United States Patent [19]

Lamm et al.

[11] E **Re. 29,640**

[45] Reissued **May 23, 1978**

[54] **CERTAIN SUBSTITUTED 2,6-DIAMINO-4-METHYL-NICOTINITRILES THE CORRESPONDING NICOTINAMIDES AND DERIVATIVES THEREOF**

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[73] Assignee: **BASF Aktiengesellschaft,** Ludwigshafen, Germany

[21] Appl. No.: **711,863**

[22] Filed: **Aug. 5, 1976**

Related U.S. Patent Documents

Reissue of:

[64] Patent No.: **3,853,895**
Issued: **Dec. 10, 1974**
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Filed: **Jan. 31, 1973**

U.S. Applications:

[63] Continuation-in-part of Ser. No. 209,431, Dec. 17, 1971, abandoned.

[30] **Foreign Application Priority Data**

Dec. 19, 1970	Germany	2062717
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Oct. 21, 1972	Germany	2251702
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Dec. 1, 1972	Germany	2258823
Dec. 2, 1972	Germany	2259103
Dec. 6, 1972	Germany	2259684
Dec. 13, 1972	Germany	2260827
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Dec. 16, 1972	Japan	47-125836
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[51] **Int. Cl.**[2] **C07D 213/57**

[52] **U.S. Cl.** ..... **260/294.9**; 260/295.5 A; 260/295.5 B; 260/295.5 T; 260/156

[58] **Field of Search** ..... 260/294.9, 295.5 A, 260/295.5 B, 295.5 T

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,433,795	3/1969	Hyden et al.	260/295.5 T
3,664,996	5/1972	Berrie et al.	260/295.5 A

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Karrer, Organic Chemistry, 4th Englsh Edition, p. 928, Elsevier Pub. Co., (NY), 1950.

Chemical and Engineering News, p. 18, Apr. 3, 1972.

Primary Examiner—Alan L. Rotman

Attorney, Agent, or Firm—Keil, Thompson & Shurtleff

[57] **ABSTRACT**

2,3,6- and preferably also 4-substituted pyridine derivatives bearing the radical of ammonia or a primary amine in the 2- and 6-positions. The compounds are eminently suitable as coupling components for the production of azo dyes, the coupling taking place in the 5-position.

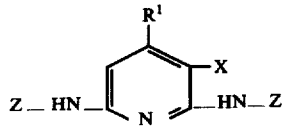
6 Claims, No Drawings

CERTAIN SUBSTITUTED 2,6-DIAMINO-4-METHYL-NICOTINITRILES THE CORRESPONDING NICOTINAMIDES AND DERIVATIVES THEREOF

Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

This application is a reissue application of U.S. Pat. No. 3,853,895 issued December 10, 1974, from U.S. Application Ser. No. 328,459, filed January 31, 1973, which in turn is a continuation-in-part of U.S. Application Ser. No. 209,431, filed December 17, 1971 (now abandoned).

This invention relates to compounds of the formula:

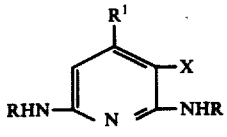


where

R^1 is hyrogen, alkyl of one to seven carbon atoms or phenyl, the radicals Z independently of one another mean hydrogen or an unsubstituted or substituted aliphatic, cycloaliphatic, araliphatic or aromatic radical and

X is cyano or carbamoyl.

More particularly, the invention relates to compounds of the formula (Ia):



(Ia)

in which

R^1 is hydrogen, alkyl of one to seven carbon atoms or phenyl,

X is carbamoyl or cyano and the radicals

R independently of one another are unsubstituted or substituted aliphatic, cycloaliphatic, araliphatic or aromatic radicals and one of the radicals R may be hydrogen and at least one of the radicals R contains an oxygen atom.

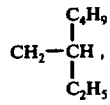
Examples of alkyl radicals R^1 are ethyl, n-propyl, isopropyl, butyl, pentyl, α-ethylpentyl and preferably methyl.

Examples of radicals Z or R are alkyl of one to eight carbon atoms which may be interrupted by oxyten atoms and which may bear hydroxy, alkoxy, cyano, cycloalkoxy, aralkoxy or aroxy as substituents, cycloalkyl and polycycloalkyl which may bear hydroxy, chloro, hydroxyalkyl, chloroalkyl or alkyl as substituents, aralkyl of seven to fifteen carbon atoms, phenyl which may bear chloro, hydroxy, alkoxy, alkyl, hydroxyalkoxy or hyroxyalkyl as substituents, or alkenyl, pyrrolidonylalkyl or carboxyalkyl.

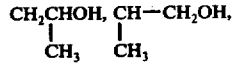
Examples of individual radicals Z or R are:

1. unsubstituted or substituted alkyl:

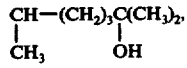
CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, i-C_4H_9, C_6H_{13},



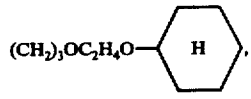
CH_2CH_2OH, $(CH_2)_3OH$,



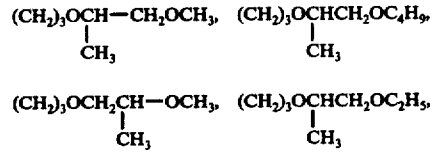
$(CH_2)_4OH$, $(CH_2)_6OH$,



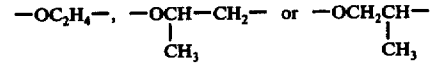
$(CH_2)_2O(CH_2)_2OH$, $(CH_2)_3O(CH_2)_4OH$, $(CH_2)_3OC_2H_4OH$, $(CH_2)_3OC_2H_4OCH_3$, $(CH_2)_3OC_2H_4OC_2H_5$, $(CH_2)_3OC_2H_4OCH(CH_3)_2$, $(CH_2)_3OC_2H_4OC_4H_9$, $(CH_2)_3OC_2H_4OCH_2C_6H_5$, $(CH_2)_3OC_2H_4OC_2H_4C_6H_5$,



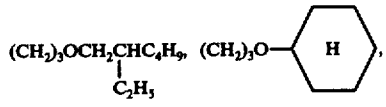
$(CH_2)_3OC_2H_4OC_6H_5$,



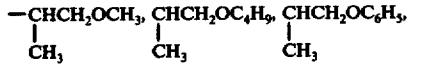
corresponding radicals in which the groupings

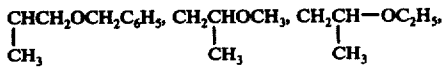


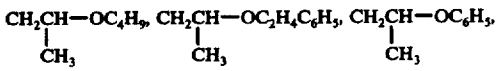
are present twice, three times or four times, $CH_2CH_2OCH_3$, $CH_2CH_2OC_2H_5$, $CH_2C_2OC_3H_7$, $CH_2CH_2OC_4H_9$, $CH_2CH_2OC_6H_5$, $(CH_2)_3OCH_3$, $(CH_2)_3OC_2H_5$, $(CH_2)_3OC_3H_7$, $(CH_2)_3OC_4H_9$,



$(CH_2)_3OCH_2C_6H_5$, $(CH_2)_3OC_2H_4C_6H_5$, $(CH_2)_3OC_6H_5$,







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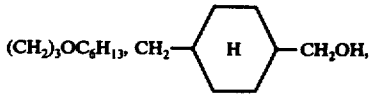
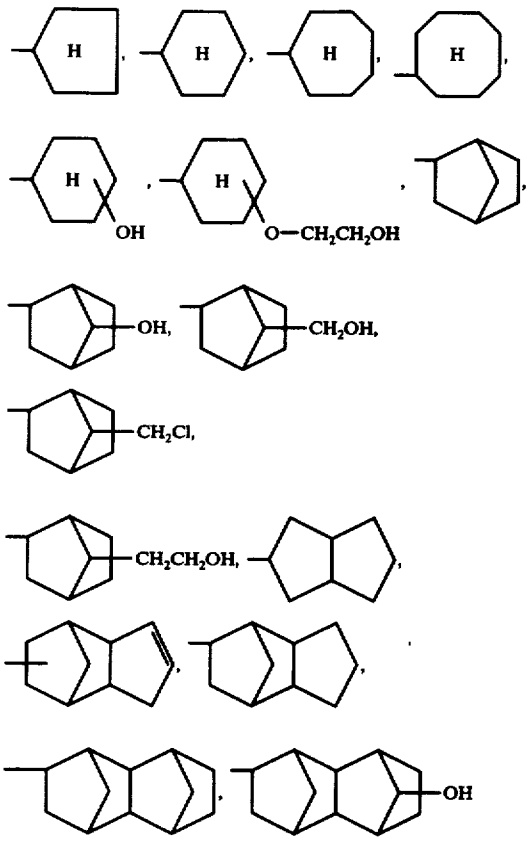
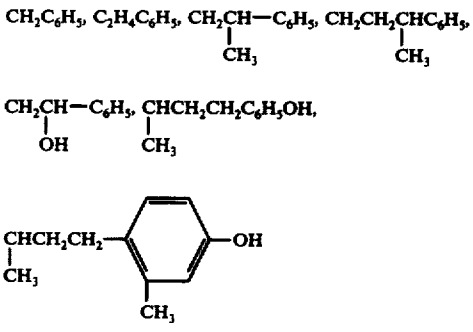


$(CH_2)_2CN$, $(CH_2)_5CN$, $(CH_2)_6CN$, $(CH_2)_7ON$ or $(CH_2)_3OC_8H_{17}$ and $C_6H_4CH_3$ instead of C_6H_5

2. unsubstituted or substituted cycloalkyl or polycycloalkyl:



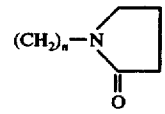
3. aralkyl:



and $C_6H_4CH_3$ instead of C_6H_5.

