Listings and/or loans of the decks for these programs will be sent on request.

Conclusions

The adaptation of the Bailar method of isomer enumeration to the computer has been shown to be rapid and reliable. It can be applied to any type of structure.

Acknowledgments.—We are grateful to the University of Iowa Computer Center and the Graduate College for computer time.

CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION,[1a]
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Metal Complexes of Azo Dyes. I. Quadridentate Complexes from Bidentate Azo Compounds and Alkanediamines or Ethanolamine[1b]

BY THEODOR A. LISS AND DONALD R. BAER

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o-Halo-*o*′-hydroxydiarylazo compounds react readily with alkanediamines or ethanolamine in the presence of copper(II) or nickel(II) salts to form in high yield the quadridentate complex of the ligand resulting from nucleophilic displacement of the halogen by the amine. The order of reactivity is I > Br > Cl > F, but even the fluoro compound reacts at room temperature. In polyhaloazo compounds only the *ortho* halogen is reactive under the reaction conditions. 4-(*o*-Bromophenylazo)-3-methyl-1-phenyl-2-pyrazolin-5-one (XI) reacts with ethylenediamine, alone or in the presence of Cu(II), to give the uncomplexed ligand XII, which can be metalized in a separate step with cupric chloride in ethanolamine. The fluoro and bromo compounds Ia and Ic, respectively, also react with ethylenediamine in the absence of metallic salts to form the quadridentate ligand XIV. The *o*-amino-*o*′-halo compounds (XVIIIc and XVIIId) react with ethylenediamine in a surprising manner to form the reduction product XX. The *o*-bromotriphenylformazan XXI reacts to form a complex of the four-nitrogen ligand XXII in which the copper is five-coordinate. The *o*-(methoxycarbonyl) azo compound XXIII reacts in one step to give the quadridentate complex XXIV.

Metal complexes of azo compounds suitably substituted in the *o,o*′ positions constitute an important class of commercial dyes.[2] Most of these dyes are based on azo compounds which are tridentate and which therefore form bicyclic metal complexes. Quadridentate and quinquidentate azo compounds which form tri- and tetracyclic metal complexes have also been reported.[2] The requisite multidentate azo compounds were first prepared and were then treated with a metal ion in a subsequent step.

The present work is concerned with the reaction of bidentate azo compounds with alkanediamines or ethanolamine in the presence of copper or nickel salts to form metal complexes of quadridentate azo compounds in one step.

The replacement of the chloro group in *o*-chloro-*o*′-hydroxyazo compounds by hydroxy, alkoxy, alkylamino, and arylamino, as well as other groups, in the presence of cupric salts was first reported by Delfs and coworkers.[3] This reaction was subsequently extended and extensively studied by Stepanov and coworkers.[4,5] Both groups were primarily interested in the new azo compounds obtained by removing the metal from the first-formed metal complexes, which themselves were not characterized.

Three isolated reports of the use of bifunctional compounds in the metal-catalyzed reaction of *o*-halo-*o*′-hydroxyazo compounds have been located. The patent literature[6] reports the use of 8-aminoquinoline and formulates the products as quadridentate complexes. Delfs[3b] mentions the use of ethanolamine in a patent example. Finally, Bamberger and Gross[7] report the treatment of *o*-chloro-*o*′-hydroxyazo dyes on a fiber with a copper compound and an *ortho*-substituted aromatic amine or a heterocyclic amine. It was suggested that the tricyclic metal complex had formed on the fiber.

The alkanediamines and ethanolamine used in the present work have the advantage of being good solvents for both the azo compounds and the metal salts and simultaneously serve as a base to neutralize the acid generated in the reaction. Much of the earlier work on metal-catalyzed reactions of *o*-halo-*o*′-hydroxyazo compounds was carried out in heterogeneous systems in which two or even three phases were present.

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[1] (a) Publication No. 419. (b) The majority of this work was included in a paper presented by D. R. Baer at the Third Internationales Farbensymposium, Interlaken, Switzerland, May 18, 1967.

[2] For a comprehensive review of metal complexes of dyes, see H. Baumann and H. R. Hensel, *Fortschr. Chem. Forsch.*, **7**, 643 (1967).

[3] (a) D. Delfs and R. Knoche, German Patent 571,859 (Sept 29, 1931); (b) D. Delfs, German Patent 658,841 (March 18, 1934); (c) D. Delfs, German Patent 738,900 (Oct 31, 1936).

[4] For paper XXII in the series, see B. I. Stepanov and M. A. Andreeva, *Soviet J. Org. Chem.*, **2**, 2171 (1966).

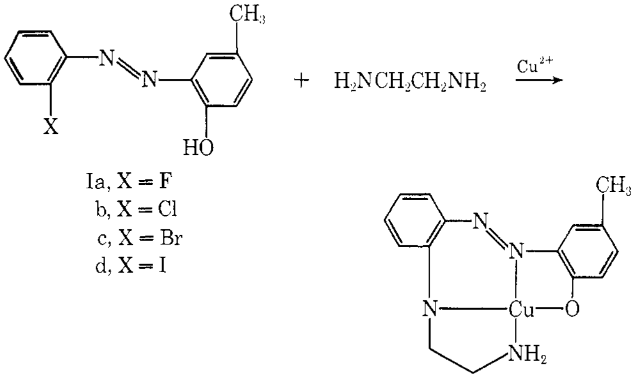
[5] A review of this work is given by B. I. Stepanov in "Recent Progress In the Chemistry of Natural and Synthetic Colouring Matters," Academic Press, New York, N. Y., 1962, pp 451–471.

[6] German Patent 748,913 (July 25, 1939).

[7] R. Bamberger and R. Gross, *Textil-Praxis*, **16**, 931 (1961); **17**, 485 (1963).

o-Halo-*o*′-hydroxyazobenzenes

When a solution of the yellow *o*-chloro-*o*′-hydroxyazo compound Ib was heated to 85–95° for several hours with 1 equiv of cupric chloride in aqueous ethylenediamine solution, a marked bathochromic shift was observed and complex II was obtained in 92% yield. The reaction also occurred at room temperature if the reaction time was lengthened.



