Preparation of Some New Aminimides

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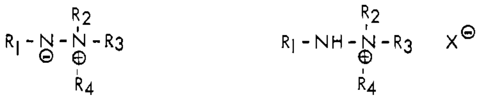
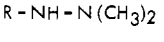
The preparation and physical properties of two new classes of aminimides, $R\text{-}\overset{\ominus}{N}\text{-}\overset{\oplus}{N}(CH_3)_3$, are described. The group R is capable of resonance stabilization of the anion, being either $R'\text{-}X\text{-}\overset{O}{\overset{\|}{C}}\text{-}$ where X is a heteroatom, or $\begin{matrix}A\\B\end{matrix}\!\!>\!C=\overset{H}{C}\text{-}$ where A and/or B are cyano or carboethoxy groups, giving rise to stable, crystalline aminimides.

STABLE aminimides or nitrogen imines (*4*), as represented by the generic formula 1, have been obtained from the quaternary hydrazides II by treatment with aqueous base where R_1 represents an aliphatic (*7, 10*) or aromatic acyl (*3*) group or an aromatic sulphonyl group (*9*), and R_2, R_3, and R_4 are aliphatic groups. Further examples of aminimides V, *a-i* have now been prepared.

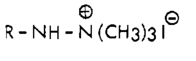


$R_1\text{-}\overset{\ominus}{N}\text{-}\overset{\oplus}{N}(R_2)(R_4)\text{-}R_3$ I $\qquad R_1\text{-}NH\text{-}\overset{\oplus}{N}(R_2)(R_4)\text{-}R_3\ X^{\ominus}$ II



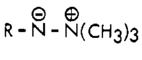
$R\text{-}NH\text{-}N(CH_3)_2$

III a-i



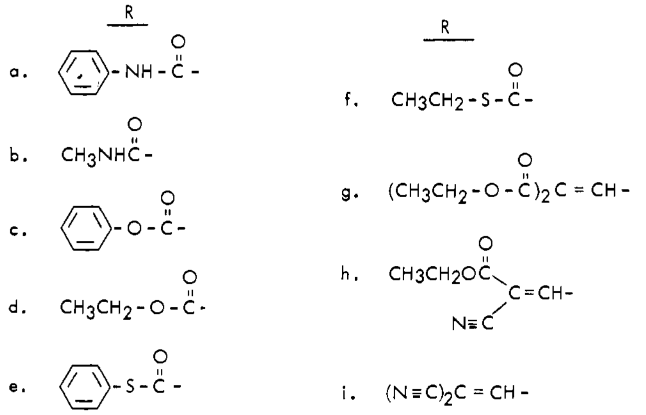
$R\text{-}NH\text{-}\overset{\oplus}{N}(CH_3)_3\overset{\ominus}{I}$

IVa-h

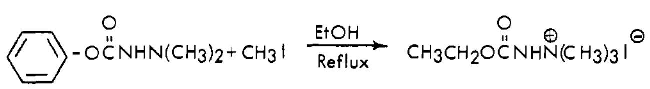


$R\text{-}\overset{\ominus}{N}\text{-}\overset{\oplus}{N}(CH_3)_3$

Va-i



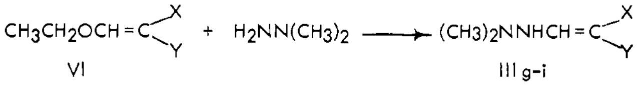
The precursors III, *a-f*, were readily prepared from the corresponding isocyanate, chloroformate, or chlorothiolformate plus 1,1-dimethylhydrazine. Methylation of III, *a*, *b*, and *d*, with methyl iodide in ethanol afforded the quaternary hydrazinium iodides IV, *a*, *b*, and *d*, in yields of approximately 60%. Attempted methylation of III, *c*, in ethanol gave primarily IV, *d*, the ethoxy derivative, by an exchange reaction of ethoxy for phenoxy, but methylation proceeded smoothly in neat methyl iodide to give IV, *c*. The ethylthio derivative III, *f*, was also methylated in neat methyl iodide to avoid any possible interchange for ethoxy, giving IV, *f*, in 50% yield. Treatment of III, *e*, the phenylthio derivative, with neat methyl iodide at room temperature did not give methylation, and treatment at elevated temperatures gave extensive decomposition. Methylation was successful using dimethylformamide as solvent, giving IV, *e*, in 60% yield. The quaternary iodides IV, *a-f*, were readily converted to the aminimides by treatment with 10% aqueous sodium hydroxide and extraction with chloroform. Physical data for the compounds in this series are given in Table I.



