OXAZOLOANTHRAPYRIDINES AND THEIR PROPERTIES

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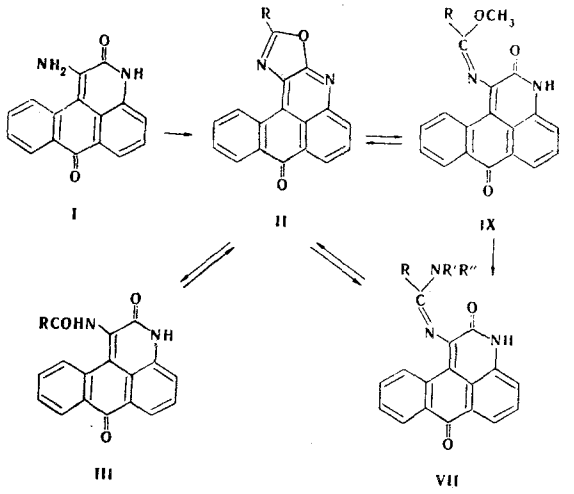
Acylation of 1-aminoanthrapyridones gives oxazoloanthrapyridines, for which reactions with opening of the oxazole ring are characteristic: 1-acylaminoanthrapyridones are formed in acid and alkaline hydrolysis, while 1-anthrapyridonylamidines and 1-anthrapyridonylimino esters, respectively, are formed by the action of amines and alkoxides. Similarly, dioxazoloanthradipyridines, which have similar properties, are formed from 1,8-diaminoanthra[1,9:-4,10]- and 1,7-diaminoanthra[1,9:5,10]dipyridones. Problems associated with the mechanism of formation of the oxazoloanthrapyridines are examined.

We have found that derivatives of a new heterocyclic polycondensed system – oxazoloanthrapyridine (oxazolo[4,5-c]-8H-dibenzo[*f*,ij]isoquinolin-8-one) – are formed in the acylation of 1-aminoanthrapyridones [1].* The reaction of 1-aminoanthrapyridone (I) with acetic, benzoic, propionic, butyric, and enanthic anhydrides proceeds to give the corresponding 2-substituted oxazoloanthrapyridines (IIa-e) in high yields and without contamination by the acylamino derivatives. Oxazoloanthrapyridines that contain substituents in the anthrone ring (IIf-i, Table 1) were similarly obtained. The acid chlorides or the acids themselves in the presence of $POCl_3$ and PCl_5 can be used in place of the carboxylic acid anhydrides. Compounds II are extremely readily hydrolyzed to 1-acylaminoanthrapyridones (III, Table 2) by the action of acids and alkalis, and III in turn can be again converted to II by the action of acid anhydrides. The latter transformation also occurs as a result of thermal dehydration of III, the conditions for which and completeness of which depend on the properties of the acyl residue. For example, 1-benzamidoanthrapyridone (IIIb) in a sealed capillary melts at a temperature close to the melting point of 1-phenyloxazoloanthropyridine (IIb, mp 292°) and undergoes complete conversion to the latter. The acetyl derivative (IIIa) does not melt on heating to 350°, but a mixture of deacylation – 1-aminoanthrapyridone (I) – and cyclization – 2-methyloxazoloanthrapyridine (IIa) – products is formed when it is heated at ~300° for 15-20 min.



*See [2] for brief communication.

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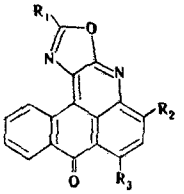
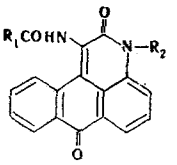
TABLE 1. Oxazoloanthrapyridines



