Experimental Section

The nmr spectra were determined on a Hitachi H-60 spectrometer with deuteriochloroform as solvent and tetramethylsilane as an internal reference. The mass spectra were obtained on a Hitachi RMU-6D mass spectrometer, using an all-glass inlet system heated to 300°. The ionizing energy was maintained at 70 eV and ionizing current at 80 μA.

Benz[a]carbazole (4).—A mixture of 1.4 g (0.005 mol) of 1,2-dihydro-2-methyl-1-(2-nitrobenzyl)isoquinoline[9] (3) and 2.5 g (0.015 mol) of triethyl phosphite was refluxed in an oil bath at 160–165° for 20 hr. After cooling, excess triethyl phosphite was removed by distillation and the residue was purified by silica gel chromatography using benzene as an eluent. Removal of the benzene fraction and recrystallization from benzene–hexane afforded 0.4 g (37%) of the benz[a]carbazole (4) as colorless needles: mp 227–228° (lit.[10] mp 228°); mass (*m/e*) 217 (M^+); ν_{max} (KBr) 3430 cm^{-1}; δ (Me_2SO) 7.10–8.65 (10 H, multiplet, aromatic protons), 12.12 ppm (1 H, singlet, NH proton, disappeared with D_2O).

Anal. Calcd for $C_{16}H_{11}N$: C, 88.45; H, 5.10; N, 6.45. Found: C, 88.62; H, 5.14; N, 6.36.

5,6-Dihydro-2,3,8,9-tetramethoxybenz[a]carbazole (6).—A mixture of 1 g (2.7 mmol) of 6′-nitrolaudanosine[11] (5) and 2.24 g (13.5 mmol) of triethyl phosphite was heated under reflux in an oil bath at 165–170° for 20 hr. After cooling the excess reagent was distilled off *in vacuo* and the residue was chromatographed on silica gel using benzene as an eluent. Evaporation of the benzene eluate and recrystallization from ethanol gave 0.35 g (38.5%) of the benz[a]carbazole derivative (6) as colorless scales: mp 202°; mass (*m/e*) 339 (M^+); ν_{max} (KBr) 3400 cm^{-1} (NH); δ ($CDCl_3$) 3.08 (2 H, triplet, J = 8 cps, C_5 or C_6 methylene protons), 3.87 (3 H, singlet, OCH_3), 3.90 (3 H, singlet, OCH_3), 3.92 (6 H, singlet, 2-OCH_3), 4.13 (2 H, triplet, J = 8 cps, C_5 or C_6 methylene protons), 6.62 (1 H, singlet, NH proton, disappeared with D_2O), 6.78, 6.80, 7.08, and 7.20 ppm (4 H, four singlets, aromatic protons).

Anal. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24, N, 4.13. Found: C, 71.00; H, 6.32; N, 4.42.

6′-Nitrolaudanosine Methiodide (7).—A mixture of 6 g of 6′-nitrolaudanosine (5), 30 ml of methanol, and 10 g of methyl iodide was heated on a water bath for 10 min, crystals of 5 being thus dissolved and then those of 7 separated in turn. After an additional 10-min heating, the crystals were collected by filtration and recrystallized from ethanol–dimethylformamide to give 7.2 g (89%) of the methiodide (7) as colorless prisms, mp 240°.

Anal. Calcd for $C_{22}H_{29}N_2O_6I$: C, 48.54; H, 5.39; N, 5.15. Found: C, 48.72; H, 5.47; N, 5.40.

6′-Aminolaudanosine Methiodide (8).—A mixture of 5.44 g (0.01 mol) of 6′-nitrolaudanosine methiodide (7) and 8.3 g (0.05 mol) of triethyl phosphite was heated under reflux in an oil bath at 160–165° for 20 hr. After removal of excess reagent, the residue was crystallized from a small amount of benzene. Recrystallization from ethanol gave 4.1 g (80.1%) of the methiodide (8) as a yellow powder: mp 231° dec; ν_{max} (KBr) 3400 cm^{-1} (NH_2 and H_2O); δ (CF_3CO_2H) 7.85, 7.50–6.60 (4 H, multiplet, aromatic protons), 4.28 (1 H, multiplet, C_1 H), 4.05, 3.99, 3.97 (12 H, three singlets, 4-OCH_3), 3.70–3.00 ppm (6 H, multiplet, C_3 H_2, C_4 H_2, and 1-benzylic proton).