The aminimides were generally obtained in high yield as crystalline solids of high purity. The phenyl substituted derivatives V, *a*, *c*, and *e*, could be further purified by crystallization. The aliphatic derivatives were hygroscopic and could not be crystallized readily, but V, *b*, and *d*, were easily sublimed, whereas V, *f*, decomposed on attempted sublimation. The aminimides V, *a-d*, are indefinitely stable at ambient temperatures, but decompose above their melting point with liberation of trimethylamine, a mode of decomposition previously noted with trimethylaminebenzimide (*1, 8*) and , apparently, a useful diagnostic test for compounds of this type. The thio analogs V, *e*, and *f*, were less stable, slowly liberating trimethylamine when stored as solids. As a result, analytical results for these materials were always somewhat low in nitrogen and high in sulfur (Table I). Decomposition of V, *e*, and *f*, in solution at ambient temperature was rapid. Observation of the PMR spectra of these compounds in deuteriochloroform over a period of hours showed a gradual decrease in intensity of the resonance owing to the trimethylammonio protons and the appearance of a peak at δ 2.25 p.p.m. assumed to be due to dissolved trimethylamine. The *N*-methyls of dimethylaminoethanol appear at δ = 2.25 p.p.m. (*6*). Other products from the decomposition of the aminimides have not been investigated.

The carbonyl stretching band in the infrared spectra of V, *a-f*, occurs at lower frequencies than in the corresponding salts IV, *a-f*, indicative of resonance involvement of the carbonyl group with the electrons on the imide nitrogen. The PMR spectra of the aminimides show a sharp singlet for the trimethyl ammonio protons in the region of δ 3.4 p.p.m., whereas the corresponding salts have a signal at approximately δ 3.7 p.p.m. The shift to higher field in the aminimides is indicative of a less positive character of the quaternary nitrogen in the ylide owing to interaction with the electrons of the imide nitrogen. The ylides could be readily converted to the original salts by treatment with hydriodic acid, indicating that no rearrangement occurred during their formation under basic conditions.

The vinyl substituted hydrazines III, *g-i*, were prepared from 1,1-dimethylhydrazine and the corresponding ethoxymethylene derivative, VI. Methylation of the hydrazines with methyl iodide alone or in ethanol was unsuccessful, an apparent mixture of the desired quaternary iodide and the hydroiodide of the starting material being obtained.



$CH_3CH_2OCH=C\begin{matrix}X\\Y\end{matrix} + H_2NN(CH_3)_2 \longrightarrow (CH_3)_2NNHCH=C\begin{matrix}X\\Y\end{matrix}$