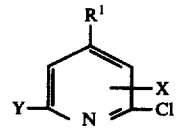
4. unsubstituted or substituted phenyl:
C_6H_5, $C_6H_4CH_3$, $C_6H_3(CH_3)_2$, $C_6H_4OCH_3$, $C_6H_4OC_2H_5$, C_6H_4OH, $C_6H_4OCH_2CH_2OH$ or C_6H_4Cl,

5. $CH_2CH=CH_2$, $(CH_2)_2COOH$, $(CH_2)_5COOH$ and



in which n is 2, 3, 4, or 6.

For the production of compounds of formula (I), compounds of formula (II):



in which

Y is chloro or a radical of the formula NHR, and

X, R and R^1 have the meanings given above may be reacted with an amine of the formula:

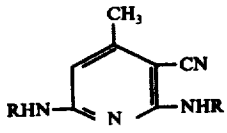
$$R—NH_2.$$

Reaction conditions which affect the exchange of the chlorine atom(s) include the temperature, the amine component, the molar ratio of the reactants and any diluent or solvent or acid-binding agent used. Amines of low boiling point may of course be reacted under superatmospheric pressure. The reaction with the amine is conveniently carried out at elevated temperature, a temperature of from about 0° to 110° C being adequate for the exchange of the first chlorine atom depending on the basicity of the amine, while temperatures in the range from about 60° to 180° C being advantageous for exchange of the second chlorine atom.

Amines of high basicity react more rapidly than those of low basicity; when exchanging the second chlorine atom it is advantageous to use an excess of amine (more than 10 percent), whereas the first chlorine atom reacts immediately with a molar amount of amine. Examples of suitable diluents or solvents which may be added are alcohols such as methanol, ethanol or isopropanol, glycols and glycol ethers such as methyl glycol, ethyl glycol or butyl glycol, hydrocarbons and halohydrocarbons such as benzene, toluene, ethylene chloride, chloroform, trichloroethylene or chlorobenzene, and also acetone, tetrahydrofuran, dimethylformamide, N-methylpyrrolidone or dimethylsulphoxide. The presence of water does not cause any disturbance.

The addition of acid-binding agents is advantageous because then the total amount of amine to be reacted is available for the exchange. Substances which do not themselves react with the chloropyridine derivatives are suitable as acid-binding agents; for example tertiary amines such as triethylamine, tributylamine, triethanolamine, ethyldiisopropylamine, caustic soda solution, sodium carbonate, magnesium oxide or calcium carbonate are suitable. In the case of inexpensive amines, an excess of the amine to be reacted may also serve as acid-binding agent.

Compounds of the formula (Ib);

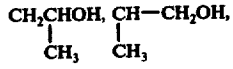


(Ib)

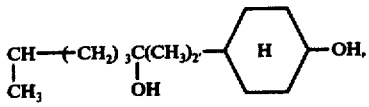
in which R has the meanings given above are of particular industrial significance.

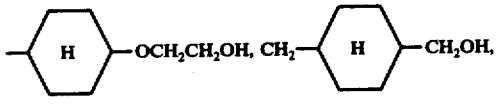
Examples of preferred radicals R containing oxygen are:

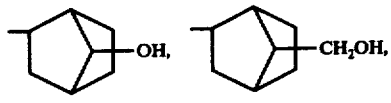
CH_2CH_2OH, $CH_2CH_2CH_2OH$,

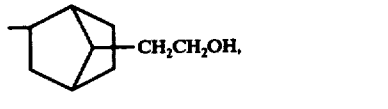


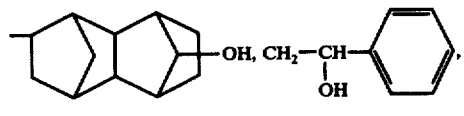
$(CH_2)_3O(CH_2)_2OH$, $(CH_2)_3O(CH_2)_4OH$, $(CH_2)_3O(CH_2)_6OH$, $(CH_2)_4OH$, $(CH_2)_6OH$, $(CH_2)_2O(CH_2)_2OH$,

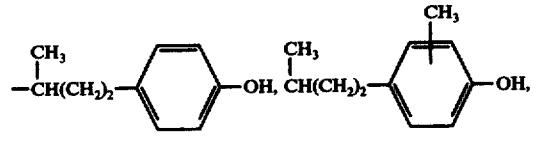


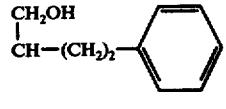




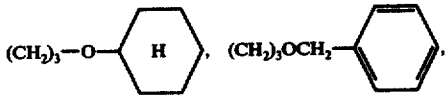


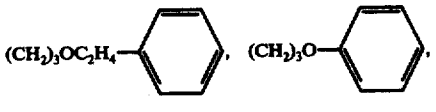






$CH_2CH_2OCH_3$, $CH_2CH_2OC_2H_5$, $CH_2CH_2OC_4H_9$, $(CH_2)_3OCH_3$, $(CH_2)_3OC_2H_5$, $(CH_2)_3OC_3H_7$, $(CH_2)_3OC_4H_9$, $(CH_2)_3OC_6H_{13}$, $(CH_2)_3OC_8H_{17}$,





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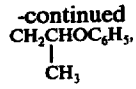
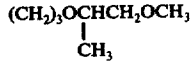


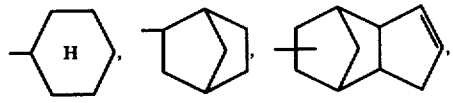
$(CH_2)_3OC_2H_4OCH_3$, $(CH_2)_3OC_2H_4OC_4H_9$,



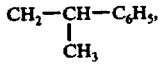
and $(CH_2)_3OC_2H_4OC_6H_5$.

Examples of preferred oxygen-free radicals which are preferably used in combination with an oxygen-containing radical R are besides H:

C_2H_5, C_3H_7, C_4H_9,



$CH_2C_6H_5$, $C_2H_4C_6H_5$, $C_3H_7C_6H_5$,



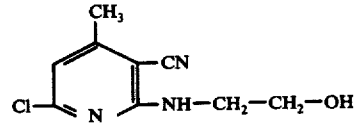
C_6H_5, $C_6H_4CH_3$, $C_6H_4OCH_3$.

The new coupling components are outstandingly suitable for the production of azo dyes by reaction with diazotized amines. The dyes which can be obtained in this way are distinguished by excellent fastness properties and by unusual brightness for azo dyes.

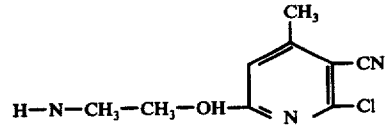
The following Examples illustrate the invention. Parts and percentages referred to are by weight unless otherwise stated.

EXAMPLE 1

187 parts of 2,6-dichloro-3-cyano-4-methylpyridine is suspended in 500 parts by volume of methanol. 80 parts of 2-hydroxyethylamine is then added at 40° to 45° C followed by 100 parts of triethylamine. The mixture is stirred for five to six hours at 45° to 50° C, about 250 parts by volume of methanol is distilled off and the residue is diluted with 1000 parts by volume of water. After acidification with 50 parts of concentrated hydrochloric acid, the whole is stirred for 1 hour, the deposited precipitate is filtered off, washed with water until neutral and dried. About 210 parts of a colorless powder of the formula:



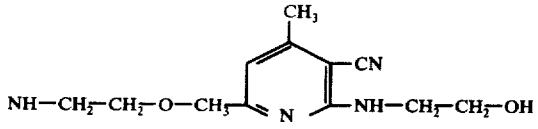
is obtained. The powder contains a minor amount of a product of the formula:



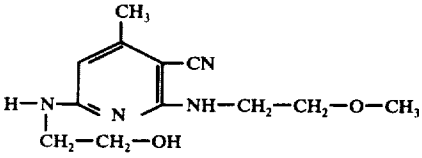
The mixture melts at 115° to 120° C.

125 parts of this powder is stirred with 300 parts by volume of methoxyethylamine for six hours under reflux.

Excess methoxyethylamine is then extensively distilled off so that the temperature may rise to 130° C and the whole is then diluted with 500 parts of water. The mixture is stirred for one hour at 0° to 10° C and the deposited precipitate is filtered off, washed with water and dried. The main product has the formula:



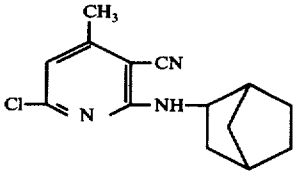
and there is a minor amount of a product having the formula:



The product is colorless and melts at 75° to 78° C.

EXAMPLE 2

A suspension of 50 parts by volume of methanol, 22 parts of norbornylamine, 37 parts of 2,6-dichloro-3-cyano-4-methylpyridine and 25 parts of triethylamine is stirred for six hours at 40° to 50° C. Then about 200 parts by volume of ice-water is added, the whole acidified to pH 1, and the precipitated product of the formula

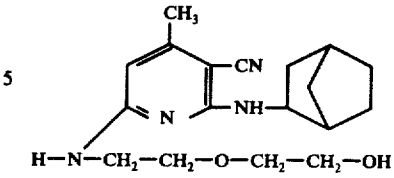


(which still contains a small proportion of 2-chloro-3-cyano-4-methyl-6-norbornylaminopyridine isomers) is filtered off, washed with water and dried. About 45 parts of a colorless powder is obtained which melts at 110° to 112° C.

45 parts of the moist powder is heated at 130° C to 140° C with 50 parts of the amine of the formula:

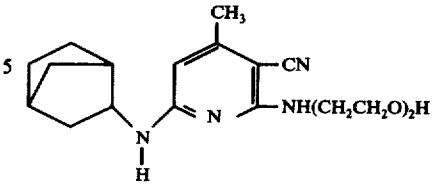
$$H_2N—CH_2—CH_2—O—CH_2—CH_2—OH$$

the water being allowed to evaporate. After stirring for 5 hours at 130° to 140° C the reaction is completed. The whole is allowed to cool and is acidified with 130 parts by volume of acetic acid. A solution of the coupling component mixture of the formulae:



(I)

and



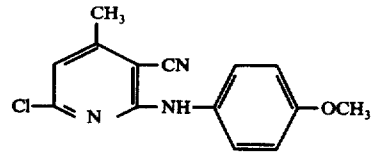
(II)

is obtained, the amount of the product of formula (II) being small.

