pyridine in 50 ml. of methanol was allowed to stand 16 hr. The solution was warmed to dissolve some precipitated material while 2–3 g. of sodium iodide was stirred in. When the solution was cooled, 3.1 g. of product was obtained. The analytical sample, which melted at 268–269°, was obtained by one crystallization from methanol.

Anal. Calcd. for $C_{15}H_{13}ClIN$: C, 45.30; H, 3.29; N, 10.57. Found: C, 45.31; H, 3.00; N, 10.55.

Reaction Products of I with Salts of Aromatic Amines. A. 7-Chloro-4-anilino-1-methylquinolinium Chloride.—A solution of 6.5 g. of I (0.02 mole) and 2.6 g. of aniline hydrochloride (0.02 mole) in 60 ml. of water was allowed to stand for 72 hr. The mixture was heated to boiling, made just neutral with ammonium hydroxide and a few grams of sodium chloride added. The yellow mat of needles was filtered and washed with cold 1:1 methanol–water. The product weighed 6.5 g. and melted at 285–286° (dec.) after two recrystallizations from acetone.

Anal. Calcd. for $C_{16}H_{14}Cl_2N_2$: C, 62.96; H, 4.62; N, 9.18. Found: C, 63.21; H, 4.80; N, 9.32.

B. 7-Chloro-4-*p*-hydroxyanilino-1-methylquinolinium chloride (VIIa).—A mixture of 16.2 g. of I (0.05 mole) and 8.0 g. of *p*-aminophenol hydrochloride (0.055 mole) was dissolved in 75 ml. of water. Within 20 minutes the product had begun to separate. After 16 hr., the solid was filtered and recrystallized from water. A yield of 10.6 g. was obtained, whose melting point was above 300°.

Anal. Calcd. for $C_{16}H_{14}Cl_2N_2O$: C, 59.82; H, 4.39; N, 8.72. Found: C, 59.57; H, 4.32; N, 8.66.

When a solution of 4.0 g. of the above salt in 350 ml. of water was made basic with concentrated ammonium hydroxide, a yellow solid (VIIIa) was precipitated. The product weighed 3.0 g. and, after two recrystallizations from dimethylformamide, the melting point was 275–277°.

Anal. Calcd. for $C_{16}H_{13}ClN_2O$: C, 67.49; H, 4.60; N, 9.84; Cl, 12.45; O, 5.62. Found: C, 67.71; H, 4.70; N, 9.75; Cl, 12.36; O, 5.80.

C. 7-Chloro-4-(4′-hydroxy-5′-diethylaminomethylanilino)-1-methylquinolinium Chloride Hydrochloride (VIIb).—A solution of 12.8 g. of I (0.04 mole) and 10.6 g. of 4-amino-2-diethylaminomethylphenol dihydrochloride[11] in 75 ml. of water was allowed to stand 24 hr. The solution was then made basic with concentrated ammonium hydroxide and the precipitated solid was filtered and washed with water. The product was dissolved in 400 ml. of acetone and then 15 ml. of concentrated hydrochloric acid was added. On storage, the precipitated gum solidified and was recrystallized by dissolving in a minimum of warm methanol and adding seven volumes of acetone. The yield was 11.8 g., m.p. 132–134° (fused at 102° and resolidified).

Anal. Calcd. for $C_{21}H_{25}Cl_2N_3O_2 \cdot HCl \cdot 3H_2O$: C, 50.76; H, 6.49; N, 8.46; Cl, 21.41. Found: C, 50.64; H, 6.59; N, 8.28; Cl, 21.60.

When a solution of 4.0 g. of the salt was dissolved in 100 ml. of water and made basic with concentrated ammonium hydroxide, 3.1 g. of the imine VIIIb was precipitated. After two recrystallizations from dilute methanol, the melting point was 143–144°.

Anal. Calcd. for $C_{21}H_{24}ClN_3O$: C, 68.19; H, 6.54; N, 11.36; Cl, 9.59. Found: C, 68.66; H, 6.97; N, 11.30; Cl, 9.81.