Anal. Calcd for $C_{22}H_{31}N_2O_4I \cdot 0.5H_2O$: C, 50.44; H, 5.92; N, 5.16. Found: C, 50.45; H, 6.28; N, 5.58.

Reduction of 6′-Nitropapaverine[12] (9) with Triethyl Phosphite.—A mixture of 5 g of 6′-nitropapaverine (9) and 11.2 g of triethyl phosphite was heated under reflux in an oil bath at 160–165° for 20 hr. After removal of the excess of the reagent, the residue was dissolved in a small amount of ethanol, whose solution was allowed to stand to separate the crystals. Recrystallization from chloroform gave 0.2 g (4.2%) of deoxygenated product (10) as yellow prisms: mp 277–278°; mass (*m/e*) 366 (M^+) (base peak) (no characteristic patterns were observed); ν_{max} (KBr) 1618 cm^{-1}; δ ($CDCl_3$) 4.00, 4.04, 4.15 (6 H, 3 H, 3 H, three singlets), 6.99, 7.07, 7.73 (each 1 H, singlets), 7.48, 8.37 (each 1 H, doublets, J = 7 cps), 10.35 (1 H, singlet). None of these disappeared with D_2O.

Anal.[13] Calcd for $C_{20}H_{18}O_5N_2$: C, 65.56; H, 4.95; N, 7.65. Found: C, 65.67; H, 5.00; N, 7.68.

Registry No.—**4**, 239-01-0; **6**, 17953-40-1; **7**, 17953-41-2; **8**, 17953-42-3.

Acknowledgment.—We wish to express our gratitude to Miss R. Hasebe and Miss T. Yamaki for the microanalyses and Miss Y. Tadano for the nmr determinations.

(13) The structure of compound **10** could not be determined.

Reissert Compound Studies. XVIII. Analogs Derived from Chloroformates[1,2a]

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The reaction of quinoline or isoquinoline and potassium cyanide with a variety of chloroformates has given rise to the formation of the Reissert compound analogs of the types **6** and **7**. The reactions of these analogs are compared with the reactions of Reissert compounds and other Reissert compound analogs.

In connection with our studies of Reissert compounds (**1** and **2**)[3] we have previously prepared analogs of the types **3**,[4] **4**,[5] and **5**[1] from the reaction of isoquinoline and potassium cyanide with carbamoyl chlorides, sulfonyl chlorides, and chlorophosphates, respectively. The corresponding analogs could not be isolated in the quinoline series.

We now wish to report on the use of chloroformates in this reaction. Reaction of isoquinoline, potassium cyanide, and a variety of chloroformates in methylene chloride–water gave compounds of the type **6**. These compounds are included in Table I. Under these same conditions quinoline reacted to give products of the type **7** which are also included in Table I. It is of interest to note that in contrast to Reissert compounds[3,6] and Reissert compound analogs **3**–**5**[1,4,5] several of these new analogs exhibited weak absorption in the nitrile region of the infrared at 220 cm^{-1}.

Since **1** undergoes a variety of reactions such as alkylation and/or rearrangement in the presence of base,[1,6,7] **3** was unreactive in base,[4] **4** underwent elimina-

(1) Part XVII: D. M. Spatz and F. D. Popp, *J. Heterocycl. Chem.*, **5**, 497 (1968).

(2) (a) Supported in part by a Research Grant (T-329) from the American Cancer Society. Portions of this material were presented at the 1st International Congress of Heterocyclic Chemistry, Albuquerque, N. M., 1967, and the 155th National Meeting of the American Chemical Society, San Francisco, Calif., 1968. (b) National Science Foundation Undergraduate Research Participant. (c) National Institutes of Health Predoctoral Fellow.