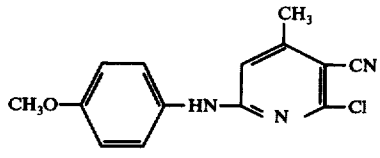
When the mixture thus obtained is coupled with p-nitroaniline a dye is obtained which dissolves in dimethylformamide to give an orange solution.

EXAMPLE 3

A mixture of 300 parts by volume of N-methylpyrrolidone, 150 parts of 2,6-dichloro-3-cyano-4-methylpyridine, 115 parts of p-anisidine and 90 parts of triethylamine is stirred for from six to 7 hours at 70° C. It is then poured while stirring onto 1500 parts of ice-water and acidified with hydrochloric acid to pH 1. About 220 parts of a colorless product of the formula:



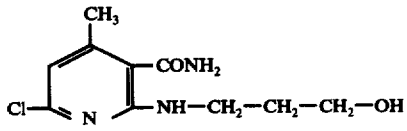
is obtained which is isolated by filtration, washing with water and drying. The powder contains a minor amount of a product of the formula:



The mixture melts at 147° to 150° C.

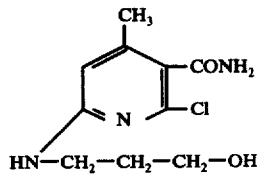
EXAMPLE 4

50 parts of 2,6-dichloro-3-carbamoyl-4-methylpyridine is stirred with 75 parts of propanolamine-1,3 for 10 hours at 90° C. The mixture is precipitated with water and acidified to pH <O. The insoluble residue is filtered off, washed with water and dried. The colourless powder melts at 210° C and probably has the formula (I):



(I)

The filtrate has caustic soda solution added to it until the pH is from 5 to 6. A crystalline precipitate is thrown down which probably has the formula (II)



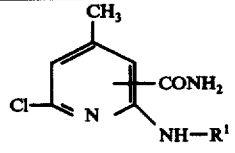
This is filtered off, washed with water and dried. The product (II) thus obtained also contains traces of the product of the formula (I) and melts at 150° to 160° C.

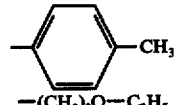
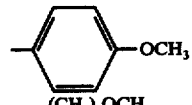
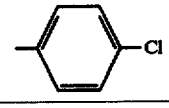
If the reaction mixture is precipitated at pH from 6 to 7, a mixture of the two isomers is obtained which has a melting point of about 143° C.

When 2,6-dichloro-3-carbamoyl-4-methylpyridine is treated analogously to the method described in Example 4, mixtures of substituted 2-aminopyridines and 6-aminopyridines are obtained, the amount of 2-amino-3-carbamoyl-4-methyl-6-chloropyridine derivatives being only slightly greater than that of the 6-aminopyridine isomers in question.

The physical properties given in Table 1 relate to mixtures.

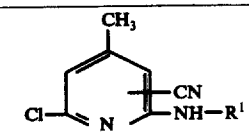
TABLE 1



Number	R^1	Melting point, ° C.
5		115–199
6	$-(CH_2)_3O-C_2H_5$	120
7	$-C_4H_9(n)$	121–122
8	$-C_6H_{13}(n)$	89–90
9	$-CH_2CH(OH)-CH_3$	140–145
10		180–190
11	$(CH_2)_3OCH_3$	105
12	$C_3H_7(n)$	124
13	CH_2CH_2OH	130
14	$(CH_2CH_2O)_2H$	110
15	CH_3	>150
16	C_2H_5	143
17		190

When 2,6-dichloro-3-cyano-4-methylpyridine is treated by a method analogous to those described in Examples 1 to 3, there are obtained (by exchange of one chlorine atom) mixtures of 2-amino-3-cyano-4-methyl-6-chloropyridine and 2-chloro-3-cyano-4-methyl-6-aminopyridine derivatives, the proportion of the 2-chloro-3-cyano-4-methyl-6-amino isomers being clearly less.

TABLE 2



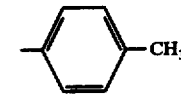
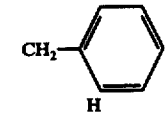
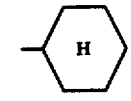
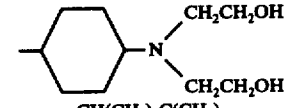
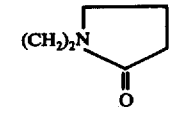
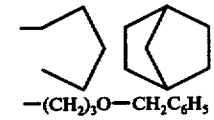
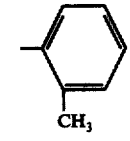
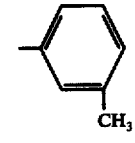
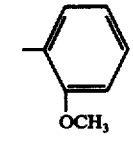
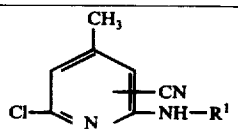
Number	R^1	Melting point, ° C.
18	$(CH_2)_5COONa$	85 - 91
19	$(CH_2)_3-CH_3$	40 - 47
20	$(CH_2CH_2O)_2H$	79 - 83
21	$(CH_2)_2OCH_3$	90 - 100
22	$C_4H_9(n)$	50 - 60
23	$C_3H_7(i)$	95 - 105
24	$(CH_2)_3OCH_3$	75 - 85 [1]
25	$CH_2CH(C_2H_5)-C_4H_9(n)$	
26	$(CH_2)_3OH$	110 - 114
27	$(CH_2)_2OH$	125
28		145 - 154
29		147 - 149
30	H	225 - 230
31		165 - 175
32		103 - 105
33	$CH(CH_2)_3C(CH_3)_2$ (CH3, OH)	Tar
34		103
35		90 - 92
36	$-(CH_2)_3O-CH_2C_6H_5$	[2]
37		105 - 110
38		170 - 185
39		147

TABLE 2-continued



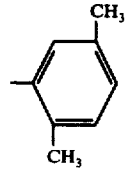
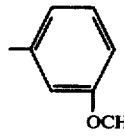
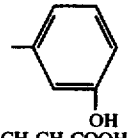
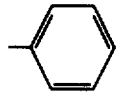
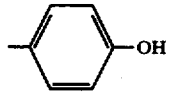
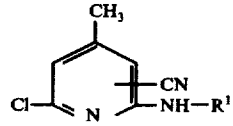
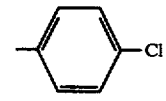
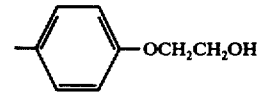
Number	R^1	Melting point, ° C.
40		120 - 128
41		170
42	$CH_2CH(C_2H_5)-C_4H_9(n)$	107 - 110
43	$CH_2CH_2-CH(CH_3)-C_6H_5$	[3]
44		185
45	CH_2CH_2COOH	170
46	$-C_{14}H_{29}$	62
47		130 - 140
48		160

TABLE 2-continued



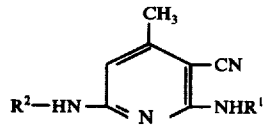
Number	R^1	Melting point, ° C.
49	$-CH_3$	140
50	$-CH_2-CH(CH_3)-OH$	80
51	$(CH_2)_3O-(CH_2)_2OH$	75 - 80
52	$(CH_2)_3O-C_3H_7(i)$	Oil
53	$CH_2CH_2-C_6H_5$	118 - 123
54	$(CH_2)_3O-C_2H_4O-C_6H_5$	Oil
55		172
56		Oil
57	$-CH_2CH(OH)-C_6H_5$	115

[1]Greasy product.
[2]Tar becoming solid on prolonged standing.
[3]Viscous oil.

When the products set out in Tables 1 and 2 are treated with aliphatic or aromatic amines at temperatures above 100° or 80° C respectively, the corresponding coupling products are obtained.

In the case of pyridine derivatives which contain a carbamoyl group the reaction has to be carried out however at the lowest possible temperature because otherwise hyrolysis and/or decarboxylation of the —$CONH_2$ group may take place.

TABLE 3



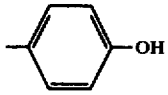
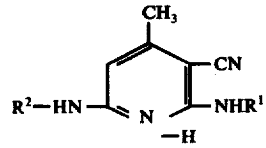
Number	R^1	R^2	Melting point, ° C.
58	CH_2CH_2OH	CH_3	125 - 130.
59	CH_2CH_2OH	$(CH_2)_3OH$	47 - 50.
60	CH_2CH_2OH	$(CH_2)_3OCH_3$	104 - 105.
61	CH_2CH_2OH	CH_2CH_2OH	156.
62	$(CH_2)_3OH$	CH_3	215 (hydrochloride).
63		$(CH_2)_3OH$	220 - 223.
64	$(CH_2)_3O(CH_2)_4OH$	H	Viscous oil.
65	$(CH_2)_3O(CH_2)_4OH$	$(CH_2)_3OH$	"
66	$(CH_2)_3O(CH_2)_4OH$	$(CH_2)_3OCH_3$	"
67	$(CH_2)_3O(CH_2)_4OH$	$(CH_2)_2OCH_3$	"
68	$(CH_2)_3O(CH_2)_6OH$	$(CH_2)_2OCH_3$	"
69	$(CH_2)_3O(CH_2)_6OH$	$(CH_2)_3OH$	"
70	$(CH_2)_3O(CH_2)_6OH$	$(CH_2)_2OH$	"
71	$(CH_2)_3O(CH_2)_6OH$	$(CH_2)_3OH$	"
72	$CH_2CH_2OCH_3$	$CH_2CH_2OCH_3$	75 - 76.
73	$CH_2CH_2OCH_3$	CH_2CH_2OH	108 - 111.
74	$CH_2CH_2OCH_3$	$C_6H_{13}(n)$	Oil which has green fluorescence.
75	$CH_2CH_2OCH_3$	—H	108.
76	$(CH_2)_3-O-CH_3$	—H	95 - 98.
77	$(CH_2)_3OH$	$(CH_2)_3OH$	84 - 87.