VI $\qquad$ III g-i

X,Y = -C≡N and/or -COOEt

Table I. Aminimides V, *a-f*, and Their Precursors

Compound	Method of Preparation	Recrystallization Solvent	Yield, %	Melting Point, ° C.	Molecular Formula	Analytical Data: Calcd.			Found			PMR Data[a] *N*-Methyl δ, P.P.M.	Infrared Carbonyl Frequency, Cm.$^{-1}$
						%N	%S	%I	%N	%S	%I		
III, *a*	A[b]	Ethanol	64	105–7	$C_9H_{13}N_3O$	23.4			23.2			2.60	1680
b	A	Benzene	81	115–19	$C_4H_{11}N_3O$	35.9			35.6			2.55	1665
c	B	Benzene-hexane	58	75–7	$C_9H_{12}N_2O_2$	15.5			15.2			2.63	1725
d	[b]	Distilled	44	45–9 0.2 mm.	$C_5H_{12}N_2O_2$	21.2			20.9			2.58	1725
e	B	Ethyl acetate	50	123–5	$C_9H_{12}N_2OS$	14.2	16.3		14.2	16.4		2.55	1660
f	B	Hexane	78	54–7	$C_5H_{12}N_2OS$	18.9	21.6		18.8	21.2		2.60	1660
IV, *a*	C	Ethanol-water	63	161–3	$C_{10}H_{16}IN_3O$	13.1		39.6	12.7		39.4	3.75	1700
b	C	Ethanol-water	66	154–7	$C_5H_{14}IN_3O$	15.2		45.8	14.9		45.7	3.70	1700
c	D	Ethanol-ether	72	117–21	$C_{10}H_{15}IN_2O_2$	8.7		39.4	8.5		39.1	3.83	1755
d	C	Ethanol-ether	60	141–2	$C_6H_{15}IN_2O_2$	10.2		46.4	10.3		46.1	3.72	1750
e	E	Ethanol	61	99–100	$C_{10}H_{15}IN_2OS$	8.3		37.6	8.1		37.0	3.77	1710
f	D	Ethanol	50	106–7	$C_6H_{15}IN_2OS$	9.7	11.0	43.8	9.5	11.2	44.4	3.77	1665
V, *a*	F	Chloroform-hexane	84	205 dec.	$C_{10}H_{15}N_3O$	21.8			22.3			3.50	1625
b	F	Sublimed-80°/0.1 mm.	82	134–8	$C_5H_{13}N_3O$	32.0			31.4			3.45	1600
c	F	Carbon tet.-chloroform	77	100–2	$C_{10}H_{14}N_2O_2$	14.4			14.4			3.39	1670
d	F	Sublimed-80°/0.1 mm.	84	95–8	$C_6H_{14}N_2O_2$	19.2			19.4			3.47	1620
e	F	Dichloromethane-hexane	60	83–5	$C_{10}H_{14}N_2OS$	13.3	15.2		13.9	14.8		3.33	1640
f	F	None	77	82–4	$C_6H_{14}N_2OS$	17.3	19.7		17.7	19.1		3.47	1595

[a] The spectra of III, *a-f*, and V, *a-f*, were determined in deuteriochloroform with tetramethylsilane as internal standard; IV, *a-f*, were run in deuterium oxide with sodium-3-trimethylsilylpropanesulfonate as internal standard. [b] Reference (5). [c] Reference (2).

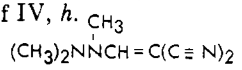
Table II. Vinylogous Aminimides V, *g-i*, and Their Precursors

Compound	Recrystallization Solvent	Yield, %	Melting Point, ° C.	Molecular Formula	Analytical Data: Calcd.		Found		NMR Data[a], δ P.P.M.	
					%N	%I	%N	%I	*N*-Methyls	Vinyl proton
III, *g*	Distilled	87	117°/0.2 mm.	$C_{10}H_{17}N_2O_4$	12.2		12.0			
h	Ethyl acetate-hexane	74	80–3	$C_8H_{13}N_3O_2$	22.9		22.2			
i	Ethyl acetate	73	131–4	$C_6H_8N_4$	41.1		40.5			
IV, *g*	2-Propanol		117–19	$C_{11}H_{21}IN_2O_4$	7.5	34.1	7.4	34.25	3.45, 3.69	8.35, 8.58
h	Methanol-ether		95–100	$C_9H_{16}IN_3O_2$	12.9	39.0	12.6	38.5	3.65	8.70
V, *g*	Chloroform-hexane	65	123–5 dec.	$C_{11}H_{20}N_2O_4$	11.45		11.3		3.25	8.70
h	Ethanol	81	193–5 dec.	$C_9H_{15}N_3O_2$	21.3		21.4		3.22	8.42
i	Water	81	222–4 dec.	$C_7H_{10}N_4$	37.3		37.3		3.22	8.20