Ia, X = F
b, X = Cl
c, X = Br
d, X = I

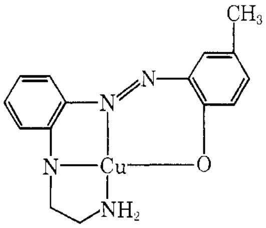
II

The structural assignment[8] is made on the basis of the elemental analysis, method of synthesis, and the infrared and visible absorption spectra. The infrared spectrum of II shows a doublet of weak to moderate intensity at 3180 and 3110 cm^{-1} (N–H stretch), which confirms the presence of a coordinated primary amino group. The infrared spectra of coordination compounds of ethylenediamine, for example, generally show doublets or even multiplets in the N–H stretching region of about 3050–3350 cm^{-1}; thus, $Cu(en)_2PtCl_4$ absorbs at 3320 and 3245 cm^{-1}.[9]

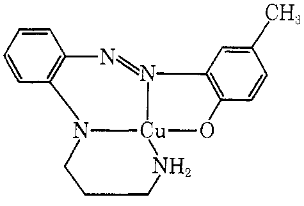
When the bromonaphthol III (Table I) was used as the halogen component, the naphthalene analog (IV, Table II) of II was obtained.

Substitution of 1,2-propanediamine for the ethylenediamine resulted in formation of complex V (Table II). Two isomers can form in this reaction as a consequence of the dissymmetry of the diamine; thin layer chromatography of the product indicated that a mixture of the two isomers was obtained.

Similarly, 1,3-propanediamine reacted with bromo compound Ic and cupric chloride to form complex VI which has two six-membered rings as well as a five-membered ring surrounding the metal atom. The absorption maximum occurs at 566 nm (DMF), which is virtually the same as that for the analog from ethylenediamine (567 nm in DMF). The infrared spectrum of VI showed a doublet of weak to moderate intensity at 3230 and 3110 cm^{-1} (N–H stretch).



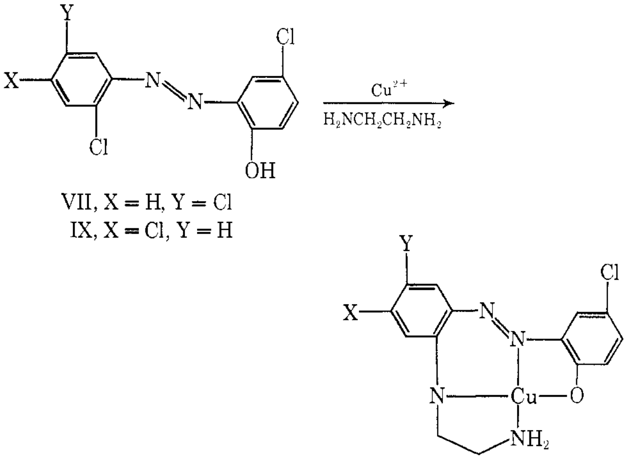
IIa



VI

As indicated above, both *o*-chloro- and *o*-bromophenylazo compounds react with alkanediamines to form copper complexes. The *o*-fluoro compound Ia was found to be somewhat less reactive but nevertheless reacted with ethylenediamine at 70–80° within several hours to give a good yield of II. The reaction even occurred slowly at room temperature; after 7 months a 70% yield of II was isolated (this long reaction time was probably not necessary). The reactivity of the fluorine in the present system contrasts with the report that no reaction was observed between 1-(*o*-fluorophenylazo)-2-naphthol and sodium methylate in the presence of copper acetate after 8 hr at 100° (methanol–dioxane solvent).[10] The iodo compound Id, as expected, was the most reactive compound in the series. Although no quantitative rate data were obtained, Id was observed to react readily at room temperature.

When polychloro azo compounds were allowed to react with ethylenediamine in the presence of cupric salts, only the *o*-chlorine was reactive under the conditions used. Thus, the trichloro compounds VII and IX yielded complexes VIII and X.



VII, X = H, Y = Cl
IX, X = Cl, Y = H

VIII, X = H, Y = Cl
X, X = Cl, Y = H

A surprising result was found in the reaction of the pyrazolinone XI with ethylenediamine. Both in the

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[8] The copper is shown coordinated to the azo nitrogen attached to the *p*-cresol ring. This assignment is arbitrary. Isomer IIa is also possible. To our knowledge there has been no report of isolation or detection of isomers of this type.

[9] D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **17**, 68 (1961).

[10] M. A. Andreeva and B. I. Stepanov, *J. Gen. Chem. USSR*, **30**, 2750 (1960).