NORTH CHICAGO, ILLINOIS

[CONTRIBUTION FROM ABBOTT LABORATORIES]

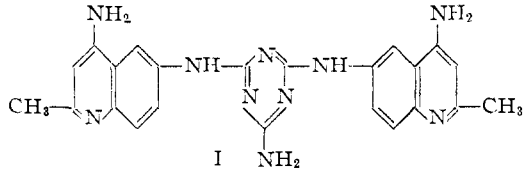
The Preparation of Some N,N′-Bis-(4-quinaldyl)-α,ω-diaminoalkanes as Potential Trypanocides[1]

BY R. U. SCHOCK

RECEIVED OCTOBER 8, 1956

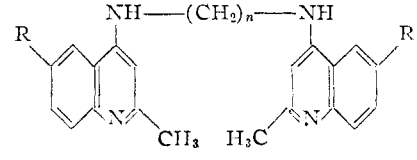
The preparation of the title compounds by reaction of substituted 4-chloro- or 4-methoxyquinaldines with α,ω-diaminoalkanes is described. Many are curative against *T. gambiense* in mice at doses comparable to standard trypanocides.

Although Suramin and Pentamidine, the two drugs used most commonly in human trypanosomiasis, are not quinoline derivatives, many 4-aminoquinaldines are active against various Trypanosoma.[2–4] A proper review of such compounds is beyond the scope of this publication; however, many fall into a general class: a bridging element combined at the 6- or 8-positions of two quinoline nuclei producing a symmetrical structure. An example of this is Surfen C (I), which found utility at one time in *T. congolense* infections.



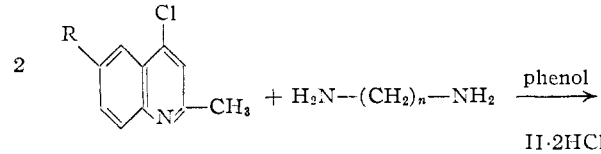
I

Since there are no recorded examples of analogous trypanocides wherein symmetry is achieved by attachment in the 4-positions, it was of interest to prepare a series of this type. The synthesis of compounds represented as II [R = NH_2, OCH_3, $N(CH_3)_2$] is the subject of this communication.



II

The preparation of this general type was accomplished according to the scheme



II·2HCl

The intermediate 4-chloroquinaldines were obtained by reaction of $POCl_3$ with the corresponding 4-hydroxyquinaldines readily available through the Conrad–Limpach reaction.[5] Reaction at 140–

(1) Presented before the Division of Medicinal Chemistry at the 129th National Meeting of the American Chemical Society, Dallas, Texas, April, 1956.

(2) H. Jensch, *Angew. Chem.*, **50**, 891 (1937); *Ann.*, **568**, 73 (1950).

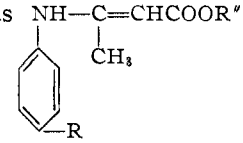
(3) L. P. Walls, *Chemistry & Industry*, 606 (1951).

(4) M. G. Pratt and S. Archer, THIS JOURNAL, **70**, 4065 (1948).

(5) R. C. Elderfield, "Heterocyclic Compounds," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1952, p. 32.

Table I

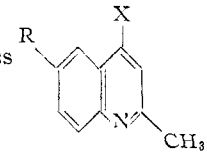
Properties of β-Anilinocrotonic Esters



R	R″	Method of prepn.	M.p., °C.	Formula	Nitrogen, % Calcd.	Found	Yield, %
$(CH_3)_2N$	CH_3	Benzene H_2O sep.	85–86	$C_{13}H_{18}N_2O_2$	11.96	12.03	79
CN	CH_3	Stand room temp.	124–125	$C_{12}H_{12}N_2O_2$	12.96	12.97	85
$N(CH_3)COCH_3$	CH_3	Benzene H_2O sep.	106–107	$C_{14}H_{18}N_2O_3$	10.68	10.84	76
COOH	C_2H_5	Reflux in alcohol	172–173	$C_{13}H_{15}NO_4$	5.62	5.71	71