[a] The spectra of IV, *g*, and *h*, and V, *g*, were determined in deuterium oxide with sodium-3-trimethylsilylpropanesulfonate as internal standard; V, *h*, and *i*, were run in dimethylsulfoxide d_6 with tetramethylsilane as internal standard.

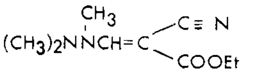
The vinylogous aminimides V, *g-i*, were obtained directly by methylation of the hydrazine with methyl iodide in ethanol containing sodium ethoxide. They are crystalline solids indefinitely stable at ambient temperature but decompose when melted with liberation of trimethylamine. The dicarboethoxy substituted derivatives V, *g*, is unstable in solution, decomposing in a matter of hours to trimethylamine and unidentified products when refluxed in chloroform. As cyano groups are substituted for the carboethoxy groups the aminimides become more stable in solution and more saltlike in character, being higher melting and less soluble in nonpolar organic solvents. The dicyano substituted derivative V, *i*, is soluble only in hot water or in highly polar solvents much as dimethyl sulfoxide and dimethylformamide. Physical data for the compounds in this series are given in Table II.

Methylation could conceivably occur on the nonterminal nitrogen of IV, *g-i*, to give a tetra-substituted hydrazine instead of the ylide derivatives, but the liberation of trimethylamine upon decomposition and the fact that the aminimides V, *g-i*, show only a single methyl peak in their PMR spectra at δ 3.25 p.p.m. rule out this possibility. From the methylation of the dicyano compound IV, *i*, in sodium ethoxide solution, there was isolated a small amount of an isomeric methylation product which showed two methyl peaks in the PMR spectrum at δ 2.66 and 3.20 p.p.m. in the ratio of 2 to 1. This product must be 1,1-dimethyl-2-β,β-dicyanovinyl-2-methyl hydrazine, VII, the result of methylation on the nonterminal nitrogen. A similar product, VIII, was obtained in small yield from methylation of IV, *h*.



$(CH_3)_2N\overset{CH_3}{\overset{|}{N}}CH{=}C(C{\equiv}N)_2$

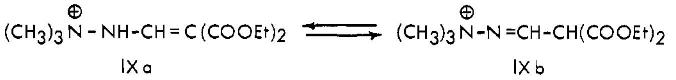
VII



VIII

The hydroiodides IV, *g*, and *h*, were prepared from the corresponding aminimides by crystallization from an alcohol-ether mixture containing hydriodic acid. Similar treatment of V, *i*, the dicyano-substituted aminimide, failed to give a salt, the aminimide crystallizing from the acidic solution. In fact, the aminimide V, *i*, could be crystallized from aqueous hydrochloric or perchloric acid with no indication of salt formation. Thus, V, *i*, is an extremely weak base owing to very effective delocalization of the negative charge by the dicyanovinyl group.