TABLE 3-continued



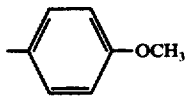
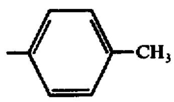
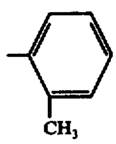
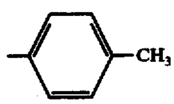
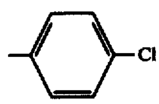
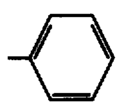
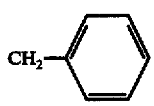
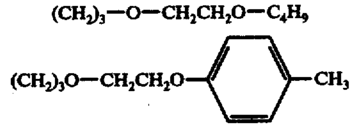
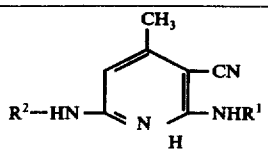
78		—H	215 - 220.
79	"	CH_2CH_2OH	137.
80	"	$—CH_2CH_2O—CH_2CH_2OH$	125 - 130.
81		$—(CH_2)_3OH$	170.
82	"	$(CH_2CH_2O)_2H$	175 - 180.
83		$(CH_2)_3OH$	169 - 170.
84		CH_2CH_2OH	155 - 158.
85	C_6H_5	$CH_2CH_2CH_2OH$	150 (hydrochloride).
86		CH_2CH_2OH	173.
87		CH_2CH_2OH	136 - 140.
88	"	$—CH_2CH_2OCH_3$	134 - 138.
89		$—CH_2CH_2OH$	90 - 95 esterified with acetic acid.
90	"	$CH_2CH_2OCH_3$	105.
91	$CH_2CH_2—C_6H_5$	$CH_2CH_2OCH_3$	60.
92	$CH_2CH_2—C_6H_5$	CH_2CH_2OH	167 - 170.
93	$C_4H_9(n)$	CH_2CH_2OH	Oil having green fluorescence.
94	$C_4H_9(n)$	$CH_2CH_2OCH_2CH_2OH$	"
95	C_2H_5	$CH_2CH_2OCH_2CH_2OH$	"
96	$CH_2CH_2OC_2H_5$	$CH_2CH_2OCH_2CH_2OH$	"
97	$(CH_2)_5CH_3$	$CH_2CH_2OCH_2CH_2OH$	"
98	$(CH_2)_3—OCH_2CH(CH_3)_2$	$CH_2CH_2OCH_2CH_2OH$	"
99	H	$(CH_2)_3—O—(CH_2)_4OH$	Viscous oil
100	H	$(CH_2)_3—O—(CH_2)_6OH$	"
101	H	$(CH_2)_3—O—(CH_2)_2OH$	"
102	H	$(CH_2)_3—O—CH_2—C_6H_5$	"
103	H	$(CH_2)_3—O—CH_2CH_2OC_6H_5$	"
104	H	$(CH_2)_3—O—CH_2CH_2—C_6H_5$	"
105	H	$(CH_2)_3—O—CH_2CH_2—OCH_3$	"
106	H	$(CH_2)_3—O—CH(CH_3)CH_2—OCH$	"
107	H	$(CH_2)_3—O—CH_2CH_2O—C_4H_9$	"
108	H		"
109	H	$—CH(CH_3)(CH_2)_3C(CH_3)_2OH$	"
110	H	$—CH_2—CH(OH)—C_6H_5$	"
111	H	$(CH_2)_3O(CH_2CH_2O)_2CH_3$	"
112	H	$(CH_2)_4O(CH(CH_3)CH_2O)_2CH_3$	"

TABLE 3-continued



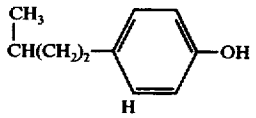
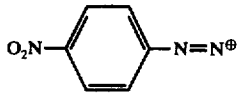
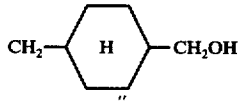
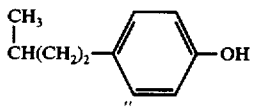
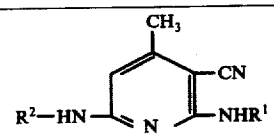
113			"
114	H	$(CH_2)_3O(CH_2)_2OH$	"
115	H	$(CH_2)_3O(CH_2)_4OH$	"
116	H	$(CH_2)_3O-(CH_2)_6OH$	"
117	H	$(CH_2)_6OH$	"
118	H	$(CH_2)_3-O-C_2H_4-O-C_3H_7$	"
			Shade on coupling with 
119	$(CH_2)_3O-C_6H_5$	$-CH_2CH_2OH$	Orange.
120	$(CH_2)_3O-C_6H_5$	$-CH_2CH_2CH_2OH$	"
121	$(CH_2)_3O-C_6H_5$	$-CH_2CH_2OCH_2CH_2OH$	"
122	$(CH_2)_3OCH_2C_6H_5$	$-CH_2CH_2OCH_2CH_2OH$	"
123	$(CH_2)_3OCH_2C_6H_5$	$(CH_2)_3OH$	"
124	$(CH_2)_3OCH_2C_6H_5$	CH_2CH_2OH	"
125	$CH_2CHOC_6H_5$ | CH_3	CH_2CH_2OH	"
126	$CH_2CHOC_6H_5$ | CH_3	$(CH_2)_3OH$	"
127	$(CH_2)_3O-CH_2CH_2C_6H_5$	$-CH_2CH_2OH$	"
128	$(CH_2)_3O-CH_2CH_2C_6H_5$	$(CH_2)_3OH$	"
129	$(CH_2)_3OCH_2CH_2OC_6H_5$	$(CH_2)_3OH$	"
130	$(CH_2)_3OCH_2CH_2OC_6H_5$	CH_2CH_2OH	"
131	$(CH_2)_3OCH_2CH_2OC_6H_5$	$-CH_2CH_2OCH_3$	"
132	$(CH_2)_3OCH_2CH_2OC_6H_5$	$-CH_2CH_2CH_2OCH_3$	"
133		$-CH_2CH_2OH$	"
134	"	$-(CH_2)_3OH$	"
135	"	$(CH_2CH_2O)_2H$	"
136	$-(CH_2)_3OCHCH_2O-C_6H_5$ | CH_3	$-CH_2CH_2OH$	"
137	$-(CH_2)_3OCHCH_2O-C_6H_5$ | CH_3	$-(CH_2)_3OH$	"
138		$-CH_2CH_2OH$	"
139	"	$-(CH_2)_3OH$	"
140	"	$-(CH_2CH_2O)_2H$	"
			Melting point, ° C.
141	$-CH_2-CH-C_6H_5$ | OH	$-CH-CH_2OH$ | C_2H_5	Viscous oil.
142	$-CH_2-CH-C_6H_5$ | OH	$-(CH_2)_3OH$	"
143	$-CH_2-CH-C_6H_5$ | OH	$-(CH_2CH_2O)_2H$	"
144	$-CH_2-CH-C_6H_5$ | OH	$-(CH_2)_2OCH_3$	"
145	$-CH_2CH-C_6H_5$ | OH	$-(CH_2)_3OCH_3$	"
146	CH_3 | $-CH_2-CH-OH$	$-CH_2-CH-C_6H_5$ | OH	"
147	$(CH_2)_6OH$	$-CH_2-CH-C_6H_5$ | OH	"
148	$(CH_2)_2O-CHCH_2OCH_3$ | CH_3	$-CH_2-CH-C_6H_5$ | OH	"