(3) F. D. Popp, *Advan. Heterocycl. Chem.*, **9**, 1 (1968).

(4) F. D. Popp, J. M. Wefer, and A. Catala, *J. Heterocycl. Chem.*, **2**, 317 (1965).

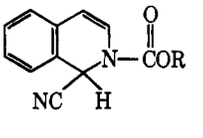
(5) J. M. Wefer, A. Catala, and F. D. Popp, *J. Org. Chem.*, **30**, 3075 (1965).

(6) W. E. McEwen and R. L. Cobb, *Chem. Rev.*, **55**, 511 (1955).

(7) F. D. Popp and J. M. Wefer, *Chem. Commun.*, 207 (1966).

TABLE I

REISSERT ANALOGS



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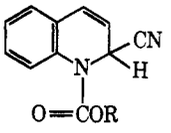
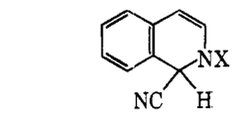


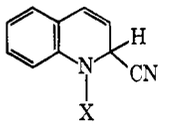
7

Type	R	Mp, °C[a]	Yield, %	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
6	CH_3	83–85	24	67.28	4.71	13.08	67.43	4.70	12.91
7	CH_3	72–73	56	67.28	4.71		67.30	4.74	
6	C_2H_5	84–86	57	68.41	5.30	12.28	68.43	5.32	12.39
7	C_2H_5	70–72	43	68.41	5.30	12.28	68.44	5.31	12.29
6	CH_2CCl_3	104–106[b]	82	47.09	2.74	8.45	47.11	2.85	8.41
6	$C_6H_5CH_2$	84–85	18	74.47	4.86	9.65	74.48	4.92	9.66
6	C_6H_5	156–158	99	73.90	4.38	10.14	73.91	4.36	10.14
6	p-$CH_3OC_6H_4$	182–183	99	70.58	4.61		70.62	4.71	

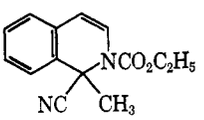
[a] Recrystallized from ethanol, unless otherwise noted. [b] Recrystallized from ethanol–water.



1, X = O=CR
3, X = O=CNR_2
4, X = SO_2R
5, X = P(O)$(OR)_2$ or P(S)$(OR)_2$
6, X = O=COR



2, X = O=CR
7, X = O=COR



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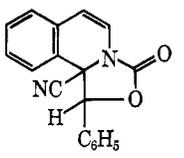

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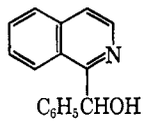

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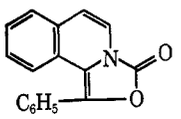

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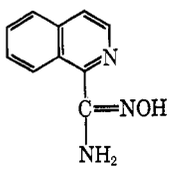

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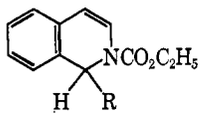
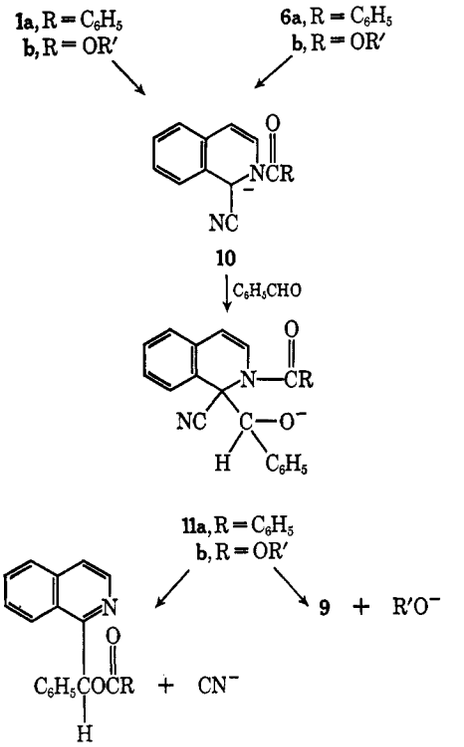


