triazin-3-thione (*XXI*)

Title compound was prepared from *XVIII* (3.5 g, 0.01 mol) by the procedure described for synthesis of *VIII* from *VI*. Crystallization from ethanol gave 4.0 g (90%) of *XXI*, m.p. 181 °C. IR spectrum: 3 420 – 3 360 (NH); 3 050 (CH aromatic); 2 220 (C≡N); 1 690 (C=O); 1 675 (exocyclic C=N); 1 200 – 1 195 (C=S). ^{1}H NMR spectrum: 7.32 – 7.38 m, 15 H (3 × C_6H_5); 9.98, 10.32 2 × brs, 2 H (2 × NH). For $C_{24}H_{17}N_7OS$ (451.5) calculated: 63.78% C, 3.76% H, 21.70% N, 7.08% S; found: 63.66% C, 3.47% H, 21.34% N, 7.41% S.

2,4-Diphenyl-5-imino-6-(4-phenylhydrazono-5-aminopyrazol-3-yl)-1,2,4-triazin-3-thione (*XXII*)

To a solution of *XXI* (4.5 g, 0.01 mol) in N,N-dimethylformamide (30 ml), hydrazine hydrate (0.5 g, 0.01 mol) was added and the reaction mixture was heated under reflux for 5 h. The solid product formed upon pouring into ice/water was collected by filtration. Crystallization from ethanol gave 3.5 g (78%) title compound, m.p. 189 °C. IR spectrum: 3 460 – 3 300 (NH_2, NH); 3 045 (CH aromatic); 1 685 (exocyclic C=N); 1 650 (C=N); 1 200 – 1 190 (C=S). ^{1}H NMR spectrum: 3.39 s, 2 H (NH_2); 7.30 – 7.37 m, 15 H (3 × C_6H_5); 8.12, 9.31 2 × brs, 2 H (2 × NH). For $C_{24}H_{19}N_9S$ (465.4) calculated: 61.88% C, 4.08% H, 27.07% N, 6.87% S; found: 62.33% C, 4.43% H, 27.39% N, 7.47% S.

7-(5-Imino-2,4-diphenyl-1,2,4-triazin-6-yl)-3-methyl-2-phenylpyrazolo[3,4-*e*]-1,2,4-triazine (*XXIV*)

A solution of *XXII* (4.6 g, 0.01 mol) in a mixture of acetic acid (30 ml) and acetic anhydride (5 ml) was heated under reflux for 12 h and then evaporated in vacuo. The remaining product was triturated in ether, collected by filtration and crystallized from ethanol, yield 4.2 g (88%), m.p. 251 – 254 °C. IR spectrum: 3 450 – 3 380 (NH); 3 050 (CH aromatic); 1 680 (exocyclic C=N); 1 660 (C=N); 1 200 – 1 195 (C=S). ^{1}H NMR spectrum: 1.39 s, 3 H (CH_3); 7.33 – 7.39 m, 15 H (3 × C_6H_5); 10.21 s, 1 H (NH). For $C_{26}H_{19}N_9S$ (489.6) calculated: 63.75% C, 3.88% H, 25.73% N, 6.53% S; found: 63.34% C, 3.87% H, 25.69% N, 6.94% S.

4-Benzylidene-4-cyano-3-oxo-2-phenylhydrazonobutyronitrile (*XXV*)

To a solution of *XIIIa* (2.1 g, 0.01 mol) in N,N-dimethylformamide (50 ml) containing piperidine (1 ml), benzaldehyde (1.0 g, 0.01 mol) was added and the reaction mixture was heated under reflux for 10 h. The solid product, formed upon dilution with water containing few drops of hydrochloric acid, was collected by filtration and crystallized from dioxane; yield 2.3 g (78%) of title compound, m.p. 233 – 236 °C. IR spectrum: 3 440 – 3 380 (NH); 3 050 (CH aromatic); 2 225, 2 215 (C≡N); 1 690 (C=O); 1 655 (C=N). ^{1}H NMR spectrum: 6.98 s, 1 H (CH=C); 7.32 – 7.35 m, 10 H (2 × C_6H_5); 8.82 brs, 1 H (NH). For $C_{18}H_{12}N_4O$ (300.3) calculated: 71.92% C, 3.99% H, 18.64% N; found: 72.43% C, 3.89% H, 18.89% N.

3-(Phenylhydrazonocyanoacetyl)coumarin (*XXVI*)

Compound *XXVI* was prepared from *XIIIa* (2.1 g, 0.01 mol) and salicylaldehyde (1.2 g, 0.01 mol) as described in precending experiment. Crystallization from N,N-dimethylformamide gave 2.8 g (90%) of *XXVI*, m.p. > 300 °C. IR spectrum: 3 460 – 3 370 (NH); 3 050 (CH aromatic); 2 220 (C≡N); 1 695, 1 680 (C=O); 1 665 (C=N). ^{1}H NMR spectrum: 7.0 s, 1 H (coumarin H-4); 7.33 – 7.37 m, 9 H (C_6H_5, C_6H_4); 10.31 s, 1 H (NH). For $C_{18}H_{11}N_3O_3$ (317.2) calculated: 68.09% C, 3.46% H, 13.24% N; found: 68.19% C, 3.66% H, 13.04% N.

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