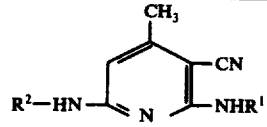
TABLE 3-continued

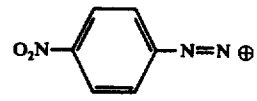


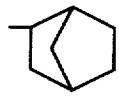
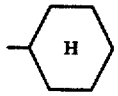
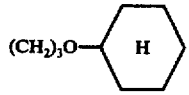
149	$(CH_2CH_2O)_2H$	$-CH_2-CH(OH)-C_6H_5$	"
150	$-CH(CH_3)(CH_2)_3C(CH_3)_2(OH)$	$-CH(CH_3)(CH_2)_3C(CH_3)_2(OH)$	"
151	$-(CH_2)_3O-(CH_2)_2OH$	$-(CH_2)_3O(CH_2)_2OH$	"
152	$-(CH_2)_3O(CH_2)_4OH$	$-(CH_2)_3O(CH_2)_4OH$	"
153	$-(CH_2)_3O(CH_2)_6OH$	$-(CH_2)_3O(CH_2)_6OH$	"
154	$-CH(CH_3)(CH_2)_3OC(CH_3)_2(OH)$	$-CH_2CH_2OH$	"
155	$-CH(CH_3)(CH_2)_3OC(CH_3)_2(OH)$	$-(CH_2)_3OH$	"
156	$-CH(CH_3)(CH_2)_3OC(CH_3)_2(OH)$	$-CH_2CH(CH_3)OH$	"
157	$-CH(CH_3)(CH_2)_3OC(CH_3)_2(OH)$	$-(CH_2CH_2O)_2H$	"
158	$-CH(CH_3)(CH_2)_3OC(CH_3)_2(OH)$	$-(CH_2)_3O-(CH_2)_2OH$	"
159	$-CH(CH_3)(CH_2)_3OC(CH_3)_2(OH)$	$-(CH_2)_3O(CH_2)_4OH$	"
160	$-CH(CH_3)(CH_2)_3OC(CH_3)_2(OH)$	$-(CH_2)_3O(CH_2)_6OH$	"
161	$(CH_2)_3OH$	$-(CH_2)_3OH$	84° bis 87° C.
162	$(CH_2CH_2O)_2H$	$-(CH_2CH_2O)_2H$	Viscous oil.
163	$-CH(CH_3)(CH_2)_3-C(CH_3)_2(OH)$	$-(CH_2)_2OCH_3$	"
164	$-CH(CH_3)(CH_2)_3-C(CH_3)_2(OH)$	$-(CH_2)_3OCH_3$	"
165	$-CH(CH_3)(CH_2)_3-C(CH_3)_2(OH)$	$-(CH_2)_3-O-C_3H_7$	"
166	$-(CH_2CH_2O)_2H$	$-CH(CH_3)(CH_2)_3-C(CH_3)_2(OH)$	"
167	$-(CH_2)_2OH$	$-CH(CH_3)(CH_2)_3-C(CH_3)_2(OH)$	"
168	$-(CH_2)_3OH$	$-CH(CH_3)(CH_2)_3-C(CH_3)_2(OH)$	"
169	$-CHCH_2OH(CH_3)$	$-CH(CH_3)(CH_2)_3-C(CH_3)_2(OH)$	"
170	$-CHCH_2OH(C_3H_7)$	$-CH(CH_3)(CH_2)_3-C(CH_3)_2(OH)$	"
171	$-CH(CH_3)-CH_2OH$	$-CH(CH_3)-CH_2OH$	"
172	$-(CH_2)_3OH$	$(CH_2)_3O-(CH_2)_2OH$	"
173	$-(CH_2)_3OH$	$(CH_2)_3O(CH_2)_4OH$	"
174	$-(CH_2)_3OH$	$(CH_2)_3O-(CH_2)_6OH$	"
175	$-(CH_2CH_2OH$	$(CH_2)_3O-(CH_2)_6OH$	"
176	$-(CH_2CH_2OH$	$(CH_2)_3O-(CH_2)_4OH$	"
177	$-CH_2CH_2OH$	$(CH_2)_3O-(CH_2)_2OH$	"
178	$CH_2CH_2OCH_3$	$(CH_2)_3O-(CH_2)_2OH$	"
179	$CH_2CH_2OCH_3$	$(CH_2)_2O-(CH_2)_2OH$	"
180	$(CH_2)_3OCH_3$	$(CH_2)_2O-(CH_2)_2OH$	"
181	$(CH_2)_3O-C_3H_7$	$(CH_2)_2O-(CH_2)_2OH$	"
182	$(CH_2)_2OCH_3$	$(CH_2)_3O-(CH_2)_4OH$	"
183	$(CH_2)_3OCH_3$	$(CH_2)_3O-(CH_2)_4OH$	"
184	$(CH_2)_3OCH_3$	$(CH_2)_3O-(CH_2)_2OH$	"

Shade on coupling with

TABLE 3-continued





185	$-CH_2CH_2OCH_2CH_2OH$	CH_3	Orange.
186	$-CH_2CH_2OCH_2CH_2OH$	C_2H_5	"
187	$-CH_2CH_2OCH_2CH_2OH$	C_3H_7	"
188	$-CH_2CH_2OCH_2CH_2OH$	C_4H_9	"
189	$-CH_2CH_2OCH_2CH_2OH$	C_5H_{11}	"
190	$-CH_2CH_2OCH_2CH_2OH$	C_6H_{13}	"
191	$-CH_2CH_2OCH_2CH_2OH$	$CH_2CHC_4H_9(n)$ | C_2H_5	"
192	$-CH_2CH_2OCH_2CH_2OH$	CH_2CH_2OH	"
193	$-CH_2CH_2OCH_2CH_2OH$	$(CH_2)_3OH$	"
194	$-CH_2CH_2OCH_2CH_2OH$	CH_2-CHOH | CH_3	"
195	$-CH_2CH_2OCH_2CH_2OH$	$-(CH_2)_3O(CH_2)_2OH$	"
196	$-CH_2CH_2OCH_2CH_2OH$		"
197	$-CH_2CH_2OCH_2CH_2OH$		"
198	$-CH_2CH_2OCH_2CH_2OH$	$(CH_2)_2OCH_3$	"
199	$-CH_2CH_2OCH_2CH_2OH$	$(CH_2)_3OCH_3$	"
200	$-CH_2CH_2OCH_2CH_2OH$	$(CH_2)_3OC_2H_5$	"
201	$-CH_2CH_2OCH_2CH_2OH$	$(CH_2)_3O-C_3H_7(n)$	"
202	$-CH_2CH_2OCH_2CH_2OH$	$(CH_2)_3O-C_3H_7(i)$	"
203	$-CH_2CH_2OCH_2CH_2OH$	$(CH_2)_3O-CH_2CH(CH_3)_2$	"
204	$-CH_2CH_2OCH_2CH_2OH$		"

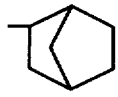
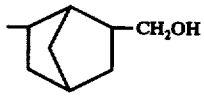
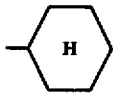
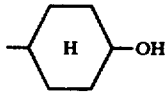
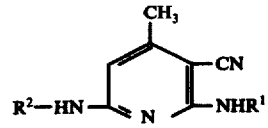
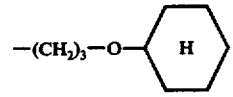
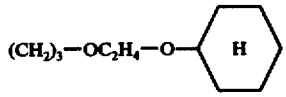
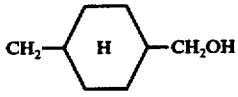
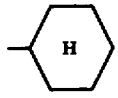
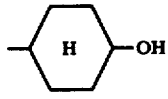
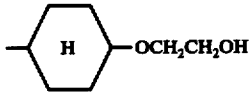
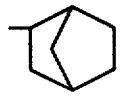
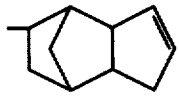
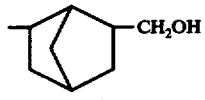
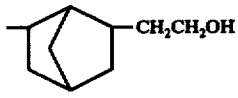
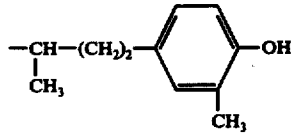
			Melting point, ° C.
205	$CH_2CH_2OCH_3$	$CH_2CH-C_6H_5$ | OH	116–117.
206	$-CH_2-CH_2OH$	$CH_2CH-C_6H_5$ | OH	188–189.
207	$-CH_2-CH_2OH$	H	>150.
208	$(CH_2)_3-COOH$	$CH_2-CH-CH_3$ | OH	185–188.
209	$(CH_2)_3-O-(CH_2)_2OH$	C_2H_5	Viscous oil.
210	$(CH_2)_3-O-(CH_2)_2OH$	$C_3H_7(n)$	"
211	$(CH_2)_3-O-(CH_2)_2OH$	$C_4H_9(n)$	"
212	$(CH_2)_3-O-(CH_2)_2OH$	$-C_5H_{11}(n)$	"
213	$(CH_2)_3-O-(CH_2)_2OH$	$C_6H_{13}(n)$	"
214	$(CH_2)_3-O-(CH_2)_2OH$		"
215	$(CH_2)_3-O-(CH_2)_2OH$		"
216	$(CH_2)_3-O-(CH_2)_2OH$		"
217	$(CH_2)_3-O-(CH_2)_2OH$		"

TABLE 3-continued



218	$(CH_2)_3-O-(CH_2)_2OH$		"
219		$-CH_2CH_2OH$	"
220	"	$-(CH_2)_3OH$	"
221	"	$(CH_2)_2O(CH_2)_2OH$	"
222		$(CH_2)_2O(CH_2)_2OH$	"
223	"	$(CH_2O(CH_2)_2OH$	"
224		$-(CH_2)_2O(CH_2)_2OH$	"
225	"	$-(CH_2)_3O(CH_2)_2OH$	"
226		$-(CH_2)_3O(CH_2)_2OH$	"
227	"	$-(CH_2)_2O(CH_2)_2OH$	"
228		$-CH_2CH_2OH$	"
229	"	$-(CH_2)_2OH$	"
230	"	$-(CH_2)_2O(CH_2)_2OH$	"
231		$-(CH_2)_2O(CH_2)_2OH$	"
232	"	$-(CH_2)_3O(CH_2)_2OH$	"
233		$-(CH_2)_3O(CH_2)_2OH$	"
234		$-(CH_2)_2O(CH_2)_2OH$	"
235	"	$-(CH_2)_2O(CH_2)_2OH$	"
236		$-(CH_2)_2O(CH_2)_2OH$	"
237		$-CH_2CH_2OH$	"
238	$CH_2CH \quad CH_2$	$-(CH_2)_2O(CH_2)_2OH$	"
239	$CH_2CH \quad CH_2$	$-(CH_2)_3O-(CH_2)_2OH$	"

Shade on coupling with

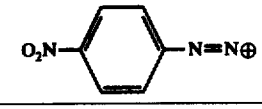
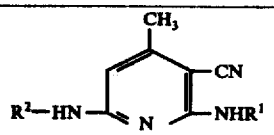