Compound	R_1	R_2	R_3	mp, °C	Empirical formula	Found, % C	Found, % H	Found, % N	Calc., % C	Calc., % H	Calc., % N	Yield, %
IIa*	CH_3	H	H	274—275	$C_{18}H_{10}N_2O_2$	75,6	3,5	10,0	75,5	3,5	9,8	97
IIb	C_6H_5	H	H	291—292	$C_{23}H_{12}N_2O_2$	79,5	3,5	8,0	79,3	3,5	8,0	83
IIc	C_2H_5	H	H	233—234	$C_{19}H_{12}N_2O_2$	75,7	3,8	9,4	75,9	4,0	9,3	83
IId	C_3H_7	H	H	216—217	$C_{20}H_{14}N_2O_2$	76,6	4,4	8,8	76,4	4,5	8,9	93
IIe	C_6H_{13}	H	H	142—143	$C_{23}H_{20}N_2O_2$	77,8	5,8	8,1	77,5	5,7	7,9	80
IIf	CH_3	CH_3	H	300—301	$C_{19}H_{12}N_2O_2$	76,0	4,0	9,5	75,9	4,0	9,3	96
IIg	CH_3	C_6H_{11}	H	279—280	$C_{24}H_{20}N_2O_2$	78,4	5,4	7,5	78,2	5,5	7,6	97
IIh	C_6H_5	CH_3	H	320—321	$C_{24}H_{14}N_2O_2$	80,1	4,1	7,9	79,6	3,9	7,7	95
IIi	CH_3	CH_3	H	303—304	$C_{19}H_{11}BrN_2O_2$	60,3	3,0	7,3	60,3	2,9	7,4	94

*Compound IIb was crystallized from chlorobenzene, while the remaining compounds were recrystallized from dioxane.

TABLE 2. 1-Acylaminoanthrapyridones

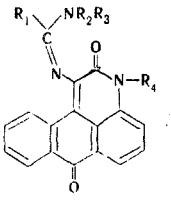


Compound	R_1	R_2	mp, °C	Empirical formula	Found, % C	Found, % H	Found, % N	Calc., % C	Calc., % H	Calc., % N	Yield, %
IIIa	CH_3	H	above350	$C_{18}H_{12}N_2O_3$	71,0	3,8	9,1	71,0	3,9	9,2	90
IIIb*	C_6H_5	H	—	$C_{23}H_{14}N_2O_3$	75,3	3,7	7,5	75,4	3,8	7,6	90
VIa	CH_3	CH_3	289—290	$C_{19}H_{14}N_2O_3$	71,9	4,3	8,7	71,6	4,4	8,8	89
VIb	C_6H_5	CH_3	250—251	$C_{24}H_{16}N_2O_3$	75,6	4,1	7,3	75,7	4,2	7,4	98

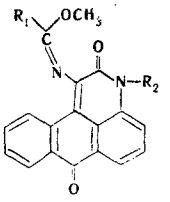
*Compound IIIb is converted to IIb on melting. Compounds IIIa,b were crystallized from aqueous acetic acid, while VIa,b were crystallized from aqueous alcohol.

It is interesting that 2-phenyloxazoloanthrapyridine (IIb) is also formed in the reaction of 1-amino-N-methylanthrapyridone (IV), which has the fixed structure of a cyclic amide, with benzoyl chloride or benzoic anhydride. It seemed most likely that the splitting out of a methyl group occurs after closing of the oxazole ring to give an intermediate, which, as a result of the realization of a lactim structure in the pyridine ring, should have a quaternary nitrogen atom and be considerably labile. The latter may lead either to demethylation or to ring opening. On the other hand, there is a probability of stabilization of this sort of compound through salt formation under the influence of a strong acid. In fact, if one cannot observe an intermediate when the reaction is carried out under the usual conditions, the reaction can be stopped at the stage involving the formation of the 2-phenyloxazoloanthra-N-methylpyridinium salt (Vb), which precipitates, by introduction into the reaction medium of a mineral acid – sulfuric or perchloric acid, for example. Treatment of Vb with benzoic anhydride or benzoyl chloride gives 2-phenyloxazoloanthrapyridine (IIb). The salts of cation Vb are readily hydrolyzed by water to give 1-benzamido-N-methylanthrapyridone (VIb, Table 2), which can be converted to salts Vb or oxazoloanthrapyridine IIb under the same conditions as in the case of the starting 1-amino-N-methylanthrapyridone (IV). Hydrolysis also proceeds by the action of air moisture, but the salts of Vb can be analyzed by using the necessary precautionary measures.