15, R = NH_2C=NOH
16, R = $CONH_2$
18, R = NH_2C=$NOCO_2C_2H_5$

SCHEME I



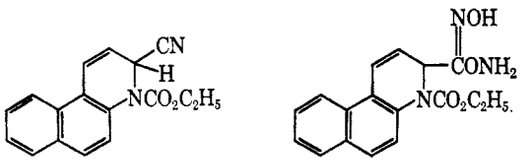
tion in base,[5] and **5** underwent alkylation or elimination in base;[1] it was thought to be of value to examine the behavior of **6** in the presence of base. Treatment of **6** (R = C_2H_5) with methyl iodide and sodium hydride in N,N-dimethylformamide[7] gave **8** in good yield. Confirmation of structure **8** was available since the compound could be readily hydrolyzed to 1-methylisoquinoline.

Treatment of **6** (R = CH_3, C_2H_5, or p-$CH_3OC_6H_4$) with benzaldehyde in the presence of n-butyllithium at −30° gave **9**. This differs, as shown in Scheme I, from the reaction of **1** with benzaldehyde. This difference is easily explained, however, when one considers that **11a** (from **1** *via* **10a**) can only reasonably lose a cyanide ion to give **12**, whereas **11b** (from **6** *via* **10b**) can also lose alkoxide and the reactions proceed through this latter route. When the reaction of **6** and benzaldehyde was carried out with sodium hydride in N,N-dimethylformamide at room temperature with no attempt to control the heat of the reaction, **13** was obtained, although in one case **14** was isolated and easily hydrolyzed by base to **13**.

Hydrolysis of **6** (R = C_2H_5) with hydrobromic acid in glacial acetic acid yielded isoquinoline which was identified as its picrate. This hydrolysis is similar to that reported for **4**[5] and **5**[1] but differs from the normal hydrolysis of a Reissert compound.[6] Treatment of **6** (R = C_2H_5) with sodium hydride gave rise to isoquinaldonitrile. This is analogous to the behavior of **4** and **5** but differs from **1** which undergoes rearrangement under these conditions.

Reaction of **6** (R = C_2H_5) with hydroxylamine by the method of Rupe and Gassman[8] yielded the amidoxime **15** together with a small amount of the amide **16**. Excess base caused the formation of **16** to be favored and none of the amidoxime was isolated. Hydrolysis of **16** with base gave isoquinaldamide. Reaction of isoquinaldonitrile with hydroxylamine

(8) H. Rupe and A. Gassman, *Helv. Chim. Acta*, **22**, 1241 (1939).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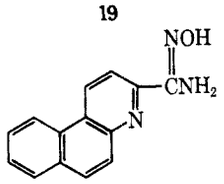
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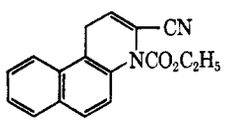
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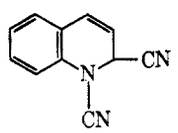
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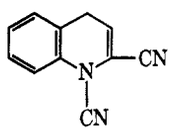
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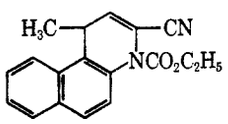
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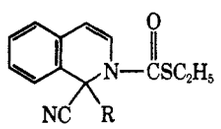
26, R = H
27, R = CH_3

yielded an amidoxime **17**. Both **15** and **17** gave a purple color with ferric chloride in ethanol, and the formation of metal complexes from these amidoximes is being studied further in this laboratory. Reaction of **15** with acetic anhydride gave the O-acetylamidoxime, but reaction of **15** with benzenesulfonyl chloride yielded a product identified as the O-carboethoxyamidoxime apparently resulting from intermolecular transethoxycarbonylation. Reaction of **15** with ethyl chloroformate yielded **18** thus confirming this structure.

