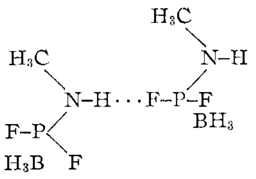
argue against significant vapor phase dissociation. In $[CH_3NH]F_2PBH_3$ intermolecular hydrogen bonding of the form would seem to be a reasonable cause of some liquid phase association and would indeed account for the fact that the entropy of vaporization of the compound $H_3CHNF_2PBH_3$ is about 1.4 cal./(mole deg.) above that for the compound $(H_3C)_2NF_2PBH_3$, in which hydrogen bonding is not expected.



Acknowledgment.—This work was supported in part by the National Science Foundation under the terms of Grant NSF-G10372 and in part under Contract AF33(616)-5874 with the U. S. Air Force, the sponsoring agency being the Aeronautical Research Laboratory of Wright Air Development Center Air Research and Development Command. Such support is gratefully acknowledged.

CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY,
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Tridentate Chelate Compounds. VI.[1] Copper(II) Complexes Derived from Pyridine-2-aldehyde-2′-pyridylhydrazone

BY JOHN F. GELDARD[2] AND FRANCIS LIONS

Received August 17, 1964

Some copper(II) coordination complexes of the tridentate chelating agent pyridine-2-aldehyde-2′-pyridylhydrazone have been prepared in which the configuration of donor atoms around the copper atom is square-planar or trigonal-bipyramidal. Reactions involving substitution of ligands coordinated at the fourth site in the square-planar complexes are reported. Some conversions of square-planar to trigonal-bipyramidal copper(II) complexes are also described. The trigonal-bipyramidal structure has been assigned to these complexes after consideration of their electrical conductivity data, infrared spectra, and elemental analyses.

Introduction

Previous work[3,4] has shown that coordination compounds can be prepared from pyridine-2-aldehyde-2′-pyridylhydrazone (1,3-di(2-pyridyl)1,2-diaza-2-propene; PAPHY; I) or heterocyclic hydrazones of similar type and copper(II) salts in which the coordinated copper atoms apparently exist in octahedral or square-planar arrangements. In this paper we report the chemistry of some of the square-planar complexes containing one PAPHY residue per copper atom. The stability of this type of PAPHY–copper(II) complex[5] has enabled us to study the substitution reactions of ligands bonded to the fourth coordination position. We also report the preparation of some complexes in which the copper atom is apparently surrounded by and bonded to five donor atoms in a trigonal-bipyramidal arrangement.

Experimental

Conductivities.—Electrical conductivities were measured with a Philips Philoscope and platinum-coated electrodes of the dip type. Unless otherwise indicated, the values quoted are given in ohm.$^{-1}$ cm.^{2} for about 10^{-3} M solutions in purified nitrobenzene at 25°.

Magnetic moments were measured on a Gouy balance at room temperature.

Preparation of the Copper(II) Complexes.[6] **Chloro(PAPHY)copper(II) Perchlorate (IIIa).**—An ethanolic solution of I (0.6 g.) and an aqueous solution of copper(II) chloride-2-water (0.5 g. in 5 ml.) were mixed and heated on a water bath. Aqueous sodium perchlorate solution was added, and, after cooling, green prisms of IIIa separated. The product was recrystallized from aqueous ethanol.

Chloro(PAPY)copper(II) (IVa).—IIIa or IIa was treated in aqueous ethanol with aqueous sodium bicarbonate solution until effervescence stopped. The solution was diluted with water and the product collected and recrystallized from benzene–petroleum ether in brown microcrystals.

Dibromo(PAPHY)copper(II) (IIb).—I (0.5 g.) and copper(II) bromide (0.55 g.) were heated together in ethanolic solution for 5 min. The mixture was cooled and the product collected.

Ammine(PAPY)copper(II) Perchlorate (Va).—Tetraamminecopper(II) sulfate–1-water (0.6 g.) in water and an ethanolic solution of I (0.5 g.) were mixed and heated for 5 min. After cooling and adding aqueous sodium perchlorate solution, the dark brown product was collected and crystallized from acetone–petroleum ether, yield 0.5 g. Vb was prepared similarly from tetraamminecopper(II) sulfate–1-water (0.6 g.) and 1-(3-methyl-2-pyrazinyl)3-(2-pyridyl)1,2-diaza-2-propene[4] (0.5 g.).