TABLE 3. N-(1-Anthrapyridonyl)amidines and Esters of N-(1-Anthrapyridonyl)iminocarboxylic Acids



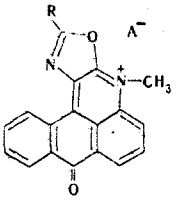
VII, VIII



IX, X

Compound	R_1	R_2	R_3	R_4	mp, °C	Empirical formula	Found, % C	Found, % H	Found, % N	Calc., % C	Calc., % H	Calc., % N	Yield, %
VIIa	CH_3	H	H	H	—*	$C_{18}H_{13}N_3O_2$	71,5	4,3	13,7	71,3	4,3	13,8	97
VIIb	CH_3	CH_3	CH_3	H	—*	$C_{20}H_{17}N_3O_2$	72,4	5,3	12,7	72,5	5,2	12,7	98
VIIc	CH_3	H	C_6H_{11}	H	—*	$C_{24}H_{23}N_3O_2$	74,3	6,2	10,6	74,7	6,0	10,9	98
VIId	CH_3	H	C_6H_5	H	—*	$C_{24}H_{17}N_3O_2$	75,7	4,5	11,2	75,9	4,5	11,0	95
VIIe	C_6H_5	CH_3	CH_3	H	—*	$C_{25}H_{19}N_3O_2$	76,2	4,9	10,4	76,3	4,8	10,6	89
VIIIa	CH_3	CH_3	CH_3	CH_3	227—228	$C_{21}H_{19}N_3O_2$	72,8	5,4	12,1	73,0	5,5	12,2	90
VIIIb	C_6H_5	CH_3	CH_3	CH_3	235—236	$C_{26}H_{21}N_3O_2$	76,5	5,1	10,2	76,6	5,2	10,3	98
VIIIc	C_6H_5	H	C_6H_5	CH_3	285—286	$C_{30}H_{21}N_3O_2$	78,9	4,7	9,0	79,1	4,6	9,2	95
VIIId	C_6H_5	H	H	CH_3	335—336	$C_{24}H_{17}N_3O_2$	75,8	4,4	11,1	75,9	4,5	11,0	98
VIIIe	C_6H_5	H	C_6H_{13}	CH_3	190—191	$C_{30}H_{29}N_3O_2$	77,8	6,1	9,3	77,7	6,3	9,0	96
IXa	CH_3	H	—	—	—*	$C_{19}H_{14}N_2O_3$	71,6	4,5	8,6	71,7	4,4	8,8	80
Xa	CH_3	CH_3	—	—	228—229	$C_{20}H_{16}N_2O_3$	72,1	4,6	8,2	72,3	4,9	8,4	94
Xb	C_6H_5	CH_3	—	—	218—219	$C_{25}H_{18}N_2O_3$	79,2	4,7	7,3	79,3	4,8	7,4	95

*Compounds VIIa-d and IXa are converted to IIa on heating, while VIIe is converted to IIb.



V a,b

a $R = CH_3$; b $R = C_6H_5$

When 1-amino-N-methylanthrapyridone (IV) is heated with acetic anhydride even up to 200° (in sealed ampuls), only 1-acetamido-N-methylanthrapyridone (VIa) is formed, and 2-methyloxazoloanthrapyridine (IIa) is not detected. At the same time, a 2-methyloxazoloanthra-N-methylpyridinium salt (Va) is formed in the presence of a mineral acid, i.e., closing of the oxazole ring also occurs during acetylation of IV, but in this case the intermediate is apparently more inclined to ring opening than to demethylation, in contrast to Vb, in which the oxazole ring is more stable. In fact, the character of the substituent in the 2 position has a pronounced effect on the stability of the oxazole ring in cations of V: a phenyl group stabilizes it much more than a methyl group. Thus the salts of the cation of Va are even less resistant to hydrolysis than the salts of Vb and are rapidly converted to 1-acetamido-N-methylanthrapyridone (VIa, Table 2) in air, but they can at the instant they are formed be introduced into reactions that confirm the structure of Va as the methyl analog of Vb.

It can be assumed that the formation of oxazoloanthrapyridines also in the case of the absence of a substituent attached to the heterocyclic nitrogen atom in the starting 1-aminoanthrapyridone also proceeds through intermediate structures similar to V (with H instead of CH_3) with subsequent splitting out of a proton. With this mechanism there is no need for prior conversion of the lactam form, in which the anthrapyridones exist [3], to the lactim form. The ease of hydrolytic opening of the oxazole ring in the oxazoloanthrapyridines compelled us to investigate the possibility of the opening of the ring under the influence not only of the hydroxyl ion but also of other nucleophiles. As nucleophilic agents we selected ammonia, amines, and alkali-metal alkoxides. Oxazoloanthrapyridines IIa,b react even in the cold with ammonia, primary and secondary amines (for example, methyl-, dimethyl-, and cyclohexylamines and aniline) to give the corresponding N-(1-anthrapyridonyl)acetamidines or N-(1-anthrapyridonyl)benzamidines (VIIa-e, Table 3). We