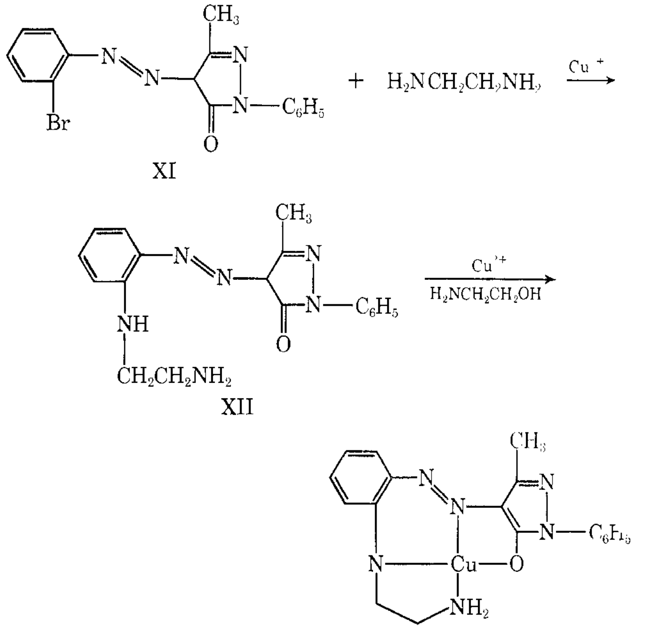
TABLE I

PROPERTIES AND ANALYSES OF *o*-HALOPHENYLAZO COMPOUNDS

Compd no.	Compd name	Recrys solvent	Mp, °C	$\lambda_{max}^{CH_3OH}$, nm	ϵ	Empirical formula	% C		% H		% Halogen		% N	
							Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Ia	2-(*o*-Fluorophenylazo)-*p*-cresol	None	80–84	397	7,800	$C_{13}H_{11}FN_2O$	67.8	68.0	4.82	5.0	8.3	8.0	12.2	12.4
Ib	2-(*o*-Chlorophenylazo)-*p*-cresol	CH_3OH	111–112[a]	403	8,100									
Ic	2-(*o*-Bromophenylazo)-*p*-cresol	CH_3OH	115–116[b]	403	7,800									
Id	2-(*o*-Iodophenylazo)-*p*-cresol	CH_3OH	108–109	401	9,000	$C_{13}H_{11}IN_2O$	46.2	46.3	3.28	3.2	37.5	37.5	8.3	8.3
III	1-(*o*-Bromophenylazo)-2-naphthol	*i*-C_3H_7OH	173–174[c]	478	18,200									
VII	4-Chloro-2-(2,5-dichlorophenylazo)-phenol	*i*-C_3H_7OH	146–147	405	8,800	$C_{12}H_7Cl_3N_2O$	47.8	47.7	2.34	2.5	35.3	35.4	9.3	9.2
IX	4-Chloro-2-(2,4-dichlorophenylazo)-phenol	*i*-C_3H_7OH	137.5–138.5	402	10,200	$C_{12}H_7Cl_3N_2O$	47.8	48.0	2.34	2.5	35.3	35.3	9.3	9.3
XI	4-(*o*-Bromophenylazo)-3-methyl-1-phenyl-2-pyrazolin-5-one	*i*-C_3H_7OH	199–200	392	21,800	$C_{16}H_{13}BrN_4O$	53.8	53.6	3.67	3.6	22.4	22.0	15.7	15.6
XVIIIc	1-(*o*-Bromophenylazo)-2-naphthylamine[d]	C_2H_5OH	156–157	463	15,700	$C_{16}H_{12}BrN_3$	58.9	58.9	3.71	3.6	24.5	24.2	12.9	13.0
XVIIId	1-(*o*-Iodophenylazo)-2-naphthylamine	CH_3OH	168–169	485 468 (shoulder)	14,700 15,500	$C_{16}H_{12}IN_3$	51.4	51.5	3.45	3.5			11.2	11.6

[a] Lit. mp 111–112.5°: M. A. Andreeva and B. I. Stepanov, *J. Gen. Chem. USSR*, **30**, 1380 (1960). [b] Lit. mp 116°: J. T. Hewitt and H. A. Phillips, *J. Chem. Soc.*, **79**, 166 (1901). [c] Lit. mp 174.5–175°: M. A. Andreeva and B. I. Stepanov, *J. Gen. Chem. USSR*, **30**, 2750 (1960). [d] Although this compound was used previously, no analyses or physical properties were reported: V. Chmatal, J. Poskocil, and Z. J. Allan, *Collection Czech. Chem. Commun.*, **24**, 494 (1959).

presence and in the absence of cupric ion, the product was the uncomplexed quadridentate compound XII.[11]



XI

XII

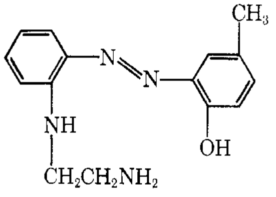
XIII

The infrared spectrum of XII (KBr pellet) shows a sharp band of weak to moderate intensity at 3390 cm^{-1} and a broad complex base at 3100–2400 cm^{-1}. The absence of the doublet characteristic of a primary amino group (N–H stretch) is probably due to bonded interactions (see below).

Evidently the cupric ion is more tightly complexed by the ethylenediamine than by XII, so that under the reaction conditions the complex of XII is not formed. The copper complex XIII was obtained by allowing XII to react with cupric chloride in aqueous ethanolamine solution. Ethanolamine forms a complex with cupric ion much less strongly than does ethylenediamine and therefore does not prevent formation of XII. The use of ethanolamine as solvent is rather specific; in solvents such as methanol and pyridine only impure copper complex was obtained. The infrared spectrum of XIII shows a multiplet in the N–H stretch region, with a very weak band at 3380 cm^{-1} and weak to moderate bands at 3250 and 3200 cm^{-1}.

The electronic spectral properties of complex XIII bear mentioning. The quadridentate compound XII has a maximum at 425 nm (ϵ 16,000) in methanol, whereas the brown copper complex XIII gives a yellow solution in methanol with a strong maximum at 415 nm (ϵ 19,800). This hypsochromic shift on metalization contrasts with the bathochromic shift observed in the analogous azobenzene derivatives XIV and II (see below).[12] In addition to the maximum at 415 nm (ϵ 19,800), complex XIII has a broad shoulder of low intensity beyond 500 nm (ϵ ~1800). In other solvents, this shoulder absorption becomes a well-defined peak at considerably longer wavelengths, with the result that solutions of XIII are deep blue. Thus, in acetone and dimethylformamide the maxima appear at 590 (ϵ 8100) and 598 nm (ϵ 8100), respectively.

The above results with the pyrazolinone compound suggested that the reaction in the azobenzene series might also occur in the absence of cupric ion. In fact, it was found that both the fluoro and bromo compounds Ia and Ic, respectively, react with ethylenediamine at 75–85° to form the quadridentate compound XIV. In a subsequent step XIV was treated with cupric sulfate in pyridine to form complex II, identical with material obtained as described earlier.



XIV

The infrared spectrum of XIV taken as a Nujol mull or KBr disk showed only a broad and complex band of weak to medium intensity at 3100–2400 cm^{-1}, with no absorption at higher frequencies. A carbon tetrachloride solution of XIV, however, showed a weak, moderately sharp doublet at 3380 and 3240 cm^{-1} expected for a primary amino group, in addition to a weak, broad band from 3100 to 2400 cm^{-1}. Thus, even in dilute solution, bonded interactions still occur in XIV; these interactions presumably represent intramolecular hydrogen bonding to the azo group.

The bromo compound Ic reacts with ethanolamine and cupric chloride at room temperature to give the complex XV in high yield. No reaction was observed at room temperature in the absence of cupric chloride. Ethanolamine could presumably react to replace the bromine with either the hydroxy or the amino end of the molecule. Since XV shows an absorption maximum at 566 nm (dimethylformamide), which is virtually the

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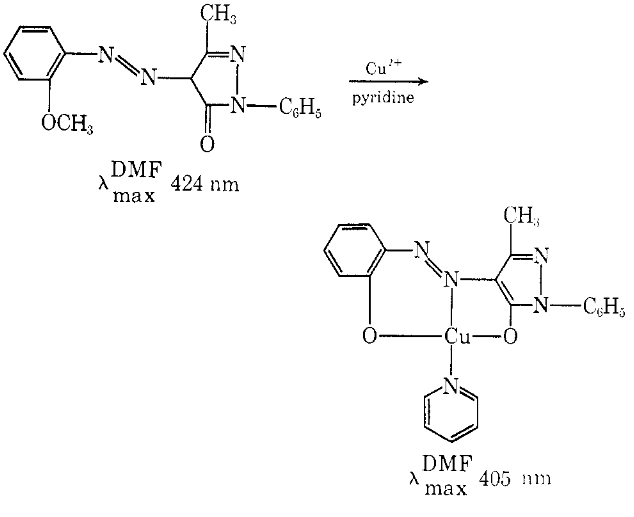
[11] The *o*-chloro analog of XI was reported to be unreacted with sodium butoxide and copper acetate in a mixture of 1-butanol and pyridine, even after 8 hr at 100°: M. A. Andreeva and B. I. Stepanov, *J. Gen. Chem. USSR*, **30**, 1380 (1960).