Table II

Properties of Intermediate Quinaldines



X	R	M.p., °C.	Formula	Nitrogen, % Calcd.	Found	Yield, %	Ref.
OH	$NHCOCH_3$	>300				85	4
Cl	$NHCOCH_3$	215–216				75	9
OCH_3	$NHCOCH_3$	231–232[a]				83	4
OH	$N(CH_3)_2$	303–305	$C_{12}H_{14}N_2O$	13.85	13.92	50	
Cl	$N(CH_3)_2$	92–93	$C_{12}H_{13}ClN_2$	12.70	13.01	89	
OH	OCH_3		$C_{11}H_{11}NO_2$	7.40	7.51	63[b]	10
Cl	OCH_3	97–98	$C_{11}H_{10}ClNO$	6.75	6.58	83	10
OCH_3	OCH_3	93–94	$C_{12}H_{13}NO_2$	71.49; 6.45[c]	71.38; 6.76	66	10
OH	NO_2	>300				70	11
Cl	NO_2	142–143				92	12
OCH_3	NO_2	195–196	$C_{11}H_{10}N_2O_3$	12.84	12.80	51	
OH	CN	297–298	$C_{11}H_8N_2O$	15.21	15.25	72	
Cl	CN	141–142	$C_{11}H_7ClN_2$	13.83	13.76	60	
OCH_3	CN	178.5–179.5	$C_{12}H_{10}N_2O$	14.14	13.99	84	
OH	$N(CH_3)COCH_3$	360 (dec.)	$C_{13}H_{14}N_2O_2$	12.17	12.26	44	
OH	$COOC_2H_5$	260–261					11
Cl	$COOC_2H_5$	113–114	$C_{13}H_{12}ClNO_2$	62.53; 4.85[c]	62.69 4.94	95	
OCH_3	$COOC_2H_5$	126–127	$C_{14}H_{15}NO_3$	68.55; 6.17[c]	68.90; 6.24	59	
OH	COOH	>300	$C_{11}H_9NO_3$	6.89	6.91	50	
OH	Cl	>300				53	12
Cl	Cl	84–85				78	12

[a] Lit. m.p. 217–218°. [b] Yield based on starting aromatic amine. [c] Carbon–hydrogen analysis.

160° in phenol[6] with an appropriate diamine yielded II directly as the dihydrochloride. In some cases the 4-methoxyquinaldines, also readily available from the 4-hydroxyquinaldines, were used with equal success under similar reaction conditions.

For the preparation of N,N'-bis-(6-amino-4-quinaldyl)-α,ω-alkanediamines, the corresponding 6-acetamido compounds were hydrolyzed in hydrochloric acid solution. In this way the colorless tetrahydrochlorides were obtained, but these reverted to the yellow sparingly soluble dihydrochlorides on crystallization from water.

Several other bis-quinaldines were planned in which R was represented as methylamino, cyano, carboxy and carbethoxy. These series failed at one of the steps in the synthesis; however, intermediates successfully prepared are listed in appropriate tables.

(6) A. R. Surrey and R. A. Cutler, This Journal, **73**, 2623 (1951), demonstrate the role played by phenol in reactions of this type.

Chemotherapeutic Results.[7]—All compounds were tested against *T. gambiense* in mice. Activity in the 6-amino series was displayed by all members with the exception of the first ($n = 2$). Maximum curative activity was evidenced in the $n = 5$–8 range. Reduced efficiency was encountered in the 6-methoxy and 6-dimethylamine series, although maximum activity was again encountered in the range $n = 6$–8.

Experimental[8]

The intermediate β-anilinocrotonic esters usually were prepared from equimolecular quantities of aromatic amine

(7) Experimental results were provided by Dr. G. F. Otto and Mr. J. C. Moetsch of these laboratories.

