carbonate, and water, dried (sodium sulfate), and evaporated. Crystallization of the residual solid from methanol gave the corresponding 4,6-diaryl-2(1*H*)-pyrimidinones (Va-c) as colorless needles.

Registry No. I, 57-13-6; IIa, 94-41-7; IIb, 20426-48-6; IIc, 959-23-9; IId, 2403-27-2; IIe, 956-02-5; IIf, 4224-96-8; IIg, 21551-47-3; IIh, 19672-63-0; III, 51863-81-1; IIj, 6332-22-5; IVa, 4113-79-5; IVb, 97691-58-2; IVc, 49593-57-9; IVd, 97691-59-3; IVe, 97691-60-6; IVf, 49593-56-8; IVg, 97691-61-7; Va, 24030-13-5; Vb, 24030-10-2; Vc, 97691-65-1; Vd, 97691-62-8; Ve, 97691-63-9; Vf, 97691-64-0; VIa, 16616-42-5; VIb, 20442-65-3; VIc, 97691-66-2.

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Reactions with Heterocyclic Amidines: Synthesis of Several New Pyrazolo[1,5-*a*]pyrimidines and Pyrazolo[1,5-*c*]-*as*-triazines

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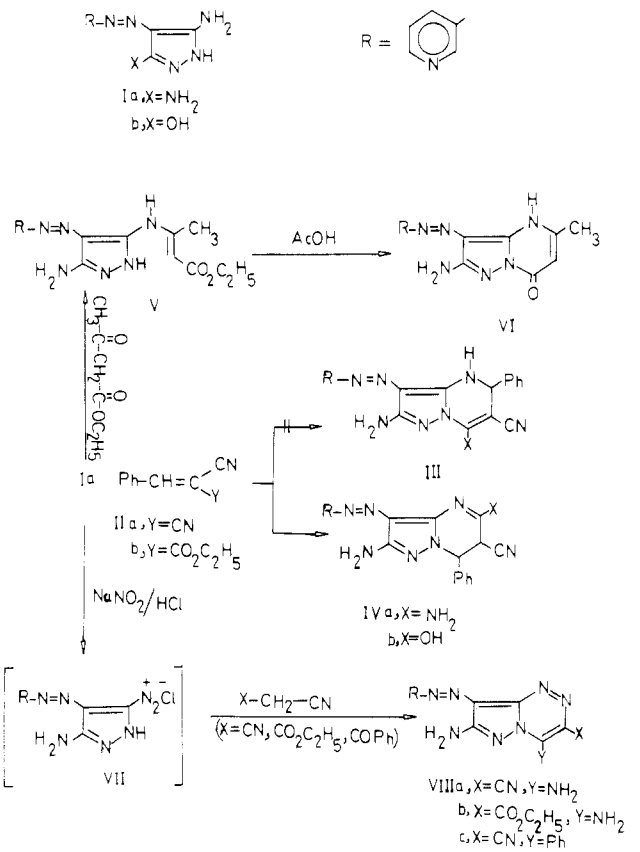
Several new pyrazolo[1,5-*a*]pyrimidines and pyrazolo[1,5-*c*]-*as*-triazines were obtained from 5-substituted-3-amino-4-(3-pyridylazo)pyrazoles (Ia,b) as starting components.

Aminopyrazoles are intermediates for the synthesis of biologically interesting pyrazole derivatives. In spite of the extensive literature reported for the chemistry of 5-aminopyrazoles (*1-3*), very little attention has been paid to the chemistry of 3,5-diaminopyrazoles (*4*) and of 3-amino-5-hydroxypyrazoles (*5*), although both compounds seem to be excellent reactants for further utility in the synthesis of fused azoles. Recently, Elnagdi et al. (*2*, *6*) have reported a new efficient synthesis of 4-arylazo-3,5-diaminopyrazoles and of 4-arylazo-3-amino-5-hydroxypyrazoles. In conjunction with this work it seemed of value to see if the reported synthesis and chemical reactivities for the above-mentioned compounds are general, and we report here the utility of 3,5-diamino-4-(3-pyridylazo)pyrazole (Ia) and 3-amino-5-hydroxy-4-(3-pyridylazo)pyrazole (Ib) (prepared following the procedure previously described by Elnagdi et al. (*2*, *6*)) for further utility in heterocyclic synthesis.

Thus, it has been found that Ia reacted with cinnamonitrile derivatives IIa,b to afford the corresponding pyrazolo[1,5-*a*]-pyrimidine derivatives IVa,b rather than the isomeric form III. Compound Ia also reacts with ethyl acetoacetate in refluxing ethanol to yield the 3-aminocrotonate derivative V. Compound V could be readily cyclized into the corresponding pyrazolo-[1,5-*a*]pyrimidine derivative VI by refluxing in acetic acid. The structure proposed for compounds IVa,b, V, and VI was established on the basis of analytical and spectral data of the resulting products. On the other hand, attempts to effect similar reactions with Ib were unsuccessful.

Compound Ia reacted with nitrous acid in presence of concentrated hydrochloric acid-acetic acid mixture to yield the corresponding diazonium salt VII which could not be isolated in pure state but its formation could be indicated via coupling with active methylene reagents. Thus, compound VII coupled with malononitrile, ethyl cyanoacetate, and benzoylacetonitrile to yield the corresponding pyrazolo[1,5-*c*]-*as*-triazines (VIIIa-c).



Experimental Section

All melting points are uncorrected. IR spectra were recorded (KBr) with a Shimadzu 408 spectrophotometer. ^1H NMR spectra obtained on an EM-390 90-MHz spectrophotometer using Me_4Si as internal indicator, and chemical shifts are expressed in ppm. Analytical data were obtained from the analytical data unit at Cairo University.

