

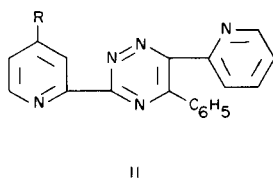
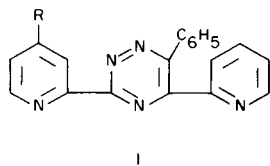
The Preparation of Certain New Diphenyl and bis(2-Pyridyl)*as*-triazines (1)

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In a previous communication (2) were described certain 3-(4-substituted phenyl)-5,6-diphenyl and -bis(2-pyridyl)*as*-triazines containing the ferriin group, which were prepared by treating the hydrazidines (picolinimidic acid hydrazides) of certain 2-cyanopyridine derivatives with benzil or 2,2'-pyridil, respectively. These all contained the ferriin group (=N-C-C-N=) and the majority of them yielded a red chelate with Fe(II).

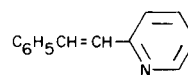
It seemed of interest to use as the diketone in this reaction an unsymmetrical compound, such as 1-phenyl-2-(2-pyridyl)ethanedione, $C_6H_5COCOC_5H_4N$. This could yield either I or II on treatment with a substituted picolinimidic acid hydrazide.



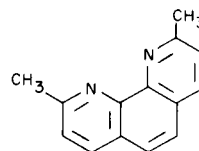
It is possible to distinguish between the two possible structures by identifying the iron(II) chelate formed by the product. An examination of spatial models reveals that compounds of structure I are capable of acting as terdentate ligands to yield iron(II) chelates in which the ratio of Fe to ligand is 1 to 2. Compounds of structure II, however, are incapable of acting as terdentate ligands but can act as bidentate ligands to yield an iron (II) chelate with three ligands per Fe(II). The identities of the iron (II) chelates formed by the products, where R is hydrogen, methyl or phenyl, were determined spectrophotometrically by the method of continuous variations (3). In each case the ratio of ligand to Fe was 3 to 1, indicating structure II. Absorption characteristics for the intensely magenta colored iron(II) chelates are given in Table I. In no case

was it possible to isolate the isomer having structure I.

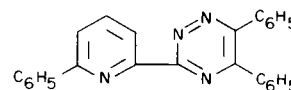
1-Phenyl-2-(2-pyridyl)ethanedione (4) was prepared by the action of selenium oxide on 1-phenyl-2-(2-pyridyl)-ethene (5).



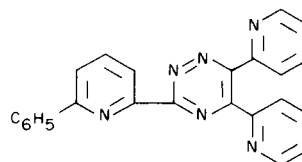
In addition to the above *as*-triazines two *as*-triazines containing hindered ferriin groups were prepared. These, like neocuproin (III), would be expected to form chelates with Cu(I) but not with Fe(II).



III



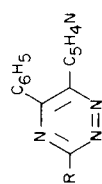
IV



V

In this category are 3-(6-methyl-2-pyridyl)- and 3-(6-phenyl-2-pyridyl)-5,6-diphenyl-*as*-triazine (IV). Also pre-

TABLE I
3-(Substituted pyridyl)-5-phenyl-6-(2-pyridyl)*as*-triazines



R	M.P. (°C)	Cryst'n Solvent	Yield %	Characteristics of Fe(II) Chelate (a)		Molecular Formula	Calculated %			Found %		
				λ max, m μ	ϵ		C	H	N	C	H	N
2-pyridyl	159-160	benzene-hexane	37.5	558	23,100	C ₁₉ H ₁₃ N ₅	73.30	4.21	22.49	73.08	4.29	22.27
4-methyl-2-pyridyl	205-206	ethanol	64.3	564	22,800	C ₂₀ H ₁₅ N ₅	73.83	4.65	21.52	73.64	4.81	21.68
4-phenyl-2-pyridyl	204-205	ethanol	92.6	565	24,400	C ₂₅ H ₁₇ N ₅	77.50	4.42	18.08	77.14	4.68	18.31

(a) Determinations indicated a mole ratio of 1/3 between Fe and ligand in the chelate.

pared were 3-(6-methyl-2-pyridyl)- and 3-(6-phenyl-2-pyridyl)-5,6-bis(2-pyridyl)*as*-triazine (V). In these compounds a new ferroin group is created and chelation with Fe (II) may occur.

The preparation of the above compounds involved condensation of the picolinimide acid hydrazides of 6-methyl and -phenyl-2-cyanopyridines (6,7) with benzil and 2,2'-pyridil, respectively. Tests on the chelating properties of these *as*-triazines will be made by Dr. Schilt.

EXPERIMENTAL

General Method of Preparation of 3-(Substituted-pyridyl)-5-phenyl-6-(2-pyridyl)*as*-triazines.