(8) Microanalyses by E. F. Shelberg, Chief Microanalyst, and staff.

(9) M. V. Rubtsov and V. I. Bunina, *J. Gen. Chem.* (*U.S.S.R.*), **14**, 1128 (1944); *C. A.*, **40**, 7194 (1946).

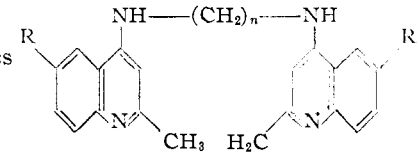
(10) M. Conrad and L. Limpach, *Ber.*, **21**, 1651 (1888).

(11) C. E. Kaslow and R. D. Stayner, This Journal, **70**, 3350 (1948).

(12) W. O. Kermack and A. P. Weatherhead, *J. Chem. Soc.*, 563 (1939).

TABLE III

PROPERTIES OF N,N'-BIS-(4-QUINALDYL)-α,ω-DIAMINOALKANES



n	R	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found	Yield, %
2	NH_2	$C_{22}H_{24}N_2 \cdot 2HCl \cdot 2H_2O$	54.88	55.00	6.28	5.91	17.46	17.11			65
3	NH_2	$C_{23}H_{26}N_6 \cdot 2HCl \cdot 4H_2O$	51.98	51.71	6.82	6.88	15.82	15.78			
3	NH_2	$C_{23}H_{26}N_6 \cdot 4HCl$	51.89	52.20	5.67	6.02	15.79	15.61	26.64	26.56	65
4	NH_2	$C_{24}H_{28}N_6 \cdot 2HCl \cdot 2H_2O$	56.58	56.10	6.73	6.65	16.50	16.83			79
5	NH_2	$C_{25}H_{30}N_6 \cdot 2HCl \cdot 3H_2O$	55.45	55.62	7.07	7.19	15.52	15.59			43
6	NH_2	$C_{26}H_{32}N_6 \cdot 2HCl$	62.27	62.00	6.83	6.92	16.76	16.67	14.14	14.04	76
6	NH_2	$C_{26}H_{32}N_6 \cdot 2HCl \cdot 2H_2O$	58.09	58.10	7.13	7.37	15.64	15.63			
7	NH_2	$C_{27}H_{34}N_6 \cdot 2HCl \cdot H_2O$	60.77	61.14	7.18	7.44	15.75	16.18			39
8	NH_2	$C_{28}H_{36}N_6 \cdot 2HCl \cdot 3H_2O$	57.62	57.64	7.60	7.57	14.40	14.86	12.15	12.03	69
9	NH_2	$C_{29}H_{38}N_6 \cdot 2HCl \cdot 2H_2O$	60.09	59.80	7.65	7.45	14.50	14.52			29
10	NH_2	$C_{30}H_{40}N_6 \cdot 2HCl \cdot 2H_2O$	60.69	60.99	7.81	7.97	14.16	14.34			57
11	NH_2	$C_{31}H_{42}N_6 \cdot 2HCl \cdot 2H_2O$	61.27	60.62	7.96	7.81	13.23	13.99			51
12	NH_2	$C_{32}H_{44}N_6 \cdot 2HCl \cdot 2H_2O$	61.82	62.12	8.11	8.17	13.52	13.91			50
4	$N(CH_3)_2$	$C_{28}H_{36}N_6 \cdot 2HCl$	63.50	63.46	7.07	7.21	15.87	15.58	13.56	13.37	61
6	$N(CH_3)_2$	$C_{30}H_{40}N_6 \cdot 2HCl$	64.62	65.02	7.59	7.77	15.07	15.22			90
7	$N(CH_3)_2$	$C_{31}H_{42}N_6 \cdot 2HCl$	65.13	64.75	7.76	7.65	14.70	14.75			61
8	$N(CH_3)_2$	$C_{32}H_{44}N_6 \cdot 2HCl$	65.62	65.74	7.92	7.70	14.35	14.27			42
9	$N(CH_3)_2$	$C_{33}H_{46}N_6 \cdot 2HCl$	66.09	66.22	8.07	7.96	14.01	13.72			54
10	$N(CH_3)_2$	$C_{34}H_{48}N_6 \cdot 2HCl$	66.54	66.47	8.15	8.29	13.70	13.51			95
4	OCH_3	$C_{26}H_{30}N_4O_2 \cdot 2HCl \cdot 2H_2O$	57.88	57.42	6.73	6.99	10.39	10.21			72
6	OCH_3	$C_{28}H_{34}N_4O_2 \cdot 2HCl \cdot 3H_2O$	57.43	57.90	7.23	7.50	9.57	9.67			77
7	OCH_3	$C_{29}H_{36}N_4O_2 \cdot 2HCl \cdot 2.5H_2O$	58.98	58.75	7.68	7.50	9.49	9.76			43
8	OCH_3	$C_{30}H_{38}N_4O_2 \cdot 2HCl \cdot H_2O$	62.48	62.38	7.33	7.62	9.70	9.98			80
9	OCH_3	$C_{31}H_{40}N_4O_2 \cdot 2HCl \cdot 3H_2O$	59.32	59.47	7.71	7.67	8.93	9.30			88
10	OCH_3	$C_{32}H_{42}N_4O_2 \cdot 2HCl \cdot 2.5H_2O$	60.75	60.75	8.13	8.05	8.86	8.89			66
6	Cl	$C_{26}H_{28}Cl_2N_4 \cdot 2HCl$	57.79	57.84	5.60	5.17	10.37	10.28			68
6	NO_2	$C_{36}H_{28}N_6O_4 \cdot 2HCl \cdot 3H_2O$					13.87	13.84			43

