Synthesis of Some Isoquinolyl-1-hydrazones and Spectrophotometric Characterization of Some of Their Transition-Metal Chelates

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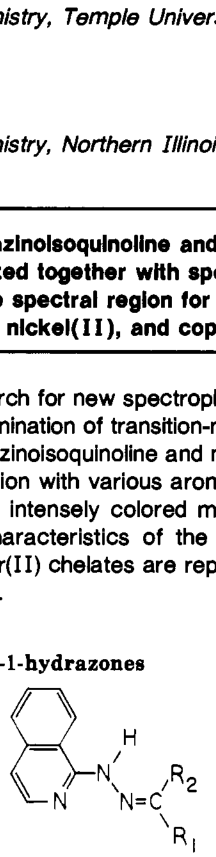
Synthesis of 1-hydrazinoisoquinoline and nine of its hydrazones is reported together with spectrophotometric data from the visible spectral region for their chelates with iron(II), cobalt(II), nickel(II), and copper(II).

Our continuing search for new spectrophotometric reagents for trace metal determination of transition-metal ions (*1*) led us to synthesize 1-hydrazinoisoquinoline and nine hydrazones derived from it by reaction with various aromatic aldehydes and ketones. All formed intensely colored metal chelates. The visible absorption characteristics of the iron(II), cobalt(II), nickel(II), and copper(II) chelates are reported here together with synthetic details.

Table I. Isoquinolyl-1-hydrazones



compd	R_1	R_2	mp, °C	cryst solvent	formula[a]
II	H	2-pyridyl	180	benzene	$C_{15}H_{12}N_4$
III	H	2-quinolyl	178	ethanol	$C_{19}H_{16}N_4O^b$
IV	H	2-quinoxalyl	223	ethanol	$C_{18}H_{15}N_5O^b$
V	H	1-isoquinolyl	195	methanol	$C_{19}H_{14}N_4$
VI	H	3-isoquinolyl	210	benzene	$C_{19}H_{16}N_4O^b$
VII	H	2-pyrryl	200	ethanol	$C_{14}H_{12}N_4$
VIII	phenyl	2-pyridyl	172	benzene	$C_{21}H_{16}N_4$
IX	2-pyridyl	2-pyridyl	173	benzene	$C_{26}H_{15}N_5$
X	methyl	2-pyridyl	139	benzene	$C_{16}H_{14}N_4$

[a] Satisfactory analyses were obtained for all compounds. [b] Monohydrate.

Experimental Section

1-Hydrazinoisoquinoline. A modification of the method of Albert and Catterall (*2*) was used. A mixture of 2.4 g of isocarbostyryl and 12 mL of phosphorous oxychloride was heated at reflux for 2 h. The excess of oxychloride was then removed by an aspirator on the steam bath. The residue was treated with an excess of a cold aqueous solution of sodium carbonate and extracted with ether. The residue, after removal of the dried ether (Na_2SO_4), was heated at reflux for 2 h with a mixture of 10 mL of hydrazine (95%) and 15 mL of absolute ethanol. On standing over night, the 1-hydrazinoisoquinoline separated in large crystals. Crystallization from benzene yielded 1.6 g (61%) of product melting at 179 °C.

Isoquinolyl-1-hydrazones. Mixtures of 0.003 M quantities of aldehyde or ketone and 1-hydrazinoisoquinoline in 20 mL of absolute ethanol were refluxed for 3 h in the presence of 2 drops of acetic acid. The solvent was then removed by evaporation and the residue crystallized from the solvent indicated in Table I.

Metal Chelates. To test for formation of colored metal chelates, 0.010 M solutions of the hydrazones in ethanol were prepared and added to 0.002 M test metal ion solutions, adjusted to known pH values with appropriate buffers. The iron(II) oxidation state was attained by addition of hydroxylamine hydrochloride as reductant. Solutions for spectrophotometric examination were prepared from accurately weighed standard metal solutions. The final solutions (in 10-mL volumetric flasks) were buffered at pH 7 with ammonium acetate and contained ethanol (50% by volume). Spectra were recorded by using a Varian 2290 spectrophotometer and a 1.00-cm cell.

Results and Discussion

For the synthesis of 1-hydrazinoisoquinoline we first attempted to prepare 1-bromoisoquinoline according to the di-

Table II. Molar Absorptivities, Wavelengths of Maximum Absorbance, and Colors of Chelates

	iron(II)		cobalt(II)		nickel(II)		copper(II)	
compd	λ, nm (color)	ϵ, L mol^{-1} cm^{-1}	λ, nm (color)	ϵ, L mol^{-1} cm^{-1}	λ, nm (color)	ϵ, L mol^{-1} cm^{-1}	λ, nm (color)	ϵ, L mol^{-1} cm^{-1}
I	590 (blue)	8 000	430[b] (orange)	9 800[a]	600 (yellow)	300[a]	540 (violet)	3 200[a]
II	579 (green)	6 070	494 (orange)	26 300	470[b] (gold)	34,000	482 (orange)	20 200
III	540 (orange)	22 000	546 (brown)	27 000[a]	512 (red)	43,500	520 (orange)	28 100
IV	605 (green)	19 900	580 (brown)	26 600	570 (brown)	49 200	564 (brown)	29 700
V	657 (orange)	11 400	*c*	*c*	*c*	*c*	*c*	*c*
VI	562 (orange)	9 560	484[b] (orange)	39 900	470[b] (gold)	33 000	480[b] (gold)	27 500
VII	522 (yellow)	4 000[a]	490[b] (green)	16 700	523 (yellow)	260	480[b] (green)	12 500
VIII	632 (yellow)	10 000[a]	516 (orange)	30 000	490[b] (orange)	43 900	520 (red)	20 300
IX	632 (yellow)	14 100	515 (orange)	25 000	500[b] (orange)	47 400	513 (orange-red)	19 500
X	585 (yellow green)	6 730	496 (orange)	29 100	470[b] (orange)	29 000	482 (orange)	19 800