were unable to find direct indications of the formation of amidines as a result of the reaction of oxazoles with amines in the literature.* On the basis of the analytical data, it could be assumed that VII are either anthrapyridones that contain an amidine grouping in the 1 position or 1-acylamino-2-aminoanthrapyridine derivatives. The fact that VII are soluble in aqueous alkali solutions and are isolated unchanged on acidification spoke in favor of the amidine structure. This indicates that anthrapyridone derivatives capable of enolization in alkaline media are formed as a result of the reaction. To prove the structure of VII, we attempted to obtain some of them by alternative synthesis using the standard method for the preparation of amidines – by the reaction of amines with N,N-dialkylamides of carboxylic acids in the presence of phosphorus oxychloride [5]. However, we found that one cannot obtain amidines by reaction of 1-aminoanthrapyridone (I) with dimethylacetamides and benzamides, since under the reaction conditions they are converted completely to oxazoloanthrapyridines IIa,b. Only traces of amidines can be observed on the chromatograms when the maximally mild conditions are used. The amidine can be obtained only when dimethylformamide is used in this reaction. The action of the latter and phosphorus oxychloride on I gave N-(1-anthrapyridonyl)-N',N'-dimethylformamidinium hydrochloride (VIIf), which on further heating is converted to the starting 1-aminoanthrapyridone (I), and the formation of an oxazoloanthrapyridine that does not contain a substituent in the 2 position (II, R = H) is not observed. It should be pointed out that the latter also is not formed in the direct formylation of I; this, in conjunction with the data presented above on the thermal cyclization of 1-acylaminoanthrapyridones (IIIa,b), indicates the effect of the substituent in the acyl residue on the formation and stability of the oxazoloanthrapyridines themselves and not only their salts (of the V type).

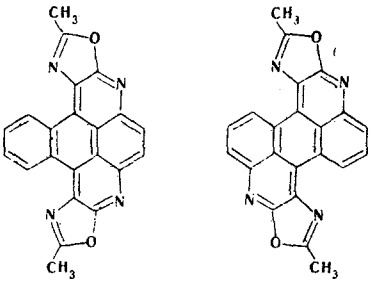
If VII have the amidine structure, then, on the basis of the data presented above, reverse transformation to oxazoloanthrapyridines should also be characteristic for them. In fact, VIIa-e are readily converted to IIa,b on heating. Since, the formation of benzoxazoles from N-(2-hydroxyphenyl)amidines is known [6], cyclization is a proof in favor of the amidine structure of VII.

Oxazoloanthrapyridinium salts (Va,b) react with ammonia and amines in analogy with oxazoloanthrapyridines IIa,b to give N-(N-methyl-1-anthrapyridonyl)amidines (VIIIa-e, Table 3). In view of the fact that the presence of a methyl group attached to the heterocyclic nitrogen atom interferes with the cyclization of the latter to oxazole derivatives, their structures can be confirmed by the synthesis of amidines from 1-amino-N-methylanthrapyridone (IV). Thus substances identical to VIIIa were obtained by reaction of IV with dimethylacetamide and $POCl_3$ with subsequent transformation of the resulting amidine hydrochloride to the base and treatment of sulfate Va with dimethylamine. The analogy in the chemical and spectral properties of VII and VIII shows that the former also have amidine structures.

The reaction of oxazoloanthrapyridines with alkali-metal alkoxides also leads to opening of the oxazole ring to give imino esters. Thus, for example, the reaction of sodium methoxide with IIa gave methyl N-(1-anthrapyridonyl)iminoacetate (IXa), the structure of which is confirmed by conversion of it to N-(1-anthrapyridonyl)-N',N'-dimethylacetamidine (VIIb) by treatment with dimethylamine; this is characteristic for imino esters [7]. Imino ester IXa is converted to 2-methyloxazoloanthrapyridine (IIa) on heating with the same ease as amidines VII. A similar reaction also occurs in the interaction of oxazoloanthrapyridinium salts Va,b with sodium methoxide. Their reactivity is so high that it enables one to obtain imino esters by the action of alcohols. For example, imino esters Xa,b (Table 3) were obtained by reaction of salts Va,b with methanol. In this reaction, as in the hydrolysis, a higher reactivity is observed for 2-methyl derivative Va – the reaction commences even in the cold – while 2-phenyl derivative Vb reacts with methanol only on heating. The complete analogy in the structures of the products of monotypic transformations of oxazoloanthrapyridine and oxazoloanthra-N-methylpyridinium salts raises no doubts about the V structure proposed for the latter.