Thiocyanato(PAPHY)copper(II) Perchlorate–1-water (IIIb).—Va was treated with one molecular proportion of perchloric acid

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[1] For the previous paper in this series see B. Chiswell, J. F. Geldard, F. Lions, and A. T. Phillip, *Inorg. Chem.*, **3**, 1272 (1964).

[2] Petroleum Research Fund Fellow of the University of Sydney.

[3] F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **80**, 3858 (1958).

[4] J. F. Geldard and F. Lions, *ibid.*, **84**, 2262 (1962); *Inorg. Chem.*, **2**, 270 (1963).

[5] R. W. Green, P. Hallman, and F. Lions, *ibid.*, **3**, 376 (1964).

[6] The full names of these complexes and their physical properties and elemental analyses are given in Table I. PAPY is deprotonated PAPHY.

TABLE I

COPPER(II) COMPLEXES OF PAPHY[a]

Compound no.	Formula	M.p., °C.	Magnetic moment, B.M.	Conductivity, ohm.$^{-1}$ cm.^{2} at 25° Nitrobenzene	Calcd., %					Found, %				
					C	H	N	X	M	C	H	N	X	M
IIb	$[CuC_{11}H_{10}N_4\cdot Br_2]$	232–235	1.8	3.1	31.3	2.4	13.3	37.9	15.1	31.2	3.0	12.3	39.2	15.7
IIc	$[CuC_{11}H_{10}N_4\cdot I_2]$	174–175	1.6	11.5	25.6	2.0	10.8	...	12.3	25.9	2.3	10.8	...	12.0
IId	$[CuC_{11}H_{10}N_4\cdot (SCN)_2]$	184–185	1.8	3.0	41.3	2.7	...	...	16.8	40.9	2.8	...	...	16.7
IIIa	$[CuC_{11}H_{10}N_4\cdot Cl]ClO_4$	...	1.8	26.1[b]	33.3	2.5	...	17.9	16.0	33.1	2.7	...	18.6	16.0
IIIb	$[CuC_{11}H_{10}N_4\cdot SCN]ClO_4\cdot H_2O$	...	...	...	33.0	2.8	16.0	8.1	14.5	33.0	2.9	16.0	8.8	14.6
IVa	$[CuC_{11}H_9N_4\cdot Cl]$	208–209	2.3	0.7	44.6	3.1	18.9	...	21.6	44.3	3.3	18.8	...	21.4
IVb	$[CuC_{11}H_9N_4\cdot Br]$	200	...	6.0	38.8	2.7	...	...	18.7	38.2	2.9	...	...	17.8
IVc	$[CuC_{11}H_9N_4\cdot I]\cdot H_2O$	240	...	6.3	32.6	2.7	...	...	...	32.7	2.7	...	...	...
IVd	$[CuC_{11}H_9N_4\cdot SCN]\cdot {}^1/_2H_2O$	162–165	...	6.6	44.0	3.1	21.4	9.8	19.4	43.7	3.1	21.0	9.7	19.5
IVe	$[CuC_{11}H_9N_4\cdot OH]$	157–160	...	8.1	47.7	3.6	...	...	22.9	47.7	3.9	...	...	20.1
Va	$[CuC_{11}H_9N_4\cdot NH_3]ClO_4$	275–280	1.7	...[c]	35.0	3.2	...	9.4	16.8	34.7	3.9	...	10.1	17.2
Vc	$[CuC_{11}H_9N_4\cdot C_{10}H_9N_3]ClO_4$	200–202	...	28.6	47.5	3.4	18.5	6.7	12.0	47.6	3.7	17.4	6.7	12.6
VIa	$[CuC_{11}H_9N_4\cdot C_5H_7O_2]$	158–160	...	...	54.3	4.5	15.6	...	17.7	53.9	4.9	15.9	...	17.7
VIb	$[CuC_{11}H_9N_4\cdot C_{10}H_9O_2]$	169–171	...	...	59.8	4.3	13.3	...	15.1	60.4	4.6	12.5	...	14.8
VIc	$[CuC_{11}H_9N_4\cdot C_9H_8O_2N]$	140–141	...	...	56.8	4.1	...	...	15.0	56.4	4.3	...	...	14.4
VId	$[CuC_{15}H_{11}N_4\cdot C_5H_7O_2]$	176–178	...	...	58.6	4.4	...	...	15.5	58.9	4.7	...	...	15.4
Vb	$[CuC_{11}H_{10}N_5\cdot NH_3]ClO_4$	...	1.8	20.0	32.2	3.7	...	8.6	15.5	32.6	4.2	...	8.7	15.6