and methyl or ethyl acetoacetate in refluxing benzene under a water separator. A few drops of concentrated hydrochloric acid served as catalyst. In some cases, the condensation was carried out by merely allowing the reactants to stand or heating in refluxing alcohol. Table I lists the properties of some of the intermediate esters not appearing in the literature. In many cases where the ester did not show signs of crystallization within a reasonable length of time, cyclization was carried out on the crude product in boiling Dowtherm A. The properties of intermediate quinaldines are listed in Table II. The following experiment will serve as a general example for the preparation of intermediates.

6-Dimethylamino-4-hydroxyquinaldine.—A mixture of 483 g. (3.55 moles) of freshly distilled *p*-dimethylaminoaniline, 412 g. (3.55 moles) and 2 ml. of concentrated hydrochloric acid in 1 l. of benzene was boiled under a reflux condenser fitted with a water separator. After 16 hr., 71 ml. of water had collected (theory is 66 ml.). The solvent was then removed at reduced pressure and the residual oil allowed to crystallize. Purification was effected by trituration with Skellysolve B. The melting point of the crude product was 82–84°. Recrystallization for analysis was carried out in cyclohexane or acetone–cyclohexane.

Cyclization.—In a 5-l. round-bottom flask fitted with a stirrer, condenser arranged for distillation and addition tube was placed 1700 ml. of Dowtherm A. The solvent was heated to boiling and 426 g. of the above crude ester added as rapidly as possible, keeping the internal temperature above 250°. The solid which separated when cool was filtered and washed with acetone.

6-Dimethylamino-4-chloroquinaldine.—To 256 g. of the above product in a 3-l. flask was added 512 ml. of phosphorus oxychloride. The mixture became orange and the solid, on shaking, gradually went into solution with evolution of heat. After standing for 1 hr., the crystalline product was triturated with 500 ml. of dry ether and quickly filtered. The cake was suspended in 1 l. of water and, with stirring, concentrated ammonium hydroxide added until permanently basic. The temperature was maintained below 30° by addition of ice. The base was filtered, washed well with water and recrystallized from dilute methanol.

The preparation of the 4-methoxyquinaldines was carried out according to that employed by Pratt and Archer[4] for 6-acetamido-4-methoxyquinaldine.