As previously reported[9] benzo[*f*]quinoline reacted with potassium cyanide and ethyl chloroformate to give the benzo analog of **6** (**19**). Reaction of **19** with hydroxylamine (this reaction differs from the reaction of **6** with hydroxylamine in that N,N-dimethylformamide was added to improve solubility) gave a mixture of four products. The expected amidoxime (**20**) was obtained in 11% yield. A small amount of benzo[*f*]quinaldamide which apparently resulted from hydrolysis of starting material was isolated. A third product, obtained in 6% yield, was **21** which apparently resulted from the hydrolysis and oxidation of **20**. The structure **21** was confirmed by treating benzo[*f*]quinaldonitrile with hydroxylamine to yield a compound identical in all respects with **21**. The major product (35% yield) of the hydroxylamine reaction was identified as **22**. The nmr spectrum of **22** showed that it was indeed the 1,4-dihydro compound by its AX_2 splitting pattern. Bramley and Johnson[10] have studied a similar series of compounds, **23** and **24**, and the nmr spectrum reported by them is consistent with this series. Seeley and coworkers[11] have studied the ultraviolet spectrum of **23** and **24**, and the spectra found in this work for **19** and **22** are consistent. Methylation of either **19** or **22** with methyl iodide in the presence of sodium hydride in N,N-dimethylformamide gave rise to the same methylated product **25**. The spectra of **25** was again consistent with the 1,4-dihydro structure, and hydrolysis of **25** yielded the known benzo[*f*]-lepidine.[12] It should be noted that alkylation of the quinoline Reissert compound (**2**) with methyl iodide occurs in the 4 position.[13]

Reaction of isoquinoline, potassium cyanide, and ethyl chlorothioformate gave **26** which is the sulfur analog of **6**. Treatment of **26** with methyl iodide and sodium hydride in N,N-dimethylformamide gave rise to the methylated product **27** in good yield. Acid-catalyzed hydrolysis of **26** gave isoquinoline.

Experimental Section[14]

Preparation of Reissert Analogs from Chloroformates.—To a mixture of 0.16 mol of isoquinoline (or quinoline) in 150 ml of methylene chloride and 0.48 mol of potassium cyanide in 40 ml of water was added 0.32 mol of the appropriate chloroformate over a 2-hr period. After an additional 4 hr of stirring, the solution was washed with water, dilute HCl, water, dilute NaOH, and water. Concentration of the methylene chloride and recrystallization yielded the products indicated in Table I.

Alkylation of 6 (R = C_2H_5).—To a mixture of 0.01 mol of **6** (R = C_2H_5) and 0.02 mol of methyl iodide in 40 ml of N,N-dimethylformamide was added with stirring 0.01 mol of a 30% sodium hydride in oil dispersion. Stirring was continued for 90 min, and the mixture was poured onto 500 g of crushed ice to give a 92% yield of solid, mp 69–70°. Recrystallization from ethanol gave **8**, mp 72–73°.

Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.40; H, 5.83; N, 11.56. Found: C, 69.41; H, 5.82; N, 11.69.

Hydrolysis of **8** with alcoholic potassium hydroxide gave 1-methylisoquinoline in 89% yield. The picrate, mp 231–233°, was identical with an authentic sample.

Condensation of 6 (R = C_2H_5) with Benzaldehyde.—To a solution of 0.005 mol of **6** (R = C_2H_5) in anhydrous ether and sufficient anhydrous dioxane to cause solution at −30° under a nitrogen atmosphere was added with stirring sufficient *n*-butyllithium solution to generate a permanent red color. To the red solution was added 3.0 ml of benzaldehyde, and the mixture was stirred at −30° for 1 hr. After stirring for an additional 13 hr at room temperature, the solution was washed with water, dilute hydrochloric acid, and water. Evaporation of the ether and recrystallization from ethanol gave a 38% yield of **9**: mp 166–167°; nmr (DMSO-d_6) τ 2.9 and 3.6 (doublets of the olefinic H's), 3.4 (singlet), 2.4 [multiplet, (9 H), of the aromatic H's].