A mixture of equimolar proportions (not to exceed 0.01 molar) of substituted picolinimide acid hydrazide and 1-phenyl-2-(2-pyridyl)ethanedione in 25 ml. of ethanol was heated at reflux for one hour. The solid separating on cooling was removed by filtration, dried, and crystallized from the solvent indicated in Table I. From the filtrates no other isomers could be isolated.

6-Methylpicolinimide Acid Hydrazide.

A mixture of 2 g. of 6-methyl-2-cyanopyridine, 3 ml. of ethanol and 5 ml. of 95% hydrazine was stirred at room temperature for 3 hours. After standing over night, 7 ml. of water was added to the clear solution, which was then extracted with ether. Removal of ether and crystallization from benzene yielded 2.2 g. (88.0%) of crystals melting at 112-113°.

Anal. Calcd. for C₇H₁₀N₄: C, 56.00; H, 6.67; N, 37.31. Found: C, 56.33; H, 6.75; N, 37.28.

6-Phenylpicolinimide Acid Hydrazide.

A mixture of 2.5 g. of 6-phenyl-2-cyanopyridine, 6.2 ml. of 95% hydrazine and 4 ml. of ethanol was allowed to stand over night. The precipitate which separated after addition of water was dried and crystallized from benzene, yielding 2.5 g. (86.3%) of pure product melting at 113-114°.

Anal. Calcd. for C₁₂H₁₂N₄: C, 67.92; H, 5.66; N, 26.40. Found: C, 68.04; H, 5.86; N, 26.38.

3-(6-Methyl-2-pyridyl)-5,6-diphenyl-*as*-triazine.

A mixture of 0.8 g. of 6-methylpicolinimide acid hydrazide, 1.2 g. of benzil and 25 ml. of ethanol was heated at reflux for 2 hours. After removal of one-half of the solvent by evaporation, followed by cooling, the *as*-triazine separated out. Crystallization from benzene-petroleum ether yielded 0.5 g. (29.4%) of pure product melting at 154-155°.

Anal. Calcd. for C₂₁H₁₆N₄: C, 77.74; H, 4.98; N, 17.27. Found: C, 78.02; H, 5.05; N, 17.36.

3(6-Phenyl-2-pyridyl)-5,6-diphenyl-*as*-triazine.

A mixture of 0.8 g. of 6-phenylpicolinimide acid hydrazide, 0.8 g. of benzil and 25 ml. of ethanol was heated at reflux for 1 hour. On cooling crystals separated. Crystallization from ethanol yielded 1.2 g. (80.0%) of pure product melting at 163-164°.

Anal. Calcd. for C₂₆H₁₈N₄: C, 80.78; H, 4.70; N, 14.50. Found: C, 81.17; H, 4.82; N, 14.38.

3-(6-Methyl-2-pyridyl)-5,6-bis(2-pyridyl)*as*-triazine.

A mixture of 0.5 g. of 6-methyl picolinimide acid hydrazide, 0.75 g. of pyridil and 16 ml. of ethanol was heated at reflux for 1

hour. After removal of ethanol, the residue was crystallized from benzene-petroleum ether. The yield of pure product melting at 139-140° was 0.7 g. (63.6%).

Anal. Calcd. for C₁₉H₁₄N₆: C, 69.94; H, 4.29; N, 25.77. Found: C, 69.54; H, 4.37; N, 25.87.

3-(6-Phenyl-2-pyridyl)-5,6-bis(2-pyridyl)as-triazine.

A mixture of 1 g. of 6-phenylpicolinimidic acid hydrazide, 1 g. of pyridil and 25 ml. of ethanol was heated at reflux for 1 hour. The precipitate which appeared on cooling was separated by filtration, and crystallized from ethanol, yielding 1.7 g. (77.8%) of as-triazine melting at 175-176°.

Anal. Calcd. for C₂₄H₁₆N₅: C, 74.23; H, 4.12; N, 21.65. Found: C, 74.22; H, 4.25; N, 21.63.

Spectrophotometric Studies.

The absorption characteristics and the identities of the iron(II) chelates were determined by Dr. A. A. Schilt. For a description of procedural details and of the reagents employed, an earlier related paper (8) may be consulted. Maximum formation of the magenta colored chelates occurs over the pH range from 4 to 7. Solubility is provided by use of ethanol-water mixtures. Extraction from aqueous solution into isoamyl alcohol is quantitative. The continuous variation studies were performed following the procedure of Vosburgh and Cooper (3).

Acknowledgment.

The author is indebted to Dr. A. A. Schilt for the elucidation of the structure of the triazines prepared from 1-phenyl-2-(2-pyridyl)-ethanedione.

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