The *N*-methyl groups of the aminimide salts IV, *g*, and *h*, resonate at lower frequency in the PMR spectra than those in the aminimides, as was the case with the other group of aminimides. The PMR spectrum of IV, *g*, in D_2O at room temperature contains two *N*-methyl peaks at δ 3.45 and 3.69 p.p.m. in a ratio of approximately 2 to 1, and two vinyl proton peaks at δ 8.58 and 8.35 p.p.m. in the same ratio. The methylene group of the ethyl ester group is composed of overlapping quartets. The same spectrum is obtained upon adding hydriodic acid to a PMR sample of the aminimide in D_2O. This phenomenon must be due to protonation of the imide on nitrogen or carbon, giving the two equilibrating tautomeric species IX, *a*, and *b*, in which the protons indicated above would have different chemical shifts. Heating the solution causes the *N*-methyl and vinyl proton resonances to coalesce to single peaks and the methylene resonance to sharpen to a quartet as expected, owing to faster proton exchange and shorter lifetimes of the tautomers. The PMR spectrum of IV, *h*, shows only one *N*-methyl peak at δ 3.65 p.p.m. and one vinyl proton peak at δ 8.70 p.p.m. The aminimide in this case is a weaker base than IV, *g*, owing to the increased delocalization of the negative charge by the cyano group, and therefore equilibration of the tautomers is rapid enough at room temperature to give the average spectrum.



$$(CH_3)_3\overset{\oplus}{N}-NH-CH=C(COOEt)_2 \rightleftharpoons (CH_3)_3\overset{\oplus}{N}-N=CH-CH(COOEt)_2$$

IX a

IX b

EXPERIMENTAL

Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected. The infrared spectra were determined as Nujol mulls on a Perkin-Elmer Infracord spectrophotometer. The PMR spectra were determined on a Varian A-60 spectrometer using the solvents and reference compounds indicated. Analytical samples were dried in vacuo (0.05 mm. of Hg) over phosphorus pentoxide at room temperature for 18 hours. Starting materials whose preparation is not described are commercially available.

Hydrazide Derivatives III, *a-f*. METHOD A–III, *a* AND *b*. To 0.5 mole of 1,1-dimethylhydrazine in 100 ml. of benzene was added slowly 0.5 mole of phenyl isocyanate (III, *a*) or methyl isocyanate (III, *b*). The mixture was stirred for 18 hours, and the solid product removed by filtration and recrystallized (Table I).

METHOD B–III, *c*, *e*, AND *f*. To 1.0 mole of 1,1-dimethylhydrazine in 400 ml. of benzene was added slowly 0.5 mole of phenylchloroformate (III, *c*), ethylchlorothiolformate (III, *f*), or phenylchlorothiolformate (III, *e*), the temperature of the mixture being kept below 40° C. by using a cooling bath if necessary. The mixture was stirred for 18 hours and 200 ml. of water was added. The organic phase was separated, washed with water, dried over $MgSO_4$, concentrated to dryness, and the products were recrystallized (Table I).

Quaternary Hydrazides IV, *a-f*. METHOD C–IV, *a*, *b*, AND, *d*. To 0.2 mole of the hydrazides III, *a*, *b*, or *d*, in 100 ml. of ethanol was added slowly 0.4 mole of methyl iodide. The solution was refluxed for 4 hours and cooled, and the precipitate was collected and recrystallized (Table I).

METHOD D–IV, *c* AND *f*. To 0.1 mole of the hydrazides III, *c*, or *f*, was added 0.5 mole of methyl iodide. The hydrazide dissolved slowly. After stirring overnight, the precipitated iodide was collected by filtration, washed with ether, and recrystallized (Table I).

METHOD E–IV, *e*. To a solution of III, *e* (3 grams) in a minimum amount of dimethylformamide (about 6 ml.) was added 4 grams of methyl iodide. The solution was left at room temperature for 3 days and then diluted with 5 volumes of ether. The product was isolated by filtration, washed with ether, and recrystallized from ethanol.

Aminimides V, *a-f*–Method F. The quaternary hydrazide IV, *a-f*, 10 grams was placed in a separatory funnel with 50 ml. of ice cold chloroform. To this slurry was added 40 ml. of ice-cold 10% sodium hydroxide solution (for IV, *f*, the ethylthio derivative, only 15 ml. of base was added). The mixture was shaken up well, the chloroform layer separated, and the aqueous phase extracted with three 50-ml. portions of cold chloroform. The aqueous phase for V, *b*, and *d*, was then continuously extracted with chloroform for 18 hours in order to obtain a good recovery. The chloroform extracts were dried over $MgSO_4$ and concentrated to dryness (for V, *e*, and *f*, the handling time in solution was kept to a minimum to prevent decomposition). The resulting solids, when well dried, had infrared spectra essentially identical to the analytical samples purified (Table I). Thus, the aminimides are obtained in high purity by this method. The imides were reconverted to the quaternary iodides by dissolving in a minimum amount of methanol, adding the calculated amount of 50% hydriodic acid, and adding ether to cause crystallization.