[12] However, a similar hypsochromic shift is observed with pyrazolinones in the tridentate series (as shown in the equation below), whereas again a bathochromic shift occurs on dealkylative metalization of *o*-hydroxy-*o′*-methoxyazobenzenes; unpublished observations.

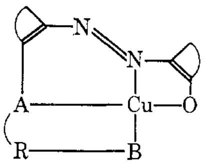


λ_{max}^{DMF} 424 nm

λ_{max}^{DMF} 405 nm

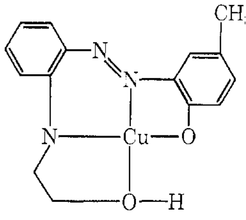
TABLE II

PHYSICAL PROPERTIES AND ANALYSES OF METAL COMPLEXES



Compd	Parent azo compd	A—R—B	Mp, °C	λ_{max}^{DMF}, nm[a]	ϵ	Empirical formula	% C		% H		% N	
							Calcd	Found	Calcd	Found	Calcd	Found
II	Ia–d	N—(CH$_2$)$_2$—NH$_2$	263 dec	567	22,600	$C_{15}H_{16}N_4OCu$	54.3	54.6	4.86	4.8	16.9	16.9
IV	III	N—(CH$_2$)$_2$—NH$_2$	209–210	573	24,800	$C_{18}H_{16}N_4OCu$	58.8	58.8	4.39	4.2	15.2	15.1
			dec	452	7,200							
V	Ic	N—CH—CH—NH$_2$ H,CH$_3$		568	21,700	$C_{16}H_{18}N_4OCu$	55.6	55.5	5.24	5.2	16.2	16.3
VI	Ic	N—(CH$_2$)$_3$—NH$_2$	211–212	566	20,200	$C_{16}H_{18}N_4OCu$	55.6	55.6	5.24	5.3	16.2	16.1
VIII	VII	N—(CH$_2$)$_2$—NH$_2$	253–254	587	21,300	$C_{14}H_{12}Cl_2N_4OCu$	43.5	43.9	3.13	3.3	14.5	14.4
				476	5,000							
X	IX	N—(CH$_2$)$_2$—NH$_2$	266–267	571	23,100	$C_{14}H_{12}Cl_2N_4OCu$	43.5	43.6	3.13	3.2	14.5	14.5
			dec									
XIII	XI	N—(CH$_2$)$_2$—NH$_2$	197–200	598[c]	8,100	$C_{18}H_{18}N_6OCu$	54.3	54.0	4.56	4.6	21.1	20.8
XVI[b]	Ic	N—(CH$_2$)$_2$—NH$_2$	296–300	630	6,500	$C_{15}H_{16}N_4ONi$	55.1	55.3	4.93	5.2	17.1	17.2
				582	6,000							
				509	16,200							
XV	Ic	N—(CH$_2$)$_2$—OH	>300	566	22,100	$C_{15}H_{15}N_3O_2Cu$	54.1	54.2	4.55	4.4	12.6	12.4
XXIV	XXIII	CN—(CH$_2$)$_2$—NH$_2$ ‖ O	274–275 dec	503	4,200	$C_{16}H_{16}N_4O_2Cu$	53.4	53.4	4.48	4.6	15.6	15.4

[a] Absorption peaks from 400 to 800 nm are listed. [b] Nickel complex. [c] See text.



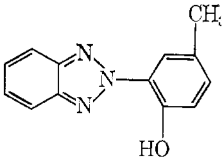
XV

same as for complex II (567 nm), it is clear that it is the amino group which is attached to the benzene ring. This assignment is confirmed by the infrared spectrum of XV, which shows no absorption in the N–H stretching region but has a broad complex band of weak intensity in the 2900–2000-cm^{-1} region. This shift of the O–H stretching vibration to lower frequency, as well as the breadth of this absorption band, evidently reflects substantial bonded interaction in XV.

A nickel complex XVI corresponding to II was obtained by a procedure similar to that for the copper complexes, *i.e.*, reaction of Ic with aqueous ethylenediamine and nickel chloride at 85–95°. Elemental analysis indicates that the octahedral positions of the nickel are not occupied by external ligands. The electronic absorption spectrum of XVI shows well-defined peaks in methanol at 618 nm (ϵ 6300) and 573 nm (ϵ 5100), with the strongest peak at 482 nm (ϵ 12,000). The analogous copper complex II shows only weak shoulder absorption beyond 600 nm and has its strongest peak at 551 nm (ϵ 20,700).

In view of the facility of the above replacement reactions with amino compounds, an attempt was made to extend the reaction to the use of ammonia.[13] This goal is particularly desirable because of the difficulty in preparing *o*-amino-*o*′-hydroxyazobenzenes (and therefore their complexes) by other routes.

For the present reaction a solvent was needed which is compatible with the aqueous copper–ammonia complex and which will solubilize the 2:1 *o*-halo-*o*′-hydroxyazo dye–copper complex which forms as an intermediate. With bromo compound Ic and cupric chloride in a mixture of glyme and ammonium hydroxide, very little reaction occurred (other than formation of the 2:1 complex, which is very soluble in the glyme) even up to 200°. The same result was observed with concentrated ammonium hydroxide in dimethyl sulfoxide at 100°. After reaction at 170° in formamide it was possible to isolate a small amount of the benzotriazole XVII, as well as unidentified products. The formation of the benzotriazole XVII suggests that replacement of the *o*-bromo substituent by amino did occur, but that under the vigorous reaction conditions the *o*-aminoazo compound thus produced was oxidatively cyclized[14] under the influence of the cupric ion. The reason for the much lower reactivity of ammonia in the replacement reaction is not clear.



XVII

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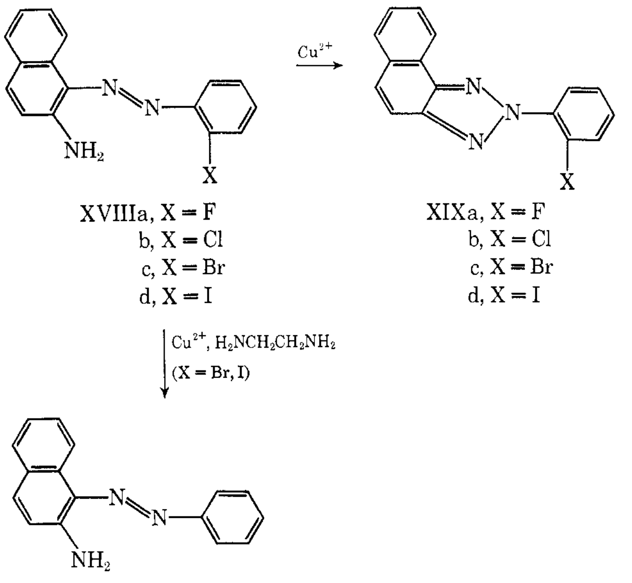
(13) In ref 3b the use of ammonia is suggested, but no specific examples are given.