N,N'-Bis-(6-dimethylamino-4-quinaldyl)-1,6-hexanediamine.—The following reaction is typical for preparations listed in Table III starting with a 4-chloroquinaldine. A mixture of 22.1 g. (0.1 mole) of 4-chloro-6-dimethylaminoquinaldine, 8.1 g. (0.05 mole) of 72% 1,6-hexanediamine and 20 g. of phenol was heated gradually in a bath to approximately 135°. At this point an exothermic reaction commenced, and the flask was removed from the bath until the temperature began to fall. The reaction was completed by heating at 150–160° for 4 hr. The hot melt was then poured into 400 ml. of cold acetone and the salt filtered and washed liberally with acetone. The crude yield was 31.2 g. Recrystallization was effected by gradual addition of concentrated hydrochloric acid to a suspension of the crude dihydrochloride in 800 ml. of hot water until solution took place. After carbon treatment, 40% sodium hydroxide solution was added to the hot filtrate to *p*H 1–2 to precipitate the salt again as the dihydrochloride. When cool, the crystalline product was separated by filtration, washed liberally with distilled water and dried at 50°.

Recrystallization of dihydrochlorides not containing a basic substituent was effected either from water or water containing a few per cent. hydrochloric acid to inhibit gelation.

N,N'-Bis-(6-amino-4-quinaldyl)-1,6-hexanediamine.—The following reaction is typical of those involving a 4-methoxyquinaldine. A mixture of 46.0 g. (0.2 mole) of 6-acetamido-4-methoxyquinaldine, 16 g. (0.1 mole) of 70% 1,6-hexanediamine and 46 g. of phenol was heated under reflux in a bath. The internal temperature fell from 135 to 108° over a 2-hr. period. At this time, the condenser was

removed and fitted for distillation. The bath temperature was raised gradually as distillation proceeded, and the internal temperature rose to 160°. After 3 hr. the melt was poured into a mixture of 200 ml. of 95% ethanol and 20 ml. of concentrated hydrochloric acid. The solution was diluted slowly with acetone until the final volume approximated 700–800 ml. The yellow solid was separated by filtration and then hydrolyzed by stirring for 4 hr. under reflux with 150 ml. of concentrated hydrochloric acid and 300 ml. of water. The colorless tetrahydrochloride was filtered and washed with 95% ethanol. Small portions could be recrystallized from 4:1 water–concentrated hydrochloric acid mixture, but few samples could be obtained in analytical purity. Recrystallization from water yielded the yellow dihydrochloride.

NORTH CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, CIBA PHARMACEUTICAL PRODUCTS, INC.]

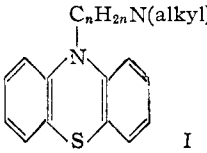
Thianaphtheno[3,2-b]indoles

BY L. H. WERNER, D. C. SCHROEDER AND S. RICCA, JR.

RECEIVED SEPTEMBER 17, 1956

A series of 10H-thianaphtheno[3,2-b]indoles was prepared by the Fischer indole reaction of phenylhydrazines with 3-hydroxythianaphthenes. These were alkylated in the 10-position with dialkylaminoalkyl chlorides. A number of these compounds showed antihistaminic activity.

Interest in the diverse and remarkable pharmacological activity of 10-dialkylaminoalkylphenothiazines (I),[1] *e.g.*, chloropromazine, promethazine and