Vinyl Hydrazines III, *g-i*. To 0.5 mole of the appropriate ethoxymethylene precursor VI (available from Kay-Fries Chemicals) in 250 ml. of methanol was added slowly 0.55 mole of 1,1-dimethylhydrazine in 50 ml. of methanol. The reaction was slightly exothermic, but did not reach reflux. The reaction was stirred for 2 hours after addition, then the solvent was removed in vacuo, and the product was purified (Table II).

Aminimides V, *g-i*. To a solution of sodium ethoxide prepared from 0.11 mole of sodium and 200 ml. of ethanol was added 0.1 mole of the hydrazine III, *g-i*, in one portion. As soon as the material dissolved, 0.15 mole of methyl iodide was slowly added, giving a slightly exothermic reaction. For V, *g*, the dicarboethoxy derivative, the reaction mixture was stirred at room temperature for 3 hours and then concentrated in vacuo to remove ethanol. The resulting gummy solid was treated with 100 ml. of water, all the material dissolving. The aqueous solution was extracted with ten 50-ml. portions of chloroform. The combined extracts were dried and concentrated to give the imide in high purity as indicated by its infrared spectrum. The sample was crystallized by dissolving in a minimum amount of chloroform at room temperature and diluting with hexane.

For V, *h*, and *i*, the reaction mixture was refluxed for 2 hours and cooled to crystallize the product, which was collected by filtration and washed with 50 ml. of cold water and 50 ml. of cold ethanol, and the products were crystallized (Table II).

Isolation of 1,1-Dimethyl-2-β,β-dicyanovinyl-2-methylhydrazine (VII). The ethanol mother liquor from the preparation of *V*, *i*, was concentrated in vacuo, and the residue was treated with 50 ml. of 0.1*N* sodium hydroxide. This solution was extracted with two 50-ml. portions of chloroform, and the extracts were dried and concentrated to give a semisolid. Crystallization from benzene gave approximately 0.5 gram of the title compound, m.p. 136–139° C. Anal. Calcd. for $C_7H_{10}N_4$: N, 37.3. Found: N, 36.70.

The PMR spectrum in deuteriochloroform with tetramethylsilane as internal standard showed single peaks at δ 2.66 p.p.m. $[(\underline{CH_3})_2N-]$, 3.20 p.p.m. $(\underline{CH_3}-\overset{N}{N}-C=)$, and 7.12 p.p.m. $(\underline{H}-\overset{N}{C}=)$ in the ratio of 6:3:1 in accord with the proposed structure, and the infrared spectrum was also consistent.

Isolation of 1,1-Dimethyl-2-β-carboethoxy-β-cyanovinyl-2-methylhydrazine (VIII). The ethanol mother liquor from the preparation of V, *h*, was worked up as in the previous experiment. From the chloroform extract was obtained a semisolid which was crystallized from benzene-hexane to give approximately 200 mg. of the title compound, m.p. 77–79° C. Anal. Calcd. for $C_9H_{15}N_3O_2$: N, 21.3. Found: N, 20.8.

The PMR spectrum in deuteriochloroform with tetramethylsilane as internal standard showed single peaks at δ 2.60 p.p.m. $[(\underline{CH_3})_2N-]$, 3.15 p.p.m. $(\underline{CH_3}-\overset{N}{N}-C=)$, and 7.55 p.p.m. $(\underline{H}-\overset{N}{C}=)$ and a triplet at 1.3 p.p.m. $(\underline{CH_3}-CH_2-O)$ and a quartet at 4.22 p.p.m. $(CH_3\underline{CH_2}-O)$ in the ratio of 6:2:1:3:2 in accord with the proposed structure, and the infrared spectrum was also consistent.