[a] Names of compounds: IIb, dibromo[1,3-di(2-pyridyl)1,2-diaza-2-propene]copper(II); IIc, diiodo[1,3-di(2-pyridyl)1,2-diaza-2-propene]copper(II); IId, dithiocyanato[1,3-di(2-pyridyl)1,2-diaza-2-propene]copper(II); IIIa, chloro[1,3-di(2-pyridyl)1,2-diaza-2-propene]copper(II) perchlorate; IIIb, thiocyanato[1,3-di(2-pyridyl)1,2-diaza-2-propene]copper(II) perchlorate–1-water; IVa, chloro-[1,3-di(2-pyridyl)1,2-diaza-2-propenato]copper(II); IVb, bromo[1,3-di(2-pyridyl)1,2-diaza-2-propenato]copper(II); IVc, iodo[1,3-di(2-pyridyl)1,2-diaza-2-propenato]copper(II)–1-water; IVd, thiocyanato[1,3-di(2-pyridyl)1,2-diaza-2-propenato]copper(II)–$^1/_2$-water; IVe, hydroxy[1,3-di(2-pyridyl)1,2-diaza-2-propenato]copper(II); Va, ammine[1,3-di(2-pyridyl)1,2-diaza-2-propenato]copper(II) perchlorate; Vc, 2,2′-dipyridylamine[1,3-di(2-pyridyl)1,2-diaza-2-propenato]copper(II) perchlorate; VIa, acetylacetonato[1,3-di(2-pyridyl)1,2-diaza-2-propenato]copper(II); VIb, benzoylacetonato[1,3-di(2-pyridyl)1,2-diaza-2-propenato]copper(II); VIc, nicotinylacetonato[1,3-di(2-pyridyl)1,2-diaza-2-propenato]copper(II); VId, acetylacetonato[1-(2-pyridyl)3-(1-isoquinolyl)1,2-diaza-2-propenato]copper(II); Vb, ammine[1-(3-methyl-2-pyrazinyl)3-(2-pyridyl)1,2-diaza-2-propenato]copper(II) perchlorate. [b] Λ_{1000} = 227.4 ohm.$^{-1}$ cm.^{2} at 25° in water. [c] Λ_{1000} = 119.3 ohm.$^{-1}$ cm.^{2} at 25° in water.

in aqueous solution and aqueous sodium thiocyanate was added until precipitation of green IIIb ceased. The product crystallized from aqueous ethanol.

Complexes of Type II.—Va in water was treated with one molecular proportion of perchloric acid and an aqueous solution of the appropriate sodium salt in excess. The product precipitated. IIc crystallized from aqueous ethanol; IId was not recrystallized.

Complexes of Type IV.—The appropriate sodium salt in water solution was added to solutions of Va in aqueous acetone. The products precipitated. IVb was not recrystallized; IVc and IVd crystallized from aqueous dimethylformamide. IVe was obtained when Va in water was treated with 2-(2-pyridyl)imidazole. The product precipitated and was collected and crystallized from benzene–petroleum ether.

(PAPY)2,2′-dipyridylaminecopper(II) Perchlorate (Vc).—Va (0.5 g.) and 2,2′-dipyridylamine (0.2 g.) were heated together in ethanol for 10 min. After cooling, the product precipitated and was collected and recrystallized from acetone–petroleum ether.

Complexes of Type VI.—The bis(β-diketone)copper(II) complex and the ligand (I or 1-(2-pyridyl)3-(1-isoquinolyl)1,2-diaza-2-propene[4]) were heated together in benzene solution in stoichiometric amounts. The solutions were concentrated and the product precipitated by the addition of sufficient petroleum ether. All VI crystallized from benzene–petroleum ether as dichroic red-green prisms.