[a] Beer's law deviation indicative of weakly formed complex. [b] Wavelength of shoulder. [c] No spectral evidence of chelate formation.

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rections of Butler, Bayer, and Gordon (*3*) but found that their directions yield 1,4-dibromoisoquinoline.

All of the hydrazones (II–X) formed water-insoluble, colored metal chelates which dissolved readily on addition of sufficient ethanol to the aqueous solutions. It is interesting that 1-hydrazinoisoquinoline (I) also formed colored chelates. In general, the pH range over which the metal chelates formed was from 3 to 11, except for the iron(II) chelates which formed between pH 5 and 9. Colors of the chelates in many cases were similar to those of their free ligands, especially those of I and VII. Listed in Table II are the colors of the iron(II), cobalt(II), nickel(II), and copper(II) chelates as well as their wavelengths of maximum absorbance and molar absorptivities.

The most promising hydrazone for use as a chromogenic reagent appears to be IV. Its chelates exhibit molar absorptivities in excess of 2×10^4 L mol^{-1} cm^{-1} which is sufficient to enable trace metal determinations at the micromolar or 0.2–2.0-μg level. Unfortunately the absorption bands of the various transition-metal chelates of IV overlap considerably so that accurate determination of one metal in the presence of the others is impractical without prior separation. Simultaneous determinations are also impractical except perhaps for iron and copper. Compound II, although less sensitive than IV, appears to be suitable for simultaneous determinations of iron, cobalt, and nickel since the respective absorption bands are better resolved.

The hydrazones in their uncomplexed form undergo a pronounced color change from intense yellow to red on acidification. They may prove useful as indicators for pH and p*K* measurements of strong acids.

Registry No. I, 15793-94-9; II, 103837-15-6; III, 103837-16-7; IV, 103837-17-8; V, 103851-10-1; VI, 103837-18-9; VII, 103837-19-0; VIII, 103837-20-3; IX, 103837-21-4; X, 103837-22-5; isocarbostyryl, 491-30-5; hydrazine, 302-01-2; 2-formylpyridine, 1121-60-4; 2-formylquinoline, 5470-96-2; 2-formylquinoxaline, 1593-08-4; 1-formylisoquinoline, 4494-18-2; 3-formylisoquinoline, 5470-80-4; 2-formylpyrrole, 1003-29-8; 2-benzoylpyridine, 91-02-1; di-2-pyridyl ketone, 19437-26-4; 2-acetylpyridine, 1122-62-9.

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Synthesis of 1,1′-Dibenzyl-5,5′:7,7′-bis(hexano)bis[6(1*H*)-cycloheptatriazolone], a Novel Heterocyclic Ring System

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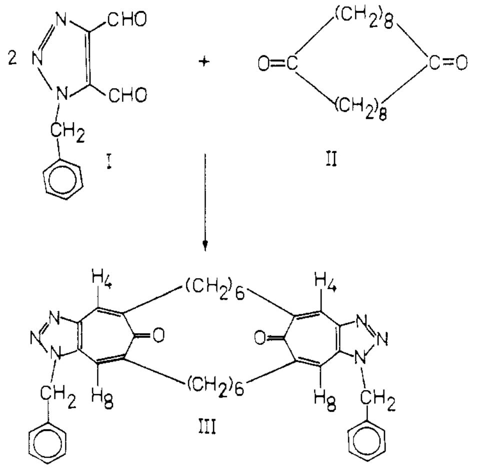
The synthesis of 1,1′-dibenzyl-5,5′:7,7′-bis(hexano)bis[6(1*H*)-cycloheptatriazolone] (III), an interesting example of a compound containing two triazoletropone systems within the same molecule, has been accomplished by the condensation reaction of 2 mol of 1-benzyl-1*H*-triazole-4,5-dicarboxaldehyde (I) with 1 mol of 1,10-cyclooctadecanedione (II).

Our continuing interest in the syntheses and reactions of triazole derivatives (*1*) has led us to prepare the novel ring system, 1,1′-dibenzyl-5,5′:7,7′-bis(hexano)bis[6(1*H*)-cycloheptatriazolone] in order to study the effect of the polymethylene bridge on the aromaticity and planarity of a system which contains two triazoletropone systems within the same molecule (*2*, *3*). The observed NMR chemical shift of 7.70 ppm from Me_4Si of the protons H_4 and H_8 can be attributed to an increase in the planarity of the triazoletropone system and also to the existence of a ring current which leads to the conclusion that this compound is aromatic in the tropone ring portion.

Experimental Section

1-Benzyl-1*H*-triazole-4,5-dicarboxaldehyde (I) was prepared according to the method of Henkel and Weygand (*4*). 1,10-



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