(14) For a discussion of the cyclization of *o*-aminoazo compounds to benzotriazoles, see K. H. Schündehütte in "Methoden der Organischen Chemie," Vol. 10/3, Houben-Weyl, Georg Thieme Verlag, Stuttgart, Germany, 1965, pp 425–430.

o-Amino-*o*′-halodiarylazo Compounds

Because of the just mentioned oxidative cyclization,[14] it was anticipated that benzotriazoles would result from the reaction of *o*-amino-*o*′-halodiarylazo compounds with ethylenediamine and cupric chloride. In fact, the cyclization of the (*o*-halophenylazo)naphthylamines XVIIIa–d to the naphthotriazoles XIXa–d has been reported to occur with cupric sulfate in hot, aqueous pyridine.[15]



XVIIIa, X = F
b, X = Cl
c, X = Br
d, X = I

XIXa, X = F
b, X = Cl
c, X = Br
d, X = I

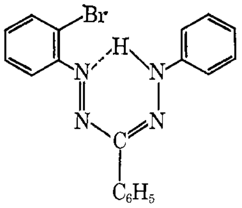
XX

Nevertheless, when XVIIIc or XVIIId (X = Br or I) was allowed to react with cupric chloride in aqueous ethylenediamine at 85–90°, an orange solid was obtained which contained neither bromine[16] nor copper. Elemental analysis suggested that the product was 1-phenylazo-2-naphthylamine (XX), which was confirmed by comparison with an authentic sample of XX.

That cupric ion plays no role in this surprising hydrogenolysis reaction was shown by the formation of XX in similar yield when the cupric chloride was omitted. This result indicates that ethylenediamine alone is responsible for the reduction (barring the presence of an unsuspected impurity in the ethylenediamine). At present only speculative mechanisms can be presented for the formation of XX. The explanation for the failure of XVIIIc and XVIIId, as well as XX, to be cyclized to the naphthotriazoles by cupric chloride in ethylenediamine is presumably that the cupric ion is tightly complexed by the ethylenediamine.[17] The cupric ion is therefore unable to interact with the relatively weakly complexing *o*-aminoazo compounds.

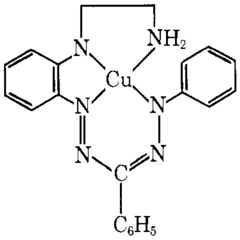
Formazans

An interesting application of the replacement of *o*-halogen by ethylenediamine was found in the formazan series. Unsubstituted 1,5-diphenylformazans are known[2] to form 2:1 complexes with divalent metals and are therefore analogous to *o*-hydroxyazobenzenes. It was therefore reasonable to examine the reaction of a halo-monosubstituted formazan with ethylenediamine and cupric chloride. The red bromo compound XXI reacted readily at 60° or more slowly at room temperature to form a deep blue copper complex in which the bromine was replaced.



XXI

Elemental analysis indicated that the product was not the simple quadridentate complex XXII but rather that it contained an additional 0.5 mol of ethylenediamine. It is possible therefore that the copper in XXII is actually five-coordinate and that one ethylenediamine molecule serves to link two units of XXII together through its amino groups. The infrared spectrum of this ethylenediamine-containing complex (XXIIa) shows only a single weak absorption in the N–H stretch region at 3200 cm^{-1}.



XXII

When water is added to a solution of XXIIa in pyridine, a new complex XXIIb is obtained which has lost the ethylenediamine-linking molecule. Elemental analysis of XXIIb is in agreement with structure XXII plus a molecule of pyridine and 0.5 mol of water. The presence of pyridine in XXIIb supports the five-coordinate nature of copper in XXIIa and was confirmed by a strong peak at m/e 79 in the mass spectrum. The infrared spectrum of XXIIb shows a weak doublet at 3330 and 3190 cm^{-1}; however, no bands due to the 0.5 mol of water could be detected. Both XXIIa and XXIIb show a strong peak at 630 nm in dimethylformamide solution.

Role of the Copper Ion

There arises the question of the importance of the metal ion in the displacement of the *o*-halogen by the amino compounds.

The Hammett σ constant for the phenylazo group is similar (0.64) to that for the cyano group (0.63) but

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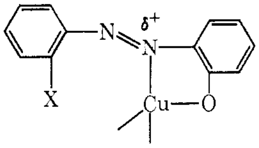
(15) V. Chmatal, J. Poskocil, and Z. J. Allan, *Collection Czech. Chem. Commun.*, **24**, 494 (1959).

(16) Reaction of the chloro analog XVIIIb with sodium butoxide and copper acetate in a mixture of 1-butanol and toluene at 100° for 8 hr was reported to result in replacement of 21% of the chlorine as chloride ion. The organic product, however, was not identified: M. A. Andreeva and B. I. Stepanov, *J. Gen. Chem. USSR*, **30**, 1380 (1960).

(17) The reaction of XVIIIa with ethanolamine is the subject of a manuscript in preparation.

somewhat lower than that for the nitro group (0.78).[18] Both of these latter groups are recognized as being strongly activating for nucleophilic displacement of *ortho*- or *para*-situated halogen atoms. This activating influence helps to explain the reactivity of halo compounds Ia, Ic, and XI with ethylenediamine in the absence of metal ion.

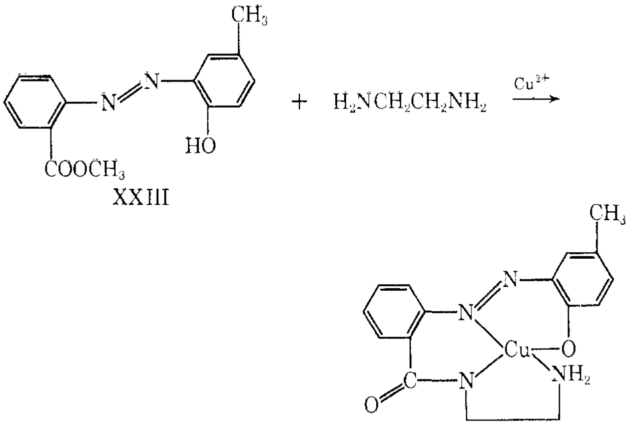
Stepanov[5] has suggested that in the 2:1 azo dye-copper complex which is probably present as an intermediate in the copper-catalyzed reactions of *o*-halo-*o*′-hydroxyazo compounds, the copper interacts with the halogen so as to weaken the carbon–halogen bond and facilitate displacement of the halogen atom. The lability of the *o*-halogen is also increased by the partial positive charge generated on the azo nitrogen in the 2:1 complex. Such effects are probably also operative in the present reactions with alkanediamines and ethanolamine, since we observed qualitatively in a number of the reactions with ethylenediamine, and especially in the reaction with ethanolamine, that the rate was higher in the presence of cupric ion than in its absence. Kinetic studies will be needed to establish the magnitude of these effects.