Anal. Calcd for $C_{18}H_{12}N_2O_2$: C, 74.99; H, 4.20; N, 9.72. Found: C, 75.06; H, 4.25; N, 9.66.

The same product was obtained using other analogs of **6**.

Treatment of 0.01 mol of **6** (R = C_2H_5) with 0.01 mol of benzaldehyde and 0.02 mol of sodium hydride as described above for the alkylation in N,N-dimethylformamide gave a 47% yield of **13**, mp 107–109°, which was identical with an authentic sample.

Use of 0.01 mol of sodium hydride in this procedure led to the isolation of a 13% yield of **14**, mp 166–168° (hexane–ethyl acetate). The nmr spectrum lacked the singlet present in the nmr spectrum of **9**.

Anal. Calcd for $C_{17}H_{11}NO_2$: C, 78.15; H, 4.24; N, 5.36. Found: C, 78.22; H, 4.07; N, 5.39.

Hydrolysis of **14** with alcoholic potassium hydroxide gave an 88% yield of **13**.

Acid Hydrolysis of 6 (R = C_2H_5).—A mixture of 0.5 g of **6** (R = C_2H_5), 10 ml of acetic acid, and 10 ml of hydrobromic acid was heated on the steam bath for 3 hr. The solution was cooled, made basic, and extracted with ether. Concentration of the ether gave a 74% yield of isoquinoline which was identified as its picrate.

Treatment of 6 (R = C_2H_5) with Sodium Hydride.—A mixture of 0.01 mol of **6** (R = C_2H_5) and 0.01 mol of a 30% sodium hydride oil dispersion was stirred for 90 min and poured onto 500 g of ice to give 0.47 g (32%) of isoquinaldonitrile, mp 87–89°,

(9) L. E. Katz and F. D. Popp, *J. Heterocycl. Chem.*, **5**, 249 (1968).
(10) R. Bramley and M. D. Johnson, *J. Chem. Soc.*, 1372 (1965).
(11) M. G. Seeley, R. E. Yates, and C. R. Noller, *J. Amer. Chem. Soc.*, **73**, 772 (1951).
(12) K. N. Campbell and I. J. Schaffner, *ibid.*, **67**, 86 (1945).
(13) V. Boekelheide and J. Weinstock, *ibid.*, **74**, 660 (1952).
(14) All melting points are corrected and taken in capillaries. Analyses by Spang Microanalytical Laboratories, Ann Arbor, Mich.

which was identical with an authentic sample. Substitution of dimethyl sulfoxide for the N,N-dimethylformamide gave an 84% yield of the nitrile.

Reaction of 6 (R = C_2H_5) with Hydroxylamine.—To 6.35 g (0.0278 mol) of 6 (R = C_2H_5) in 140 ml of absolute methanol at −8° was added a cooled solution of 0.64 g (0.0278 g-atom) of Na and 1.22 g (0.0278 mol) of hydroxylamine hydrochloride in 40 ml of absolute methanol. The mixture was stirred at −8° for 50 min and filtered to give 2.24 g of starting material. The filtrate was evaporated, and 3.64 g of solid was obtained. Recrystallization from ethanol gave **15**: mp 153–155°; ir (KBr) 3480, 3430, 3345, 1680, 1662, 1030 cm^{-1}.

Anal. Calcd for $C_{13}H_{15}N_3O_3$: C, 59.80; H, 5.79; N, 16.10. Found: C, 59.74; H, 5.83; N, 16.16.

After the isolation of **15**, 0.02 g of **16**, mp 183–185°, was obtained from the filtrate: ir (KBr) 3420, 3300, 3220, 1715, 1670, 1030 cm^{-1}.

Anal. Calcd for $C_{13}H_{14}N_2O_3$: C, 63.66; H, 5.75; N, 11.42. Found: C, 63.61; H, 5.67; N, 11.33.