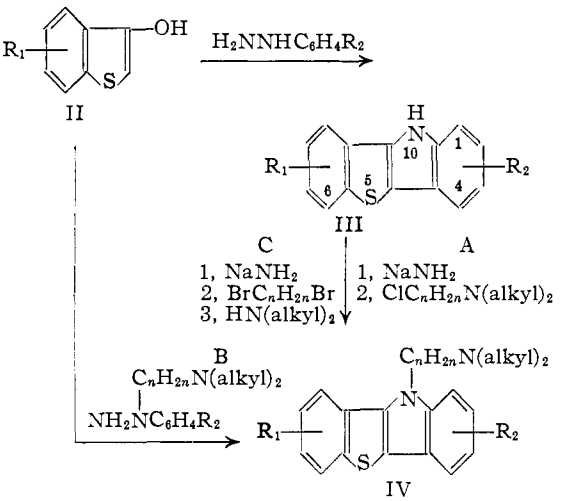


I

profenamine, induced us to synthesize 10-substituted thianaphtheno[3,2-b]indoles (IV) (Table I). The preparation of this type of compound had been studied previously by McClelland and D'Silva[2] and Dalgliesh and Mann.[3] However, their studies did not include compounds with basic sidechains at the 10-position.

The thianaphthenoindoles prepared in this series were obtained by a Fischer indole reaction of appropriately substituted 3-hydroxythianaphthenes (II)[4] with phenylhydrazines in glacial acetic acid. These 10H-thianaphtheno[3,2-b]indoles are easily obtained as they crystallize readily from the reaction mixture. In most cases, the basic sidechain was then attached by conversion to the sodio-derivative with sodium amide and treatment with a dialkylaminoalkyl chloride (procedure A). Three additional approaches also were studied. In general, the procedure we have designated as A gave the best yields. 3-Hydroxythianaphthenes (II) can react directly with N^2-substituted phenylhydrazines to give 10-substituted thianaphtheno[3,2-b]indoles (procedure B). This method was, for example, used to prepare 10-(2-diethylaminoethyl)-thianaphthenoindole (Table I, 4) and 10-(5-diethylamino-2-pentyl)-7-methoxythianaphthenoindole (Table I, 50).

The reaction of the sodio-derivative of III with an alkylene dibromide and treatment of the 10-(ω-bromoalkyl)-thianaphthenoindole with a secondary amine (procedure C) also gave the desired compounds (IV), but in a poorer yield than procedure A. The fourth approach studied is illustrated by the following example: 7-methoxy-10-(2-piperi-



R_1 = H, halogen, CH_3, OCH_3, OC_2H_5
R_2 = H, Cl, OCH_3, NO_2

dinoethyl)-thianaphthenoindole (Table I, 46) can be prepared by $LiAlH_4$ reduction of the piperidide of 7-methoxythianaphthenoindoleacetic acid (Table I, 48). In addition, 10-(3-aminopropyl)-thianaphthenoindole (Table I, 3) was prepared by the $LiAlH_4$ reduction of 10-(2-cyanoethyl)-thianaphthenoindole.[3]

Dalgliesh and Mann[3] had found that a substituent in the 4-position of the 3-hydroxythianaphthene or in the 2-position of the phenylhydrazine blocked the formation of the thianaphthenoindole ring system. We have reinvestigated the reaction between 6-chloro-3-hydroxy-4-methylthianaphthene and phenylhydrazine in acetic acid and found that 7-chloro-9-methyl-thianaphthenoindole is formed (Table I, 64). Likewise, we were able to prepare the 9-chloro- (Table I, 23) and the 8,9-dichlorothianaphthenoindole (Table I, 58) from 4-chloro- and 4,5-dichloro-3-hydroxythianaphthene, respectively. On the other hand, we can

(1) P. Viaud, *J. Pharm. and Pharmacol.*, **6**, 361 (1954).
(2) E. W. McClelland and J. L. D'Silva, *J. Chem. Soc.*, 227 (1932).
(3) C. E. Dalgliesh and E. G. Mann, *ibid.*, 653 (1947).
(4) A large number of substituted 3-hydroxythianaphthenes have been prepared as intermediates in the synthesis of thioindigos. They have been reviewed by H. D. Hartough and S. L. Meisel in "The Chemistry of Heterocyclic Compounds. Compounds with Condensed Thiophene Rings," A. Weissberger, Consulting Editor, Interscience Publishers, Inc., New York, N. Y., 1954, pp. 63-79.