Quaternary Hydrazines IV, *g* and *h*. The aminimide V, *g*, 5 grams in 20 ml. of 2-propanol was treated with 3 ml. of 50% hydriodic acid. Ether was added to the cloud point, and the solution was cooled to give IV, *g*, which could be recrystallized from 2-propanol. A similar procedure using methanol in place of 2-propanol gave the iodide IV, *h*. All attempts to prepare an acid salt of V, *i*, using hydriodic, hydrochloric, or perchloric acid in alcohols or water resulted in recovery of the crystalline imide.

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LITERATURE CITED

(1) Gibson, M.S., Murray, A.W., *J. Chem. Soc.* **1965**, p. 880.
(2) Hinman, R.L., *J. Am. Chem. Soc.* **78**, 1645 (1956).
(3) Hinman, R.L., Flores, M., *J. Org. Chem.* **24**, 660 (1959).
(4) Johnson, A.W., "Ylide Chemistry," p. 266, Academic Press, New York and London, 1966.
(5) Renouf, E., *Chem. Ber.* **13**, 2169 (1880).
(6) "Varian NMR Spectra Catalog," Varian Associates, 1962.
(7) Wawzonek, S., Chua, J., Yeakey, E.L., McKillip, W., *J. Org. Chem.* **28**, 2376 (1963).
(8) Wawzonek, S., Gueldner, R.C., *Ibid.*, **30**, 3031 (1965).
(9) Wawzonek, S., Meyer, D., *J. Am. Chem. Soc.* **76**, 2918 (1954).
(10) Wawzonek, S., Yeakey, E., *Ibid.*, **82**, 5718 (1960).

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Metal Complexes of Cyanoformamidines, Oxamidines, and Oxalimidates

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The preparation and physical characteristics of copper and nickel complexes of a number of cyanoformamidines, oxamidines, and oxalimidates are described. Cyanoformimidates failed to produce complexes under the conditions used.

In THE investigation of the reactions of cyanogen with organic compounds (*5–11*), it was often found useful or necessary to convert the product into a derivative which could be stored for long periods of time without deterioration. Recently, references have been made to the utilization of oxamidines and oxalimidates in syntheses or analytical processes (*1–4*). Since many of these compounds are unstable, a number of metal complexes are reported which have been accumulated over the years, whose stability and solubility might make them of interest in the research areas indicated.

The molecular formulas, physical appearance, and melting points for all complexes are given in Tables I, II, and III. No attempt was made to determine the actual structure of any complex. However, details characteristic of the preparation of each class are given in the Experimental section. The procedure given leads to the complex described and does not preclude the possibility that a change in method might yield a complex of different metal to substrate ratio

Table I. Metal Complexes of Cyanoformamidines

R	*x*	Appearance	M.P., ° C.
		$(R_2NC_2N_2)_2Cu \cdot xH_2O$	
Ethyl	2	Light red powder	203–4 dec.
n-Propyl	2	Light red powder	207–8 dec.
n-Butyl	2	Red needles	184–5 dec.
n-Amyl	2	Red needles	185–6 dec.
Allyl	2	Red crystals	201–3 dec.
		$(R_2NC_2N_2)Ni \cdot xH_2O$	
Ethyl	1	Bright yellow powder	314–7 dec.
n-Butyl	1	Bright yellow powder	245–8 dec.
n-Butyl	2	Orange yellow powder	243–5 dec.[a]
n-Amyl	1	Bright yellow powder	227–30 dec.
n-Amyl	2	Orange yellow powder	185–8 dec.

[a] Color change, orange to yellow at 170° to 80° C.