Use of 0.01 g-atom of Na to 0.0046 mol of **6** gave only **16**.

Hydrolysis of 16.—A mixture of 0.02 g of **16** and 0.10 g of potassium hydroxide in 5 ml of ethanol was refluxed for 15 min and concentrated. The residue was dissolved in water and extracted with ether. Concentration of the ether gave isoquinaldamide which was identical with an authentic sample.

Preparation of 1-Amidoxamidoisoquinoline (17).—To a solution of 0.62 g (0.0044 mol) of isoquinaldonitrile in 20 ml of methanol at −10° was added with stirring a cooled solution of 0.305 g (0.0044 mol) of hydroxylamine hydrochloride and 0.11 g (0.0044 g-atom) of Na in methanol. The mixture was stirred at −10° for 30 min and concentrated to give a solid which was washed with water. Crystallization of the solid from a minimum of ethanol and then methanol gave 0.185 g (23%) of **17**, mp 126–128°.

Anal. Calcd for $C_{10}H_9N_3O$: C, 64.20; H, 4.85. Found: C, 64.32; H, 4.95.

Reaction of 15 with Acetic Anhydride.—A mixture of 5 ml of acetic anhydride and 0.11 g (0.0004 mol) of amidoxime **15** was heated for 30 min at 100° and then concentrated to give a solid. Recrystallization from ethanol gave the O-acetylamidoxime, mp 135–136°.

Anal. Calcd for $C_{15}H_{17}N_3O_4$: C, 59.40; H, 5.65; N, 13.87. Found: C, 59.45; H, 5.61; N, 13.82.

Reaction of 15 with Benzenesulfonyl Chloride.—A mixture of 0.62 g (0.0024 mol) of the amidoxime **15**, 10 ml of pyridine, and 0.65 g (0.0035 mol) of benzenesulfonyl chloride was stirred at 0° for 5 hr and then concentrated. Treatment of the residue with hexane and methylene chloride caused a solid to form, and recrystallization from toluene gave 0.055 g (7%) of a solid (**18**): mp 133–134°; ir (KBr) 3430, 3375, 1765, 1710, 1635, 1577, 1020 cm^{-1}.

Anal. Calcd for $C_{16}H_{19}N_3O_5$: C, 57.50; H, 5.75; N, 12.60. Found: C, 57.74; H, 5.76; N, 12.55.

This same product **18** was obtained in 74% yield by the reaction of **15** and ethyl chloroformate in pyridine at 0°.

Reaction of 19 with Hydroxylamine.—To a mixture of 2.75 g (0.001 mol) of **19**,[9] 50 ml of methanol, and 50 ml of N,N-dimethylformamide was added a cooled solution of 0.23 g (0.001 mol) of sodium and 0.80 g (0.001 mol) of hydroxylamine hydrochloride in 20 ml of methanol. The mixture was stirred at −8° for 80 min and concentrated *in vacuo*. When all of the methanol was removed, the solution was added to 450 g of ice, and a crude solid collected. Chromatography of this solid on alumina gave four components. Elution with benzene gave 0.98 g (35%) of a solid (**22**): mp 135–136° (ethanol); ir (KBr) 2250, 1715, 1030 cm^{-1}; uv 218 mμ (log ε 4.68), 238 (4.63) [the starting material **19** had no ir peak at 2250 cm^{-1} and had uv peaks at 207 mμ (log ε 4.34), 243 (4.63), and 319 (3.63)]; nmr (CCl_4) a quartet (2 H) and triplet (3 H) at τ 5.6 and 8.6 (ethyl), a multiplet at 2.0–2.8 (6 H, aromatic), and an AX_2 pattern at 3.6 (1 H) and 6.3 (2 H).

Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.45; H, 5.07; N, 10.05. Found: C, 73.28; H, 4.98; N, 10.24.

The next component further elution with benzene had mp 239° and was identical with an authentic sample of benzo[*f*]-quinaldamide.

Elution with ethanol gave 0.145 g (6%) of solid **21**, mp 211–213° from benzene. This sample was identical with the material described below.