TABLE 3-continued



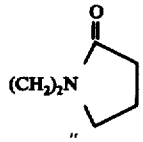
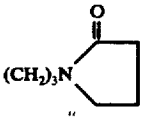
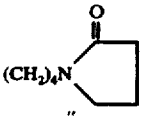
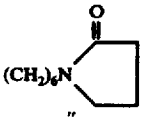
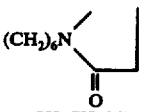
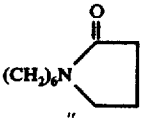
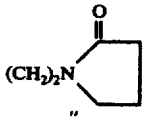
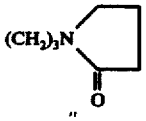
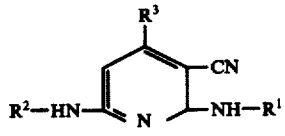
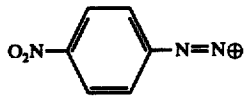
240		$-C_2H_5$	Orange.
241	"	$-C_3H_7(n)$	"
242	"	$-C_4H_9(n)$	"
243	"	$-C_6H_{13}(n)$	"
244	"	$-(CH_2)_2OH$	"
245	"	$(CH_2)_2O-(CH_2)_2OH$	"
246	"	$(CH_2)_2O(CH_2)_2OH$	"
247	"	$(CH_2)_3O-(CH_2)_4OH$	"
248		$-C_2H_5$	"
249	"	$-C_3H_7(n)$	"
250	"	$-C_4H_9(n)$	"
251	"	$-C_6H_{13}(n)$	"
252	"	$-(CH_2)_2OH$	"
253	"	$-(CH_2)_3OH$	"
254	"	$-(CH_2)_2O(CH_2)_2OH$	"
255	"	$-(CH_2)_3O(CH_2)_2OH$	"
256	"	$-(CH_2)_3O(CH_2)_4OH$	"
257		$-C_2H_5$	"
258	"	$-C_3H_7$	"
259	"	$-C_4H_9$	"
260	"	$-CH_2CH_2OH$	"
261	"	$-(CH_2)_3OH$	"
262	"	$-(CH_2)_2O(CH_2)_2OH$	"
263	"	$-(CH_2)_2OCH_3$	"
264	"	$(CH_2)_3O(CH_2)_2OH$	"
265	"	$(CH_2)_3O(CH_2)_4OH$	"
266		C_2H_5	"
267	"	$C_3H_7(n)$	"
268	"	$C_4H_9(n)$	"
269	"	$C_6H_{13}(n)$	"
270	H		Golden yellow.
271		$-CH_2CH_2OH$	Orange.
272	"	$(CH_2)_2OH$	"
273	"	$(CH_2)_2O(CH_2)_2OH$	"
274	"	$(CH_2)_3O(CH_2)_2OH$	"
275	"	$(CH_2)_2O(CH_2)_4OH$	"
276	"	$(CH_2)_2OCH_3$	"
277	"	$(CH_2)_3OCH_3$	"
278		$(CH_2)_3OCH_3$	Orange.
279	"	$(CH_2)_2OCH_3$	"
280		$(CH_2)_2OCH_3$	"
281	"	$(CH_2)_3OCH_3$	"

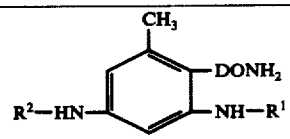
TABLE 4

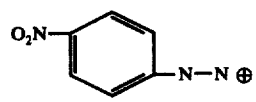




Number	R^1	R^2	R^3	Shade coupling with
282	$CH_2CH_2C_6H_5$	CH_2CH_2OH	H	Orange.
283	$CH_2CH_2C_6H_5$	CH_2CH_2OH	$-C_2H_5$	"
284	$CH_2CH_2C_6H_5$	$(CH_2)_3OH$	$-C_2H_5$	"
285	$CH_2CH_2C_6H_5$	$(CH_2)_2O(CH_2)_2OH$	H	"
286	$CH_2CH_2C_6H_5$	$(CH_2)_2O(CH_2)_2OH$	C_2H_5	"
287	$CH_2CH_2C_6H_5$	CH_2CH_2OH	$C_3H_7(n)$	"
288	$CH_2CH(OH)C_6H_5$	CH_2CH_2OH	H	41
289	$CH_2CH(OH)C_6H_5$	CH_2CH_2OH	$C_3H_7(n)$	"
290	$CH_2CH(OH)C_6H_5$	$(CH_2)_3OH$	$C_3H_7(n)$	"
291	$CH_2CH(OH)C_6H_5$	$(CH_2)_3OH$	H	"
292	$CH_2CH(OH)C_6H_5$	$(CH_2)_3OH$	C_2H_5	"
293	CH_2CH_2OH	CH_2CH_2OH	$-CHC_4H_9(n)$, C_2H_5	"
294	CH_2CH_2OH	CH_2CH_2OH	$-C_5H_{11}(n)$	"
295	$CH_2CH_2OCH_3$	$(CH_2CH_2O)_2H$	$-C_6H_5$	"
296	$(CH_2)_3OCH_3$	$(CH_2CH_2O)_2H$	$-C_6H_5$	"
297	H	$CH_2CH(OH)C_6H_5$	H	Golden yellow.
298	H	$CH_2CH(OH)C_6H_5$	$-C_3H_7(n)$	"
299	H	$(CH_2)_3O(CH_2)_4OH$	H	"
300	H	$(CH_2)_3O(CH_2)_2OH$	H	"

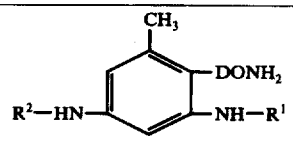
TABLE 5



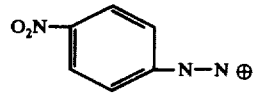


Number	R^1	R^2	Shade after coupling with
301	$-CH_2CH_2CH_2OCH_3$	$(CH_2)_3OH$	Red.
302	$-CH_2CH_2-C_6H_5$	$-CH_2CH_2OH$	Red.
303	$-CH_2CH_2-C_6H_5$	$-(CH_2)_3OH$	Red.
304	$-CH_2-CH(OH)-C_6H_5$	$-(CH_2)_3OH$	Red.
305	$-CH_2-CH(OH)-C_6H_5$	$-(CH_2)_2OH$	Red.
306	$-(CH_2)_3O-CH_2C_6H_5$	$-(CH_2)_2OH$	Red.
307	$-(CH_2)_3O-CH_2C_6H_5$	$-(CH_2)_3OH$	Red.
308	$-(CH_2)_3OCH_2CH_2O-C_6H_5$	$-(CH_2)_3OH$	Red.
309	$-(CH_2)_3OCH_2CH_2OC_6H_5$	$-(CH_2)_2OH$	Red.
310	$-(CH_2)_2O(CH_2)_2OH$	$-(CH_2)_2OCH_3$	Red.
311	$-(CH_2)_2O(CH_2)_2OH$	$-(CH_2)_3OCH_3$	Red.
312	$-(CH_2)_2OCH_3$	$-(CH_2)_2O(CH_2)_2OH$	Red.
313	$-(CH_2)_3OCH_3$	$-(CH_2)_2O(CH_2)_2OH$	Red.
314	$-H$	$-(CH_2)_2O(CH_2)_2OH$	Yellowish red.
315	$-H$	$-(CH_2)_3O(CH_2)_2OH$	"
316	$-H$	$-(CH_2)_2O(CH_2)_4OH$	"
317	$-CH_2-CH_2OH$	$-CH_2CH_2-C_6H_5$	Red.
318	$-(CH_2)_3OH$	$-CH_2CH_2-C_6H_5$	Red.

TABLE 5-continued



Shade after coupling with



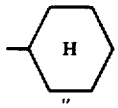
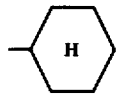
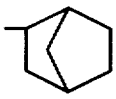
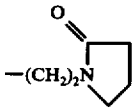
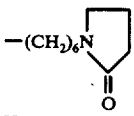
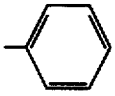
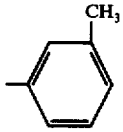
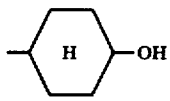
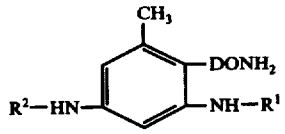
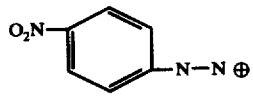
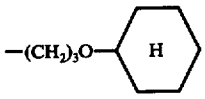
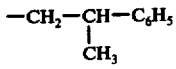
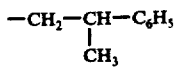
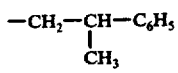
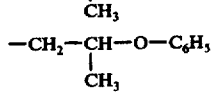
Number	R^1	R^2	
319	$-(CH_2)_3OCH_3$	$-CH_2CH_2-C_6H_5$	Red.
320	$-CH_2-CH_2-C_6H_5$	$-(CH_2)_3OCH_3$	Red.
321	$-CH(CH_3)(CH_2)_3C(CH_3)_2(OH)$	$-CH_2CH_2OH$	Red.
322	$-CH(CH_3)(CH_2)_3C(CH_3)_2(OH)$	$-(CH_2)_3OH$	Red.
323	$-CH(CH_3)(CH_2)_3C(CH_3)_2(OH)$	$-(CH_2)_2O(CH_2)_2OH$	Red.
324		$-CH_2-CH_2OH$	Red.
325	"	$-(CH_2)_3OH$	Red.
326	"	$-(CH_2)_2O(CH_2)_2OH$	Red.
327	"	$-(CH_2)_3-O-(CH_2)_2OH$	Red.
328	$-C_4H_9(n)$	$-(CH_2)_3-O-(CH_2)_2OH$	Red.
329	$-C_4H_9(n)$	$-(CH_2)_2O(CH_2)_2OH$	Red.
330	$-(CH_2)_2O(CH_2)_2OH$	$-C_4H_9(n)$	Red.
331	$-(CH_2)_2O(CH_2)_2OH$		Red.
332		$-(CH_2)_2O(CH_2)_2OH$	Red.
333		$-(CH_2)_3OH$	Red.
334		$-(CH_2)_3OH$	Red.
335	H	$-(CH_2)_2OH$	Red.
336		$-(CH_2)_2OH$	Bluish red.
337	"	$-(CH_2)_3OH$	"
338	"	$-(CH_2)_2O(CH_2)_2OH$	"
339		$-(CH_2)_2O(CH_2)_2OH$	"
340	$-(CH_2)_2OH$	$-(CH_2)_2OH$	Red.
341	$-(CH_2)_3OH$	$-(CH_2)_3OH$	Red.
342	$-(CH_2)_3O(CH_2)_4OH$	$-(CH_2)_3OH$	Red.
343	$-(CH_2)_3O(CH_2)_2OH$	$-(CH_2)_2OCH_3$	Red.
344	$-(CH_2)_3O(CH_2)_2OH$	$-(CH_2)_3OCH_3$	Red.
345	$-(CH_2)_3O-(CH_2)_2OH$	$-(CH_2)_3OCH_3$	Red.
346	$-H$	$-(CH_2)_2O(CH_2)_2OH$	Yellowish red.
347		$-CH_2-CH_2-OH$	Red.
348	"	$-(CH_2)_3OH$	Red.
349	"	$-(CH_2)_2O-(CH_2)_2OH$	Red.