In at least one instance, however, namely, the conversion of the pyrazolinone compound XI to XII in the presence of cupric ion, it is apparent that cupric ion does not participate. Since quadridentate XII does not form a complex with cupric ion in ethylenediamine solution and since bidentate XI is undoubtedly a weaker complexing agent than quadridentate XII, an intermediate copper complex of XI cannot play a significant role in the formation of XII.[19,20]

o-Hydroxy-*o*′-(methoxycarbonyl)azobenzene

The concept of allowing a bidentate azo compound having a labile group to react with ethylenediamine to form a quadridentate complex was extended to an *o*-hydroxy-*o*′-(methoxycarbonyl)azobenzene. Thus, when the ester XXIII was treated with cupric chloride and aqueous ethylenediamine at 70–80°, it was possible to isolate after purification the complex XXIV. The visible absorption maximum underwent a marked bathochromic shift from 401 nm (ε 6700) to 503 nm (ε 11,200) (both in dimethylformamide).



The presence of the coordinated primary amino group is confirmed by the weak doublet in the infrared spectrum at 3360 and 3230 cm^{-1}. In the carbonyl region the band at highest frequency appears at 1620 cm^{-1} (weak to medium intensity). It is likely that this band represents aromatic C=C stretching vibration. A band of strong intensity appears at 1590 cm^{-1} and this band is tentatively assigned to the amide carbonyl. In any case it is clear that bonding of the copper to the amide nitrogen shifts the carbonyl absorption strongly to longer wavelength.

As in the case of complexes of *o*-carboxy-*o*′-hydroxyazobenzene, there is no ambiguity about which of the azo nitrogens in XXIV is bonded to metal. Since a seven-membered ring would result if the other azo nitrogen were involved, structure XXIV is much more likely.

Magnetic Susceptibility

The magnetic susceptibilities of a number of the complexes described above were determined. The nickel complex XVI was found to be diamagnetic, which indicates that the complex has a square-planar geometry around the nickel atom. All of the copper complexes examined (including II, VI, XV, and XXIV) had magnetic moments equal to or greater than the spin-only value, $\mu_{eff} = 1.73$. The magnetic moments for the copper complexes establish the oxidation state Cu(II) d^9 but indicate very little about the geometry of the complexes, since the moment for this state is almost independent of stereochemistry. The results do suggest that no significant interaction between copper atoms is occurring. X-Ray examination would be required to establish the stereochemistry of the copper complexes with certainty.

Experimental Section

All melting points are uncorrected. Infrared spectra were determined with Perkin-Elmer infrared spectrophotometers, Models 621 and 221, and were taken as Nujol mulls unless otherwise indicated. The electronic spectra were measured with a Cary Model 14 recording spectrophotometer. The magnetic susceptibilities were determined on a Faraday balance which was calibrated with HgCo(SCN)$_4$.

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[18] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

[19] It is recognized that even in the reactions of *o*-hydroxyphenylazo compounds, only a small portion of the cupric ion may actually be complexed by the starting azo compound, because the major portion is complexed by the alkanediamine. Stability constants which have been reported for cupric ion with ethylenediamine (K_1 = 11[20a]) and 2-phenylazo-*p*-cresol (K_1 = 9.67[20b]) in 75% dioxane support this view, although it is clearly not possible to extrapolate these values from 75% dioxane to aqueous ethylenediamine. In any case the acceleration by cupric ion is then all the more remarkable. In the case of the more weakly complexing ethanolamine, a larger portion of the cupric ion will be complexed by the starting azo compound. It is thus not surprising that the cupric ion caused a large rate increase in the ethanolamine reaction.

[20] (a) L. G. Uitert and W. C. Fernelius, *J. Am. Chem. Soc.*, **76**, 375 (1954); (b) F. A. Snavely, as cited in "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964, p 680.

The *o*-halophenylazo compounds in Table I (except compounds XVIIIc and XVIIId) were prepared by coupling the diazotized haloamine to the appropriate coupling component under alkaline conditions. XVIIIc and XVIIId were prepared by coupling to 2-amino-1-naphthalenesulfonic acid under acid conditions. The solvents used for recrystallization are listed in Table I; a Soxhlet apparatus was used in some cases.[21]

Reaction of *o*-Halophenylazo Compounds with Ethylenediamine and Cupric Chloride. (a) **Ib.**—To a solution of 2.5 g of Ib in 25 ml of ethylenediamine was added a solution of 1.75 g of $CuCl_2 \cdot 2H_2O$ in 5 ml of water plus 10 ml of ethylenediamine. The mixture was warmed to 85–90° for about 3 hr and then cooled to room temperature. The needles of II which formed were collected and washed with water, yielding 1.45 g. A second crop was obtained by adding an equal volume of water to the filtrate at 85°. The crystals were collected at room temperature, yielding 1.6 g; total yield, 3.05 g (90%). The analytical sample of II was obtained by recrystallizing the crude product from methanol (Soxhlet).[21]

(b) **Ia and Id.**—The fluoro and iodo analogs Ia and Id, respectively, were similarly treated with ethylenediamine and $CuCl_2 \cdot 2H_2O$. The yield of II isolated from the fluoro analog after 4–5 hr at 70–80° was 72%, whereas the yield was 70% after 7 months at room temperature. Shorter reaction periods at room temperature were not tried. The iodo analog gave a 75% yield (no attempt was made to isolate a second crop) of II after 4 hr at room temperature.

(c) **Additional *o*-Halophenylazo Compounds.**—Similar concentrations and reaction conditions were used for reaction of III, VII, and IX with ethylenediamine, and for the reaction of Ic with 1,2-propanediamine. The details of these reactions are listed in Table III. No attempt was made to obtain maximum yields.

