

The Further Preparation of 1,2,4-Triazines and 1,2,4-Triazolines Containing the Ferroin Group

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Previous communications from this laboratory (1,2) described 5,6-diphenyl- and bis (2-pyridyl)-*as*-triazines related to 6-cyano-2,2'-bipyridine and three cyanodiazines. The present work involves the preparation of 5,6-dimethyl-*as*-triazines (I-IV) and 3-substituted 1,2,4-triazolines (V-XII) related to the above four nitriles.

The preparation of the dimethyl triazines involves the reaction of the corresponding carboxamide hydrazone (hydrazidine) with 2,3-butanedione in ethanol solution. The 1,2,4-triazolines resulted when the hydrazidines were similarly treated with benzaldehyde and pyridine-2-carboxaldehyde, respectively. Similar triazolines have recently been reported from this laboratory (3).

It is of interest that the structure assigned to the first

such compound thus prepared (by the action of 2-picoline-carboxamide hydrazone on benzaldehyde) was that of a Schiff base (4). We have shown that the cyclic structure is correct by dehydrogenation to a compound which has been shown to be identical with the triazole prepared by Potts (5) by heating 2-picolinylhydrazidebenzenesulfonate with benzonitrile.

3-(4-Pyrimidyl)-*as*-triazino[5,6-*f*][4,7]phenanthroline (XIII) was synthesized by the action of 4,7-phenanthroline-5,6-dione in ethanol on pyrimidine-4-carboxamide hydrazone. The corresponding derivatives of the other diazines have already been prepared (2).

The above compounds, will be tested for their chelating ability for Fe(II) and Cu(I) by Dr. Alfred Schilt.

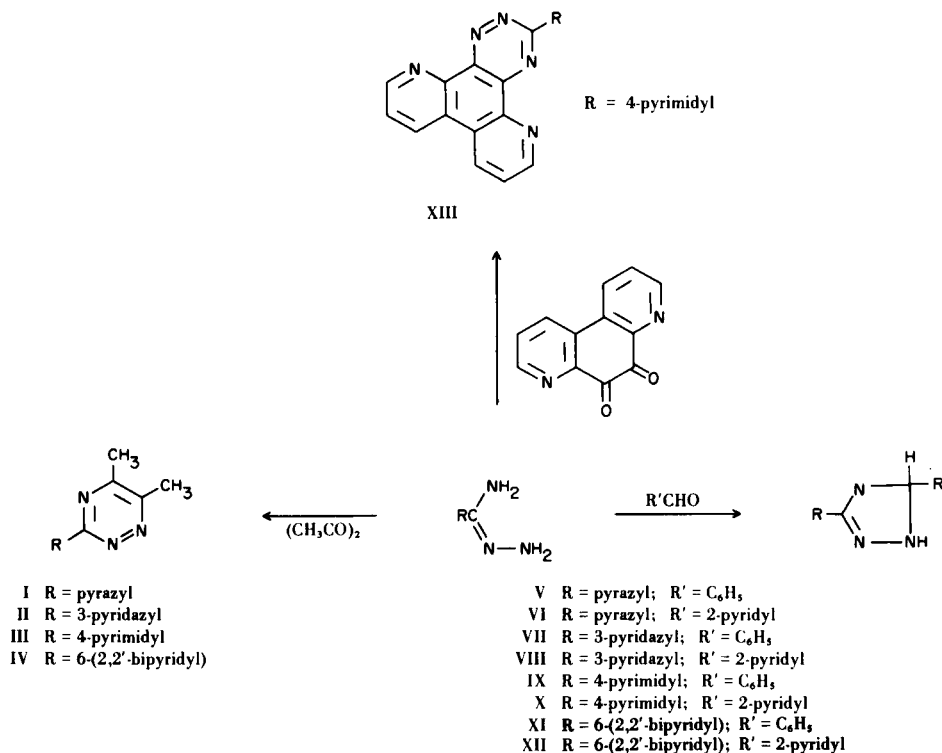
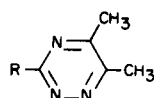
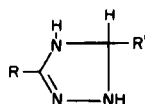