Further elution with ethanol gave 0.33 g (11%) of solid **20**, mp 182–183° from ethanol.

Anal. Calcd for $C_{17}H_{17}N_3O_3$: C, 65.65; H, 5.50; N, 13.50. Found: C, 65.49; H, 5.48; N, 13.70.

Preparation of 23.—To a mixture of 0.715 g (0.0035 mol) of benzo[*f*]quinaldonitrile and 20 ml of methanol was added a solution of 0.08 g (0.0035 mol) of sodium and 0.25 g (0.0035 mol) of hydroxylamine hydrochloride in 10 ml of methanol. After stirring in the cold for 30 min, 0.47 g (56%) of solid was collected and recrystallized from ethanol to give **23**, mp 211–212°, identical with that reported above.

Anal. Calcd for $C_{14}H_{11}N_3O$: C, 70.97; H, 4.68; N, 17.72. Found: C, 70.97; H, 4.71; N, 17.69.

Methylation of 19 and 22.—To a solution of 0.133 g (0.0005 mol) of **22** in 5 ml of N,N-dimethylformamide at 0° was added 0.10 g (0.012 mol) of 30% sodium hydride in oil with stirring. To the purple solution was then added a few drops of methyl iodide. After disappearance of the color, the solution was poured on ice, and 0.11 g (78%) of solid **25**, mp 152–153° from ethanol, was obtained: nmr (CCl_4) τ 2.0–2.7 (multiplet, 6 H, 3.5 (doublet 1 H, H_2), 5.8 (multiplet, 3 H, H_1 and CH_2 of ethyl), 8.5 (multiplet 6 H, two CH_3).

Anal. Calcd for $C_{18}H_{16}N_2O_2$: C, 74.00; H, 5.58; N, 9.58. Found: C, 74.02; H, 5.60; N, 9.60.

In a similar manner **19** gave the same product.

Hydrolysis of 25 to Benzo[*f*]lepidine.—A small amount of the methylated compound **25** was refluxed with alcoholic potassium hydroxide. Concentration gave a solid, mp 98–100° from hexane (lit.[14] mp 100–101° for benzo[*f*]lepidine).

Preparation of Sulfur Analog 26.—Use of ethyl chlorothiolformate and isoquinoline in the preparation of **6** described above gave a 44% yield of **26**, mp 107–108° from ethanol.

Anal. Calcd for $C_{13}H_{12}N_2OS$: C, 63.91; H, 4.95; N, 11.47. Found: C, 63.89; H, 4.90; N, 11.41.

Alkylation of 26.—Reaction of **26** with methyl iodide as described above for the preparation of **8** from **6** gave a nearly quantitative yield of **27**, mp 79–81° from ethanol.

Anal. Calcd for $C_{14}H_{14}N_2OS$: C, 65.09; H, 5.46; N, 10.84. Found: C, 65.16; H, 5.61; N, 10.71.

Acid Hydrolysis of 26.—Hydrolysis of **26** with acetic acid–hydrobromic acid as described above for the hydrolysis of **6** gave isoquinoline, isolated as its picrate.

Registry No.—**6** (R = Me), 17954-40-4; **6** (R = Et), 17954-22-2; **6** (R = CH_2CCl_3), 17954-24-4; **6** (R = CH_2Ph), 17954-25-5; **6** (R = Ph), 17954-26-6; **6** (R = *p*-$MeOC_6H_4$), 17954-27-7; **7** (R = Me), 17954-21-1; **7** (R = Et), 17954-23-3; **8**, 17954-28-8; **9**, 17954-29-9; **14**, 17954-30-2; **15**, 17954-31-3; **15** (O-acetylamidoxime, 17953-94-5; **16**, 17954-32-4; **17**, 17954-33-5; **18**, 17954-34-6; **20**, 17954-36-8; **21**, 17954-41-5; **22**, 17954-35-7; **25**, 17954-37-9; **26**, 17954-38-0; **27**, 17954-39-1.