TABLE 5-continued



Shade after coupling with

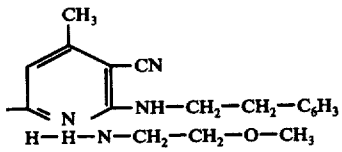


Number	R^1	R^2	
350		$-(CH_2)_2O-(CH_2)_2OH$	Red.
351	"	$(CH_2)_2OH$	Red.
352	"	$-(CH_2)_3OH$	Red.
353		$-(CH_2)_3OH$	Red.
354		$-(CH_2)_2OH$	Red.
355		$-(CH_2)_2-O-(CH_2)_2OH$	Red.
356		$-CH_2-CH_2-OH$	Red.

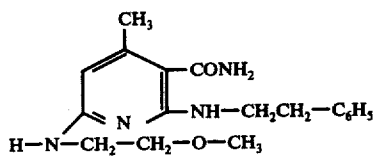
The Examples described in the above Tables are prepared by always first introducing the radical R^1.

EXAMPLE 357

25 parts of the coupling component of the formula:



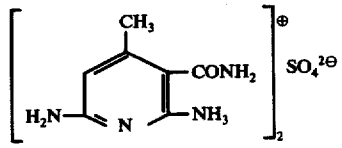
is stirred with 75 parts of 90 percent sulphuric acid for six to eight hours at 80° to 100° C. The reaction mixture is then precipitated on 500 parts of ice, adjusted to pH 4 to 6 by adding caustic soda solution and extracted with ethyl acetate. After the extractant has been evaporated about 20 parts of the coupling component of the formula:



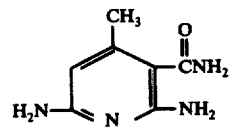
is obtained as a dark oil. A red dye is obtained therefrom after coupling with diazotized p-nitroaniline

EXAMPLE 358

30 parts of 2,6-diamino-3-cyano-4-methylpyridine is stirred with 200 parts by volume of concentrated sulphuric acid for ten hours at 50° C. The whole is then allowed to cool, 250 parts of ice is added and it is left overnight. The deposited precipitate is filtered off and washed witht acetone. After drying, 36 parts of a colourless powder of the formula:

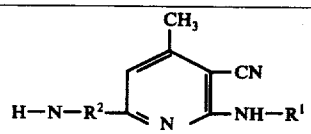


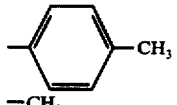
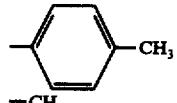
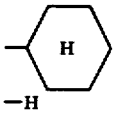
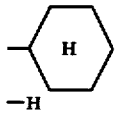
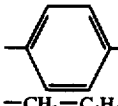
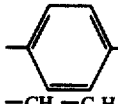
is obtained which melts at 250° C with decomposition. The free base of the formula:



is obtained from the salt by a conventional method.

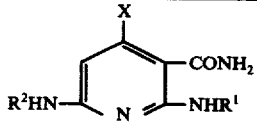
TABLE 6



Number	R^1	R^2	Melting point, °C.
359	$-C_6H_5$	$-C_6H_5$	128–130
360			178
361	$-CH_3$	$-CH_3$	140–150
362	$-CH(CH_3)_2$	$-CH(CH_3)_2$	118–120
363	$-C_3H_7(n)$	$-C_3H_7(n)$	122–123
364	$-CH_2-CH=CH_2$	$-CH_2-CH=CH_2$	77
365	$-C_4H_9(n)$	$-C_4H_9(n)$	97
366	$-C_6H_{13}(n)$	$-C_6H_{13}(n)$	Oil
367			193
368	$-H$	$-H$	225
369			175
370	$-CH_2-C_6H_5$	$-CH_2-C_6H_5$	170
371	$-CH_2-CH_2-C_6H_5$	$-CH_2-CH_2-C_6H_5$	110
372	$-C_2H_5$	$-C_2H_5$	[1]205 [1]
373	$-C_6H_5$	$-C_4H_9(n)$	115
374	C_6H_5	H	([2])
375	$C_4H_9(n)$	H	100
376	C_2H_5	$-C_6H_5$	218–220
377	$-CH_2CH_2C_6H_5$	$-H$	100
378	$-CH_2-CH(CH_3)-C_6H_5$	$-CH_2-CH(CH_3)-C_6H_5$	Ca.60
379	$-H$	$-CH_2-CH_2-C_6H_5$	Ca. 100, [1]188
380	$-C_8H_{17}(n)$	$-H$	Oil
381	$-C_{14}H_{29}$	$-H$	Ca.90–105
382	$-H$	$-CH_2-CH(CH_2)-C_6H_5$	Tar
383	$-CH_2-CH(CH_3)-C_6H_5$	$-H$	Tar
384	$-CH_2-CH_2-CN$	$-CH_2-CH_2-CN$	170–176
385	$-CH_2-CH_2-CN$	$-CH_2-CH_2-C_6H_5$	Ca.120
386	$-H$	$-(CH_2)_5CN$	142

[1]Hydrochloride.
[2]Tarry: becomes solid after prolonged standing.

Table 7



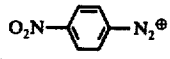
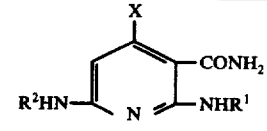
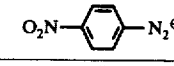
Ex.	X	R^1	R^2	Shade when coupled with 
387	CH_3	H	CH_2CH_2OH	Yellowish red.
388	CH_3	H	$(CH_2)_3OH$	"
389	CH_3	H	$CH_2-CH(OH)-C_6H_5$	"
390	CH_3	H	$CH_2CH_2C_6H_5$	"
391	C_3H_7	C_6H_5	CH_2CH_2OH	Bluish red.
392	C_3H_7	C_6H_5	$(CH_2)_3OH$	"
393	C_3H_7	C_6H_5	$(CH_2)_2O(CH_2)_2OH$	"
394	C_3H_7		$(CH_2)_2O(CH_2)_2OH$	"
395	C_3H_7	"	CH_2CH_2OH	"

Table 7-continued

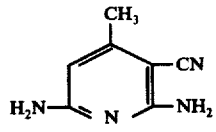


Ex.	X	R^1	R^2	Shade when coupled with 
396	C_3H_7	"	$(CH_2)_3OH$	"
397	H	C_6H_5	$(CH_2)_3OH$	"

EXAMPLE 398

190 parts of 2,6-dichloro-3-cyano-4-methylpyridine, 750 parts of isopropanol and approx. 300 parts of ammonia are stirred in an autoclave for 15 hours at 180° C. The mixture is allowed to cool, excess ammonia is evaporated and 450 parts by volume of isopropanol is distilled off. The residue is mixed with approx. 600 parts of

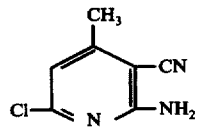
water, the pH is adjusted to approx. 0 with concentrated hyrochloric acid and the solution filtered. Then 50 percent caustic soda solution is added until the pH of the mixture is approx. 9, the mixture allowed to cool to 0°–10° C and then filtered, and the residue is washed with water and dried. 130 to 145 parts of a colorless powder of the formula



is obtained which melts at 225° C.

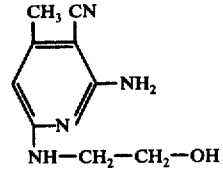
EXAMPLE 399

300 parts of 2,6-dichloro-3-cyano-4-methylpyridine is mixed with about 500 parts by volume of liquid ammonia and treated in an autoclave for 2 hours at approx. 80° C. Excess ammonia is allowed to evaporate, the residue is diluted with approx. 2500 parts by volume of water, and the pH is adjusted to 0 to 1 with hydrochloric acid. The insoluble residue is filtered off, washed with water and dried. Approx. 260 parts of a colorless powder of the formula



which contains a minor amount of the isomeric 2-chloro-3-cyano-4-methyl-6-aminopyridine and melts at 210° C is obtained.

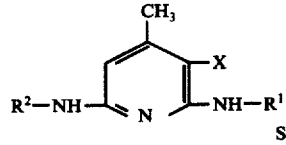
168 parts of this powder is mixed with about 170 parts of β-hydroxyethylamine and 170 parts by volume of isopropanol. The mixture is heated for 7 to 10 hours under reflux, the solvent is distilled off, the residue is diluted with about 400 parts of water, and the pH is adjusted to 1 to 2. A deep-colored solution of about 192 parts of the coupling component of the formula



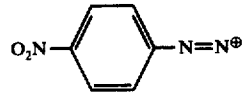
is obtained, a minor portion of which consists of 2-amino-4-methyl-5-cyano-6-β-hydroxyethylaminopyridine.