Discussion

Preparation of Complexes.—In aqueous solutions, copper(II) ion reacts with one molecular proportion of I to form complexes in which the metal is either four- or five-coordinate. Copper(II) salts will react with two molecular proportions of I in concentrated ethanolic solutions if no other ligands are present.[4] In these 2:1 complexes, the copper ion is apparently six-coordinate. Copper(II) chloride and bromide both react with one molecular proportion of I to form dihalo(PAPHY) complexes (IIa and IIb, respectively) in which the copper is apparently five-coordinate. Dissolution of IIa in hot aqueous ethanolic solutions of sodium perchlorate causes the formation of chloro(PAPHY)-copper(II) perchlorate (IIIa). Treatment of either IIa or IIIa with sodium bicarbonate solution leads to evolution of carbon dioxide and formation of the deprotonated chloro(PAPY)copper(II) (IVa). The use of sodium hydroxide solution instead of sodium bicarbonate leads to a partial replacement of the halogen coordinated to copper by hydroxyl and a mixture of complexes is obtained. Interaction of IIa, IIIa, or IVa with other ligands (*e.g.*, amines) which might reasonably be expected to replace the coordinated halogen leads similarly to mixtures.

The admixture of aqueous tetraamminecopper(II) sulfate and ethanolic PAPHY solutions causes the formation of ammine(PAPY)copper(II) ion. The complex was isolated as the perchlorate salt (Va). The ammonia liberated by the reaction deprotonates the coordinated ligand I. In the same way, Vb was obtained from tetraamminecopper(II) sulfate and 1-(3-methyl-2-pyrazinyl)3-(2-pyridyl)1,2-diaza-2-propene.[4] Va and Vb were dark brown uni-univalent electrolytes.

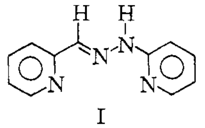
The ammine group of Va is easily replaced by other ligands. The replacement reactions can be divided into two types—those where the ligand is protonated

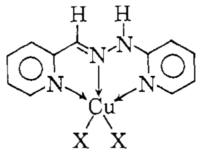
TABLE II

THE INFRARED SPECTRA OF THE COPPER(II) COMPLEXES VIa, VIb, VIc, AND VId[a]

VIa	VIb	VIc	VId	Assignment[b]
1605 s	1608 sh	1608 sh	1614 sh	Pyridine 1. This band and the C=O, C=C overlap extensively
	1600 sh			
1599 s	1596 s	1594 s	1603 s	C=O and C=C
1576 m	1560 m	1586 sh	1584 w	Pyridine 2
1520 s	1518 s			Unassigned
1499 s	1500 sh		1502 s	Unassigned
1469 w	1470 m	1463 m	1454 w	Pyridine 3
1446 s	1445 s	1444 s	1443 m	Pyridine 4
1421 s	1417 s	1416 s	1416 s	Unassigned
1405 s	1402 sh		1400 sh	Unassigned
1361 m	1358 m			Combination band or $\delta_s(CH_3)$
1295 s	1293 s	1295 s	1290 s	Unassigned
1284 w	1282 w		1282 w	Possibly $\nu(C\text{–}C) + \nu(C\text{–}CH_3)$, ν_2
1266 w	1266 w		1270 w	Combination band or the ν_2 band
	1262 w		1260 w	
1249 s	1247 s	1248 m	1248 w	Unassigned
			1228 m	Unassigned
			1221 m	Unassigned
1216 w	1213 w	1216 s	1213 m	Unassigned
			1184 s	Unassigned
1137 s	1134 s	1135 m	1135 s	Ring vibrations, C–H deformations
1008 s	1005 s		1004 s	Possibly a symmetric ring vibration With C–H deformations

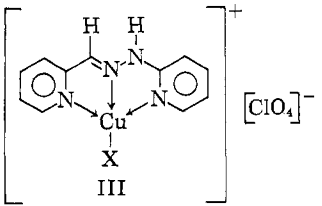
[a] Spectra were measured on chloroform solution. The range quoted is 1700 to 1000 cm.$^{-1}$. [b] Assignments are based on the analysis of C. H. Kline and J. Turkevich, *J. Chem. Phys.*, **12,** 300 (1944) (pyridine vibrations), and K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, N. Y., 1963, pp. 216–220. Compound VId exhibits a metal–oxygen stretching vibration at 456 cm.$^{-1}$. The other complexes were not examined for this band. s, strong; m, medium; w, weak; sh, shoulder.