Reaction of Ia with Cinnamonitrile Derivatives IIa,b. A suspension of an equimolecular amount (0.01 mol) of Ia and

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Table I. List of the Newly Synthesized Compounds

compd (color)[a]	mp, °C	yield, %	cryst solv[b]	IR, cm^{-1}	^1H NMR, ppm
IVa (yellow)	>280	80	b	3400–3200 (NH_2 and NH); 2200 (CN); 1650 (C=N)	
IVb (yellow)	>280	82	b	3400–3200 (NH_2 and NH); 2200 (CN); 1640 (C=N)	3.2 (m, br, 2 H, 2 CH); 3.6 (br, 2 H, NH_2); 6.8–8.6 (m, 10 H, pyridyl and phenyl protons)
V (yellow)	>280	75	c	3400, 3250 (NH_2 and NH); 1680 (conjugated ester CO); 1640 (C=N)	1.3 (t, 3 H, CH_3); 2.4 (s, 3 H, CH_3); 3.6 (br, 2 H, NH_2); 4.2 (q, 2 H, CH_2); 5.85 (s, 1 H, methine CH); 7.4–8.6 (m, 6 H, pyridyl and NH protons)
VI (yellow)	>280	78	d	3450, 3250 (NH_2 and NH); 1690 (ring CO); 1640 (C=N)	2.3 (s, 3 H, CH_3); 4.0 (br, 2 H, NH_2); 6.9–8.6 (m, 7 H, aromatic and NH protons)
VIIIa (buff)	>280	92	b	3400–3200 (NH_2); 2200 (CN); 1650 (C=N); 1610 (C=C)	
VIIIb (brown)	235	90	b	3400, 3300–3100 (NH_2); 1680 (ester CO); 1620 (C=C)	1.3 (t, 3 H, CH_3); 3.8 (br, 2 H, NH_2); 4.2 (q, 2 H, CH_2); 7.4–8.2 (m, 5 H, pyridyl protons); 8.4 (br, 2 H, NH_2)
VIIIc (brown)	>280	88	b	3450–3200 (NH_2); 2200 (CN); 1640 (C=N)	6.8–8.2 (m, 10 H, pyridyl and phenyl protons); 8.5 (br, 2 H, NH_2)

[a] Satisfactory elemental analyses were found. [b] Ethanol. [c] DMF. [d] Acetic acid.

the appropriate amount of IIa,b in ethanol (50 mL) was refluxed with piperidine (1 mL) until the reaction was complete (TLC control) (time ranges from 2 to 4 h). The solvent was triturated with a little water and then acidified with concentrated hydrochloric acid. The resulting solid products were collected by filtration and crystallized from the proper solvent (cf. Table I).

Ethyl β-[5-Amino-4-(3-pyridylazo)pyrazol-3-yl]amino-crotonate (V). A mixture of Ia (0.01 mol) and ethyl acetoacetate (1.0 mL) in ethanol (50 mL) were heated on a boiling water bath for 2 h. The solvent was then evaporated in vacuo and the remaining product poured onto water. The solid product, formed on standing, was collected by filtration and crystallized from the proper solvent (cf. Table I).

Cyclization of V. A solution of V (2 g) in acetic acid (50 mL) was heated under reflux for 3 h. The solvent was then evaporated in vacuo then triturated with water. The solid product, so formed, was collected by filtration and crystallized from the proper solvent (cf. Table I).

Reaction of Diazotized Ia with Active Hydrogen Compounds. A solution of 0.01 mol of diazotized Ia (prepared following the procedure described by Elnagdi et al. (*7*)) was added to a solution of an appropriate active hydrogen compound in ethanol. (The diazonium salts should be used directly. Gradual decomposition in solution takes place on standing. *Caution*: Care should be taken in attempting isolation of diazonium salts or the diazo compounds in the solid state as some of these diazo compounds explode readily.) The solid product was collected by filtration and crystallized from the proper solvent (cf. Table I).

Registry No. Ia, 97732-47-3; IIa, 2700-22-3; IIb, 2025-40-3; IVa, 97732-48-4; IVb, 97732-49-5; V, 97732-50-8; VI, 97732-51-9; VII, 97732-52-0; VIIIa, 97732-53-1; VIIIb, 97732-54-2; VIIIc, 97732-55-3; $CH_2(CN)_2$, 109-77-3; $EtOC(O)CH_2CN$, 105-56-6; $PhC(O)CH_2CN$, 614-16-4.

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Synthesis of Some 3-(Arylimino)-5-(ethylethylidenehydrazido)-1,2,4-dithiazolidines

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The synthesis of 3-(arylimino)-5-(ethylethylidenehydrazido)-1,2,4-dithiazolidines has been described by the oxidative debenzylation of the corresponding 1-(ethylethylideneamino)-5-aryl-2-*S*-benzyliso-4-thiobiurets. These compounds have been characterized by the direct oxidation of the corresponding 2,4-dithiobiurets and also by IR spectra.

Our earlier work (*1*, *2*) on the synthesis of 3-(arylimino)-5-(phenylbenzylidenehydrazido)-1,2,4-dithiazolidines led us to prepare 3-(arylimino)-5-(ethylethylidenehydrazido)-1,2,4-dithiazolidines as new analogues for evaluation of the biological activity of this class of compounds. It was of interest to assess the effect of alkyl substituted thiosemicarbazone moiety in the resulting dithiazolidene derivatives.

Experimental Section

S-Benzylisoethyl methyl ketone thiosemicarbazone and the related 1-(ethylethylideneamino)-5-aryl-2-*S*-benzyliso-4-thiobiurets (Table I), 3-(arylimino)-5-(ethylethylidenehydrazido)-

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