TABLE III

Complex	Reaction temp, °C	Time, hr	% yield (crude)	Recrys solvent
IV	50	5	73	Methanol[21]
VIII	90	4.5	60	Acetone[21]
X	90	10	27	(1) Methanol[21] (2) Ethylenediamine–water
V	60	1	64	Acetone[21]

Reaction of Ic with 1,3-Propanediamine and Cupric Chloride.—To a solution of 2.9 g of Ic in 40 ml of 1,3-propanediamine was added a solution of 2.5 g of $CuCl_2 \cdot 2H_2O$ in 5 ml of water plus 15 ml of 1,3-propanediamine. The mixture was heated at 65–75° for 5 hr, after which an addition of 2.5 g of cupric chloride in 5 ml of water was made. Heating was continued for about 16 hr, and the needles of VI were then collected at room temperature; yield, 1.75 g (51%). Purification was effected by twice dissolving the solid in 1,3-propanediamine and then precipitating the solid by the dropwise addition of water.

Reaction of XI with Ethylenediamine. (a) **In Presence of Cupric Chloride.**—To a solution of 3.6 g of XI in 25 ml of ethylenediamine was added a solution of 2.5 g of $CuCl_2 \cdot 2H_2O$ in 5 ml of water plus 10 ml of ethylenediamine. The mixture was heated at 75–80° for 12 hr, after which 65 ml of water was added by drops at room temperature. The yellow solid which formed was filtered off to give 2.9 g (86%) of XII; mp 165–169° dec; $\lambda_{max}^{CH_3OH}$ 425 nm (ϵ 16,100).

(b) **In Absence of Cupric Chloride.**—A solution of 3.6 g of XI in 25 ml of ethylenediamine was heated under nitrogen at 75–80° for about 22 hr. The mixture was cooled and 25 ml of water was added by drops at 40° or less. The yellow solid which formed was filtered off and washed with cold methanol and then with water; yield, 3.1 g (92%). After recrystallization from pyridine, the yellow crystals of XII melted at 166–168° dec (inserted at 162°) and gave the analysis shown below; $\lambda_{max}^{CH_3OH}$ 425 nm (ϵ 16,000). The infrared spectra of both samples of XII, prepared in the presence and absence of $CuCl_2 \cdot 2H_2O$, were identical. *Anal.* Calcd for $C_{18}H_{20}N_6O$: C, 64.3; H, 5.99; N, 25.0. Found: C, 64.3; H, 6.1; N, 24.7.

Reaction of XII with Cupric Chloride.—To a solution of 1.9 g of XII in 50 ml of ethanolamine was added a solution of 0.8 g of $CuCl_2 \cdot 2H_2O$ in 10 ml of ethanolamine plus 1 ml of water. After 15 min, 15 ml of water was added by drops. The rods which separated were filtered off and washed with methanol and then with water to give 1.06 g (90%) of XIII; mp 197–200°.

Formation of XIV.—A solution of 11.6 g of Ic in 120 ml of ethylenediamine was heated for 22 hr at 80–85°, after which 60 ml of water was added by drops at room temperature. The solid which formed was filtered off and recrystallized from methanol to give 4.3 g (40%) of XIV, mp 130–132°; $\lambda_{max}^{CH_3OH}$ 467 nm (ϵ 13,700). The thin layer chromatogram (Silica Gel G, 4:1 ethyl acetate–isopropyl alcohol) showed a single orange spot. *Anal.* Calcd for $C_{15}H_{18}N_4O$: C, 66.7; H, 6.71; N, 20.7. Found: C, 66.7; H, 7.0; N, 20.4.

When the fluoro compound Ia was allowed to react under similar conditions (26 hr at 75°), XIV was obtained in 79% yield.

Reaction of XIV with Cupric Chloride.—To a solution of 0.54 g (0.002 mol) of XIV in 8 ml of pyridine at room temperature was added by drops a solution of 0.55 g (0.0022 mol) of $CuSO_4 \cdot 5H_2O$ in 3 ml of water plus 3 ml of pyridine. After 3 ml more of water was added, the crystals of II were filtered off; yield, 0.44 g (66%). This product was identical with II prepared from Ib in one step as described above.

Reaction of Ic with Ethanolamine and Cupric Chloride.—To a slurry of 2.9 g of the azo compound Ic in 60 ml of ethanolamine was added at room temperature a solution of 2.0 g of $CuCl_2 \cdot 2H_2O$ in a mixture of 4 ml of water and 10 ml of ethanolamine. The mixture soon became homogeneous and blue-red. The mixture was stirred at room temperature overnight, after which the red crystals of crude XV were filtered off; yield, 3.4 g. The analytical sample was obtained by twice recrystallizing the crude sample from acetone (Soxhlet).[21]

Reaction of Ic with Ethylenediamine and Nickel Chloride.—To a solution of 2.9 g of the azo compound Ic in 25 ml of ethylenediamine at 75° was added a warm solution (75°) of 2.5 g of $NiCl_2 \cdot 6H_2O$ in 5 ml of water and 10 ml of ethylenediamine. After 1 hr 12 ml of water was added and the temperature was raised to 85–95° for several hours. The needles of XVI were filtered off at room temperature; yield, 2.2 g (67%). The analytical sample was twice recrystallized from acetone (Soxhlet).[21] The infrared spectrum (Nujol) shows a doublet of weak to medium intensity at 3230 and 3110 cm^{-1}.

Reaction of Ic with Ammonia and Cupric Chloride.—A mixture of 5.8 g of Ic, 5 g of $CuCl_2 \cdot 2H_2O$, and 10 ml of concentrated ammonium hydroxide in 80 ml of formamide plus 6 ml of water was heated in an autoclave for 22 hr at 170°. A portion of the solid obtained from this reaction mixture was washed with methanol and then treated with hot isopropyl alcohol. The filtrate was concentrated on a hot plate, after which there was isolated in the cold 0.18 g of XVII (mp 129–132°), identified by comparison with the infrared spectrum and melting point (131–132°) of an authentic sample of XVII.

Formation of 1-Phenylazo-2-naphthylamine (XX) from XVIIIc and XVIIId.—To a solution of 3.3 g of XVIIIc in 25 ml of ethylenediamine was added a solution of 3.0 g of $CuCl_2 \cdot 2H_2O$ in 7 ml of water and 5 ml of ethylenediamine. The resulting solution was heated at 85–90° for about 24 hr, after which 25 ml of water was added by drops at room temperature. The semisolid which separated from solution was filtered off, washed with water, and then dissolved in benzene. This dried (Na_2SO_4) benzene solution was then chromatographed on a column of silicic acid which contained 10% water by weight. The orange fraction which was eluted with benzene was collected, and the benzene was removed under vacuum to give 1.5 g (60%) of crude XX, mp 87–92°.

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[21] The recrystallization was effected by extracting the solid with the indicated solvent in a Soxhlet apparatus; the crystals which formed in the receiver were then collected.

Recrystallization from cyclohexane afforded 0.93 g of orange needles, mp 99–100°; (lit.[22] mp 102–104°); $\lambda_{\max}^{CH_3OH}$ 443 nm (ϵ 14,000). The same product was obtained from XVIIId.