TABLE I
3-Substituted 5,6-Dimethyl-1,2,4-Triazines



	R	Yield %	M.P. °C	Cryst'n Solvent	Formula	Calcd. %			Analysis Found %		
						C	H	N	C	H	N
I	Pyrazyl	27.2	110-111	benzene-pet. ether	C ₉ H ₉ N ₅	57.74	4.85	37.41	57.57	4.83	37.16
II	3-Pyridazyl	38.9	150	benzene	C ₉ H ₉ N ₅	57.74	4.85	37.41	57.25	4.75	37.89
III	4-Pyrimidyl	30.0	116-117	benzene-pet. ether	C ₉ H ₉ N ₅	57.74	4.85	37.41	57.72	4.93	36.95
IV	6-(2,2'-Bi-pyridyl)	81.3	149-150	benzene	C ₁₅ H ₁₃ N ₅	68.43	4.98	26.60	68.69	5.06	26.29

TABLE II
3,5-Disubstituted-1,2,4-Triazolines



	R	R'	Yield %	M.P. °C	Cryst'n Solvent	Formula	Calcd. %			Analysis Found %		
							C	H	N	C	H	N
V	Pyrazyl	C ₆ H ₅	90.0	164	ethanol	C ₁₂ H ₁₁ N ₅	63.99	4.92	31.09	63.80	4.94	31.31
VI		2-C ₅ H ₄ N	72.2	190	ethanol	C ₁₁ H ₁₀ N ₆	58.40	4.46	37.15	58.20	4.50	37.53
VII	3-Pyridazyl	C ₆ H ₅	75.8	173	ethanol	C ₁₂ H ₁₁ N ₅	63.99	4.92	31.09	63.60	5.01	31.11
VIII		2-C ₅ H ₄ N	72.2	204	ethanol	C ₁₁ H ₁₀ N ₆	58.40	4.46	37.15	58.29	4.43	37.60
IX	4-Pyrimidyl	C ₆ H ₅	90.9	155	ethanol	C ₁₂ H ₁₁ N ₅	63.99	4.92	31.09	63.72	5.04	30.98
X		2-C ₅ H ₄ N	69.2	179	ethanol	C ₁₁ H ₁₀ N ₆	58.40	4.46	37.15	58.16	4.54	37.08
XI	6-(2,2'-Bi-pyridyl)	C ₆ H ₅	58.8	135	ethanol	C ₁₈ H ₁₅ N ₅	71.74	5.02	23.24	71.81	5.07	23.46
XII		2-C ₅ H ₄ N	89.3	181	ethanol	C ₁₇ H ₁₄ N ₆	67.54	4.67	27.80	67.45	4.85	27.69

EXPERIMENTAL

Preparation of 3-Substituted 5,6-Dimethyl-1,2,4-triazines.

A mixture of one molar proportion of the appropriate carboxamide hydrazone, a slight molar excess of 2,3-butanedione, and 20 ml. of ethanol was heated at reflux for 2.5 hours. The solvent was then removed by evaporation and the residue crystallized from the solvent indicated in Table I.

Preparation of 3,5-Disubstituted-1,2,4-Triazolines.

A mixture of one molar proportion of the requisite carboxamide hydrazone, 2 molar portions of benzaldehyde or pyridine-2-carboxaldehyde, and 20 ml. of ethanol was heated at reflux for 2.5 hours. The solvent was then removed and the triazoline crystallized from the solvent mentioned in Table II.

3-(4-Pyrimidyl)-*as*-triazino[5,6-*f*][4,7]phenanthroline (XIII).

A mixture of 1 g. of pyrimidine-4-carboxamide hydrazone, 1.5 g. of 4,7-phenanthroline-5,6-dione and 25 ml. of ethanol was heated at reflux for one hour. The residue obtained after evaporation of the solvent was crystallized from dimethylformamide and dried at 110°. The yield of product melting at 380° was 1.4 g. or 60.9%.

Anal. Calcd. for C₁₇H₉N₇: C, 65.57; H, 2.92; N, 31.51. Found: C, 65.58; H, 2.84; N, 31.60.

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