I


II

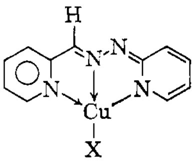
IIa, X = Cl IIc, X = I

IIb, X = Br IId, X = SCN


III

IIIa, X = Cl

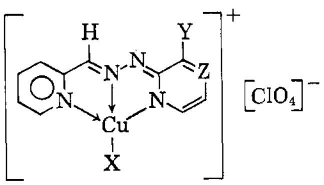
IIIb, X = SCN

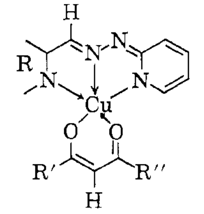

IV

IVa, X = Cl IVd, X = SCN

IVb, X = Br IVe, X = OH

IVc, X = I


V


VI

Va, $X = NH_3$; $Y = H$; $Z = CH$

Vb, $X = NH_3$; $Y = CH_3$; $Z = N$

Vc, $X = C_{10}H_9N_3$; $Y = H$; $Z = CH$

VIa, $R = 2\text{-}C_5H_4N$; $R' = R'' = CH_3$

VIb, $R = 2\text{-}C_5H_4N$; $R' = CH_3$; $R'' = C_6H_5$

VIc, $R = 2\text{-}C_5H_4N$; $R' = CH_3$; $R'' = 3\text{-}C_5H_4N$

VId, $R = 2\text{-}C_9H_6N$; $R' = R'' = CH_3$

by addition of one molecular proportion of perchloric acid prior to replacement of the ammine group and those where it is not. Examples of the first type of reaction are the replacements of the ammine group with excess iodide or thiocyanate ion to give the five-coordinate complexes IIc and IId. Thiocyanato(PAPHY)copper(II) perchlorate (IIIb) can be isolated as an intermediate in the formation of IId. IIc is steel gray in color, IId brown, and IIIb green. Examples of the second type of reaction are the replacements of the ammine group with bromide, iodide, and thiocyanate ions to give the four-coordinate complexes IVb, IVc, and IVd, respectively.

Ammine(PAPY)copper(II) perchlorate reacts with 2,2′-dipyridylamine in aqueous acetone solution to form the brown uni-univalent electrolyte Vc. Here, the dipyridylamine is probably bonded to copper by the σ-donor electrons of one of the aromatic nitrogen atoms. Similar treatment of Va with 2-(2-pyridyl)imidazole leads to the formation of the hydroxy complex IVe instead of the expected 2-(2-pyridyl)imidazolato(PAPY)copper(II) or 2-(2-pyridyl)imidazole(PAPY)copper(II) perchlorate.

When I and bis(acetylacetonato)copper(II) are heated together in boiling benzene solution, the intensely brown acetylacetonato(PAPY)copper(II) (VIa) is formed. This neutral complex is very soluble in benzene, chloroform, alcohols, acetone, etc., but is only very slightly soluble in water. Similarly, bis(benzoylacetonato)copper(II) and bis(nicotinylacetonato)copper(II) react with I to give VIb and VIc, respectively. Both are similar to VIa in their properties. The generality of this reaction is further illustrated by treating bis(acetylacetonato)copper(II) in boiling benzene solution with 1-(2-pyridyl)3-(1-isoquinolyl)1,2-diaza-2-propene.[4] The resulting compound VId was distinguished by its intense reddish purple color in solution.

Structure of the Complexes.—Without complete X-ray structural analysis, it is not possible to assign unequivocal structures to the copper complexes described in this paper. The usual stereochemistry of copper(II) complexes is a square-planar arrangement of four donor atoms at normal bond distances around the metal ion with one or two more elongated bonds normal to the plane. The X-ray structural analysis of a five-coordinate zinc(II) complex has been reported[7]; it shows a tridentate ligand (terpyridine) and two halogen atoms all bonded to zinc in a trigonal-bipyramidal arrangement. The corresponding copper(II) complex was shown to be isomorphous with the zinc compound and therefore likely to have the same structure. More recently, the X-ray structural analysis of bis(bipyridine)copper(II) iodide was reported,[8] showing the copper to have a trigonal-bipyramidal configuration.