When the cupric chloride was omitted from the above reaction with XVIIId, a 62% yield of XX was isolated. An authentic sample of XX was prepared by coupling phenyldiazonium chloride to 2-naphthylamine. The two samples had the same R_f value on thin layer chromatography (Silica Gel G, 2:1 benzene–cyclohexane) and had very similar visible and infrared spectra.

1-(*o*-Bromophenyl)-3,5-diphenylformazan (XXI).—To a mixture of 12.9 g (0.075 mol) of *o*-bromoaniline and 22 ml of concentrated hydrochloric acid in 75 ml of water at 5° was added by drops a solution of 5.2 g of sodium nitrite in 15 ml of water. The excess nitrous acid was then destroyed by adding a small amount of sulfamic acid. The coupler solution was made by adding a solution of 15 g (0.076 mol) of benzaldehyde phenylhydrazone in 150 ml of pyridine to a solution of 15 g of sodium hydroxide in 375 ml of methanol. The cold diazonium solution was then added by drops to the coupler solution at 5–8°. Stirring was continued at 3–5° for 45 min, after which the crystals of XXI which had formed were filtered off and washed in turn with methanol and water; yield 13.8 g; mp 133–138°. After a recrystallization from isopropyl alcohol the solid melted at 155–156°; yield 8 g (28%); $\lambda_{\max}^{DMF}$ 486 nm (ϵ 14,600). *Anal.* Calcd for $C_{19}H_{15}BrN_4$: C, 60.2; H, 3.99; N, 14.8; Br, 21.1. Found: C, 60.2; H, 4.0; N, 14.7; Br, 20.5.

Reaction of XXI with Ethylenediamine and Cupric Chloride.—To the red solution of 2.5 g (0.0066 mol) of XXI at 60° was added a solution of 1.2 g (0.007 mol) of $CuCl_2 \cdot 2H_2O$ in 3 ml of water and 10 ml of ethylenediamine. The mixture was deep blue after 10 min at 60° and was then cooled to room temperature and stirred overnight at room temperature. The blue diamond-shaped plates of XXIIa which had formed were filtered off and washed with methanol; yield, 1.2 g (42%); mp 220–222° dec; $\lambda_{\max}^{DMF}$ 620 nm (ϵ 17,400), 500 (4500). When a similar reaction was carried out entirely at room temperature over a 22-hr period, the yield of complex XXIIa was 62%. *Anal.* Calcd for $C_{21}H_{20}N_6Cu \cdot 0.5C_2H_8N_2$: C, 58.7; H, 5.37; N, 21.8; Cu, 14.1. Found: C, 58.6; H, 5.3; N, 21.6; Cu, 13.7.

To a solution of 0.2 g of XXIIa in 30 ml of pyridine was added 15 ml of water by drops. The crystals of XXIIb which separated were collected and washed with water; yield, 0.09 g; mp 200–204 dec; $\lambda_{\max}^{DMF}$ 620 nm (ϵ 21,300), 500 (5600). *Anal.* Calcd for $C_{21}H_{20}N_6Cu \cdot C_5H_5N \cdot 0.5H_2O$: C, 61.5; H, 5.16; N, 19.3. Found: C, 61.5; H, 5.2; N, 19.6.

Coupling of Methyl Anthranilate to *p*-Cresol.—To a solution of 15.1 g of methyl anthranilate in 200 ml of water plus 20 ml of concentrated hydrochloric acid at 0–5° was added slowly 20 ml of 5 *N* sodium nitrite. After 15 min the excess nitrous acid was destroyed by adding sulfamic acid. This diazonium solution was then added slowly at 0–5° to a mixture of 16 g of *p*-cresol, 5.6 g of sodium hydroxide, and 200 ml of water.

The product turned crystalline near the end of the addition of the diazonium solution. The pH was maintained at 10–11 by adding 30% sodium hydroxide until the test for diazo was negative. The yield of crude XXIII was 23.6 g (87%); after recrystallization from methanol, the yield was 19.9 g (73%); mp 63–64°. The infrared spectrum shows a strong band at 1727 cm^{-1} (C=O stretch). *Anal.* Calcd for $C_{15}H_{14}N_2O_3$: C, 66.6; H, 5.22; N, 10.4. Found: C, 66.7; H, 5.3; N, 10.4.

Reaction of XXIII with Ethylenediamine and Cupric Chloride.—A solution of 5.1 g of $CuCl_2 \cdot 2H_2O$ in 10 ml of water was added slowly to a solution of 5.4 g of XXIII in 40 ml of ethylenediamine. The mixture was then heated overnight at 70–80°, after which 60 ml of water was added by drops at room temperature. The resulting solid was filtered off, washed with a 2:1 water–ethylenediamine mixture, followed by water; yield, 6.1 g. A 2-g portion of this solid was extracted with 125 ml of hot methanol and the resulting solution was chromatographed on a silicic acid (5% water content) column, using methanol as the eluent. The main orange fraction was collected and concentrated to dryness to give 0.88 g of XXIV. The product gave a single spot on thin layer chromatography and was recrystallized (Soxhlet)[21] from methanol before analysis; yield, 0.59 g. *Anal.* Calcd for $C_{16}H_{16}N_4O_2Cu$: C, 53.4; H, 4.5; N, 15.6. Found: C, 53.4; H, 4.6; N, 15.4.

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[22] T. A. Lawson, *Ber.*, **18**, 798 (1885).

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gem-Dibasic Ligands with Phosphorus, Sulfur, and Nitrogen Sites, and Some Borane Derivatives[1]

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Three *gem*-dibasic ligands, dimethylphosphinomethyldimethylamine [$(CH_3)_2PCH_2N(CH_3)_2$] (pcn), dimethylphosphinomethyl methyl sulfide [$(CH_3)_2PCH_2SCH_3$] (pcs), and dimethylaminomethyl methyl sulfide [$(CH_3)_2NCH_2SCH_3$] (ncs) were prepared using chloromethyldimethylamine or chloromethyl methyl sulfide as starting materials. All three are colorless liquids of low vapor pressure (5–10 mm at room temperature), pcn and pcs being very inflammable in air. Monoborane adducts, H_3Bpcn, H_3Bpcs, and H_3Bncs, form readily with diborane. The only stable diadduct was H_3BpcnBH_3. A new borane cation type was demonstrated in the preparation of CH_3pcnBH_3^+.

The preparation and characterization of some 1,3-dihetero skeletons were conducted as a part of a synthetic program in small ring chemistry. Of special interest in this program were compounds with two different heteroatom base sites that could be used to incorporate functional chemistry into complexes without the complication of chelate formation or polymerization.

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