A greenish yellow dye may be obtained by coupling with diazotized 2-aminobenzonitrile.

TABLE 8



Shade when coupled with



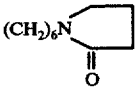
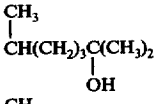
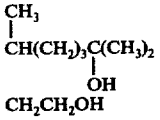
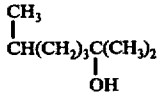
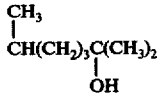
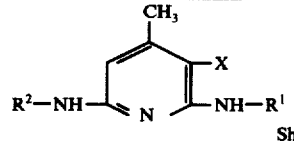
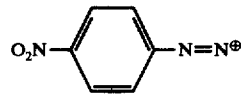
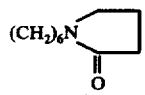
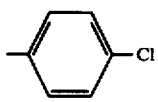
No.	R^1	R^2	X	
400	H	CH_3	CN	Golden yellow.
401	H	C_2H_5	CN	"
402	H	C_3H_7	CN	"
403	H	$C_2H_4OCH_3$	CN	"
404	H	$C_2H_4OCH_3$	$CONH_2$	Yellowish red.
405	H	$C_3H_6OCH_3$	$CONH_2$	"
406	H	$C_3H_6OCH_3$	CN	Golden Yellow.
407	H	C_4H_9(n)	CN	Yellow orange.
408	H	C_4H_9(n)	$CONH_2$	Yellowish red.
409	H	$CH_2CH=CH_2$	CN	Golden yellow.
410	H		$CONH_2$	Yellowish red.
411	H		CN	Orange.
412	H		$CONH_2$	Red.
413		CH_2CH_2OH	$CONH_2$	Red.
414		$(CH_2)_3OH$	$CONH_2$	Red.

TABLE 8-continued



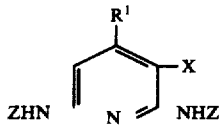
Shade when coupled with



No.	R^1	R^2	X	
415	CH_2CH_2OH		$CONH_2$	Red.
416		CH_2CH_2OH	$CONH_2$	Red. (M.P. 150–153° C.)

We claim:

1. A compound of the formula

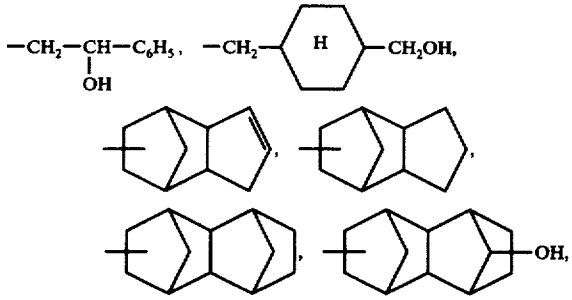


in which:

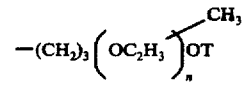
R^1 is hydrogen, alkyl of one to seven carbon atoms or phenyl;

X is cyano or carbamoyl; and

each Z, independently of one another, is hydrogen, alkyl of one to eight carbon atoms, hydroxyalkyl of two to eight carbon atoms, cyanoalkyl of two to seven carbon atoms, alkoxyalkyl of two or three carbon atoms in the alkyl and one to eight carbon atoms in the alkoxy, cyclohexoxypropyl, benzyloxypropyl, β-phenyl-ethoxypropyl, phenoxypropyl, tolyloxypropyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, hydroxycyclohexyl, β-hydroxyethoxycyclohexyl, norbornyl, hydroxynorbornyl, hydroxymethylnorbornyl, chloromethylnorbornyl, β-hydroxyethylnorbornyl, bicyclooctyl, phenylalkyl or tolylalkyl of one to four carbon atoms in the alkyl, phenyl, phenyl substituted by methyl, methoxy, ethoxy, hydroxy, chloro or β-hydroxyethoxy, allyl, carboxyethyl, carboxypentyl, ω-pyrrolidonylalkyl of two to six carbon atoms in the alkyl,



$-(CH_2)_2O(CH_2)_2OH$, $-(CH_2)_3O(CH_2)_4OH$, $-(CH_2)_3O(CH_2)_6OH$,

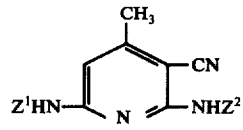


or $-(CH_2)_3(OC_2H_4)_nOT$,

n being 1, 2, 3 or 4, and

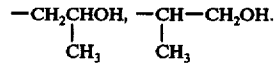
T being hydrogen, alkyl of one to four carbon atoms, benzyl, phenylethyl, cyclohexyl, phenyl or tolyl.

2. A compound as claimed in claim 1 of the formula

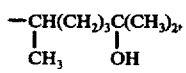


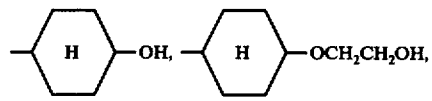
in which:

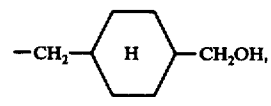
Z^1 is an oxygen-containing radical selected from the group consisting of $-CH_2CH_2OH$, $-CH_2CH_2CH_2OH$,



$-(CH_2)_3O(CH_2)_2OH$, $-(CH_2)_3O(CH_2)_4OH$, $-(CH_2)_3O(CH_2)_6OH$, $-(CH_2)_4OH$, $-(CH_2)_6OH$, $-(CH_2)_2O(CH_2)_2OH$,







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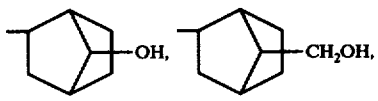
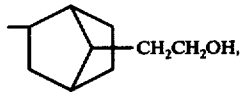
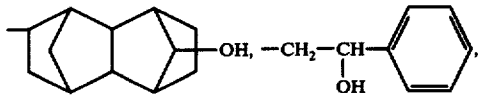
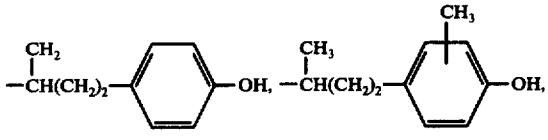
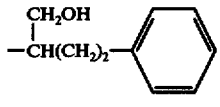


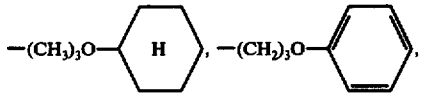


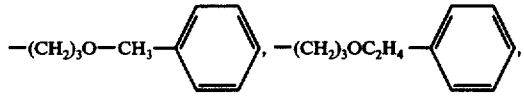


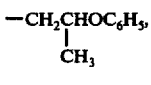




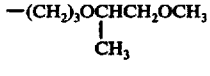
—$CH_2CH_2OCH_3$, —$CH_2CH_2OC_2H_5$, —$CH_2CH_2OC_4H_9$, —$(CH_2)_3OCH_3$, —$(CH_2)_3OC_2H_5$, —$(CH_2)_3OC_4H_9$, —$(CH_2)_3OC_3H_7$, —$(CH_2)_3OC_6H_{13}$, —$(CH_2)_3OC_8H_{17}$,







—$(CH_2)_3OCH_2CH_2OCH_3$, —$(CH_2)_3OC_2H_4OC_4H_9$,

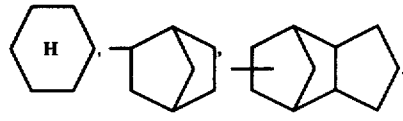


and

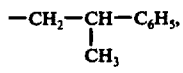
—$(CH_2)_3OC_2H_4OC_6H_5$; and

Z^2 is hydrogen, an oxygen-containing radical as defined for Z^1 or an oxygen-free radical selected from the group consisting of

—C_2H_5, —C_3H_7, —C_4H_9,

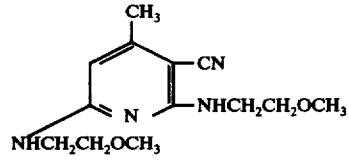


—$CH_2C_6H_5$, —$C_2H_4C_6H_5$, —$C_3H_7C_6H_5$,

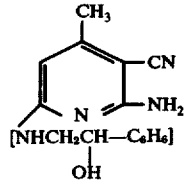


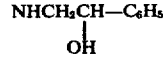
—C_6H_5, —$C_6H_4CH_3$ and —$C_6H_4OCH_3$.

3. The compound of the formula

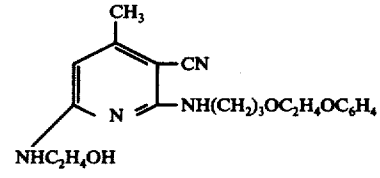


4. The compound of the formula

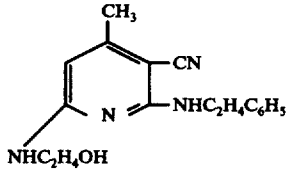




5. The compound of the formula



6. The compound of the formula



* * * * *

UNITED STATES PATENT OFFICE

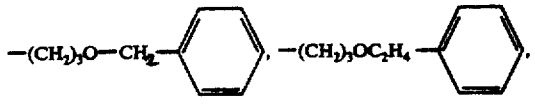
CERTIFICATE OF CORRECTION

Patent No. Re. 29,640 Dated May 23, 1978

Inventor(s) Lamm et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In Claim 2, col. 37, at 40, please change the formula to read:



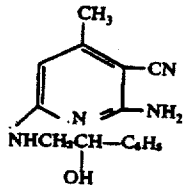
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. Re. 29,640 Dated May 23, 1978

Inventor(s) Lamm et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In Claim 4, col. 38, at 25, please change the formula to read:



Signed and Sealed this

Twenty-fourth Day of October 1978

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

DONALD W. BANNER
Commissioner of Patents and Trademarks