The conductivity data of the complexes III, IV, and V indicate a square-planar structure for these. In the complexes of type II, the tridentate PAPHY and two anionic ligands (halide or thiocyanate) appear to be bonded to the copper atom; the complexes are nonelectrolytes in nonpolar solvents. By analogy,[7,8] these are assigned a trigonal-bipyramidal structure.

The complexes of type VI are also assigned a trigonal-bipyramidal stereochemistry. The highly crystalline nature of some of these shows that they are not chance equimolecular mixtures of bis(PAPY)copper(II)[4] and the bis(β-diketone)copper(II) complexes. The infrared spectra (Table II) of these compounds show the presence of a deprotonated molecule of I and a β-diketone residue both bonded to the copper atom. The C=O and C=C stretching vibrations are assigned to bands at somewhat higher frequencies than those in bisacetylacetonatocopper(II). A tetragonal pyramidal structure is also possible for these complexes.

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(7) D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, 594 (1956).

(8) G. A. Barclay and C. H. L. Kennard, *Nature*, **192**, 425 (1961).

Notes

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3,5,6-Tri(2-pyridyl)1,2,4-triazine, a New Tridentate Chelating Agent, and Some of Its Metal Coordination Complexes

BY JOHN F. GELDARD[1]

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Multidentate chelating agents in which the donor atoms are sp^2-hybridized nitrogen atoms are usually of the strong ligand field type. Ligands such as terpyridine [2,6-di(2-pyridyl)pyridine], bipyridine, or 1,10-phenanthroline all cause spin pairing in the derived octahedral iron(II) complexes but not in the cobalt(II) and manganese(II) complexes. The donor nitrogen atom may be located in pyridine or other heterocyclic rings or in azomethine linkages such as hydrazones[2] or Schiff bases.[3]

Tridentate chelating agents of suitable low symmetry having such donor nitrogen atoms are interesting because they can make possible the study of some stereochemical problems associated with octahedral coordination.

In this paper the preparation of a new tridentate chelating agent, 3,5,6-tri(2-pyridyl)1,2,4-triazine (I), is described. The spectra, stereochemistry, and physical properties of its coordination complexes with some transition metal salts are discussed.

Experimental

Conductivities.—All electrical conductivities were measured with a Philips Philoscope and platinum coated electrodes of the dip-type. Values are given in ohm.$^{-1}$ cm.^{2} at 25° for about 10^{-3} *M* solutions in purified nitrobenzene and water.

Magnetic Moments.—Magnetic moments were measured on a Gouy balance at room temperature.

Electronic Absorption Spectra.—Spectra were measured in 95% ethanol using a Perkin-Elmer Model 4000A spectrophotometer.

1,2,5-Tri(2-pyridyl)5-amino-3,4-diazapent-2,4-dien-1-one (II).—A cold solution of 2-picolinicamidrazone[4a] (10 g.) in N-methyl-2-pyrrolidone (60 ml.) was added slowly with stirring to a solution of 2,2′-pyridil[4b] (16 g.) in N-methyl-2-pyrrolidone (30 ml.) at 100°. A white solid separated out toward the end of the addition. The mixture was cooled and the product collected. It crystallized from pyridine in cream-colored needles, m.p. 188–189°; the yield was 21 g.

Anal. Calcd. for $C_{18}H_{14}N_6O$: C, 65.4; H, 4.3. Found: C, 65.5; H, 4.6.

3,5,6-Tri(2-pyridyl)1,2,4-triazine (I).—II (15 g.) was heated in boiling N,N-dimethylformamide (25 ml.) until a clear yellow solution was obtained. The solution was cooled and diluted with water. The yellow precipitate was collected and recrystallized from aqueous N,N-dimethylformamide, m.p. 186–187°. The yield was 13 g.

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(1) W. A. Noyes Laboratory, University of Illinois, Urbana, Ill.

(2) F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **80**, 3858 (1958).

(3) F. Lions and K. V. Martin, *ibid.*, **79**, 2733 (1957).

(4) (a) W. J. van der Burg, *Rec. trav. chim.*, **74**, 257 (1955); (b) commercial product.