Acylation of 1,8-diaminoanthra[1,9:4,10]- and 1,7-diaminoanthra[1,9:5,10]dipyridones, which we previously synthesized in [8], leads to closing of two oxazole rings, as a result of which we obtained dioxazoloanthradipyridines (for example, XI and XII), for which facile opening of the oxazole rings during hydrolysis and in reactions with amines and alkoxides is also characteristic. For example, as a result of the reaction of XI and XII with butylamine, we obtained anthradipyridones with two amidine groupings (XIII, XIV), which, like amidines VII, are again cyclized on heating to form XI and XII. The structures of dioxazoles XI and XII are confirmed by the analytical data and chemical properties and by the IR spectra, which do not contain bands of the stretching vibrations of the carbonyl groups.

* Data on the preparation of amidines by the action of amines on pyronoxazoles were published after completion of this portion of the research [4].



XI XII

Amidines that are the products of the reaction of 2-alkyloxazoloanthrapyridines with ammonia and aliphatic primary and secondary amines have intense luminescence; this, in conjunction with the ease and completeness of the reaction, makes, in our opinion, the oxazoloanthrapyridines interesting reagents for use during analysis of other investigated substances that contain an aliphatic amino group.

EXPERIMENTAL

Oxazoloanthrapyridines (IIa-i). A mixture of 1 g of I or substituted I and 10 g of the carboxylic acid anhydride was refluxed for 20-30 min, cooled, and filtered. The filtrate was washed with alcohol.

2-Methyloxazoloanthrapyridine (IIa). A. This compound was obtained from I via the method described above.

B. Three drops of $POCl_3$ were added to a suspension of 1 g of I in 4 ml of acetic acid, during which I dissolved and the mixture turned red. It was then refluxed for 10-15 min, after which it was cooled, and the precipitated needles were removed by filtration and washed with alcohol to give the product in 93% yield.

C. The compound was obtained from IIIa by methods A or B (the yields were 90 and 88%, respectively).

D. A 0.1-g (0.38 mmole) sample of I was heated in 7.5 ml (0.10 mole) of dimethylacetamide up to 80°, 0.1 ml (0.001 mole) of $POCl_3$ was added, and the mixture was stirred at 130° for 1 h. It was then cooled and filtered to give 0.08 g (73%) of IIa.

E. A 0.8-g sample of imino ester IXa was refluxed in chlorobenzene for 5 h, after which the mixture was cooled and filtered. The solid was washed with ether to give 0.68 g (94%) of IIa.

2-Phenyloxazoloanthrapyridine (IIb). A. This compound was obtained from I or IV via the usual method.

B. A mixture of a 0.1-g sample of I, IV, or VIb and 6 ml of benzoyl chloride was refluxed for 15-20 min, after which it was cooled and filtered to give the product in 89% yield.

C. A mixture of 0.1 g (0.4 mmole) of I and 3 g (20 mmole) of dimethylbenzamide was heated to 120°, three drops of $POCl_3$ were added, and the mixture was cooled and filtered to give 0.12 g (90%) of IIb.

D. A 0.1-g sample of amidine VIIe was refluxed in 30 ml of dioxane for 1 h, after which it was cooled, and the precipitated needles were removed by filtration to give 0.084 g (95%) of IIb.

2-Phenyloxazoloanthra-N-methylpyridinium Salts (Vb). A suspension of 0.5 g of IV or VIb in 20 ml of benzoyl chloride or benzoic anhydride containing four drops of 95% H_2SO_4 was stirred at 100° for 30 min, after which the mixture was cooled and filtered, and the precipitated product was washed with ether to give 0.75 g (90%) of Vb sulfate. Similarly, using $HClO_4$ in place of H_2SO_4 we obtained Vb perchlorate. Found: C 62.1; H 3.4; Cl 7.5; N 6.0%. $C_{24}H_{15}ClN_2O_6$. Calculated: C 62.3; H 3.3; Cl 7.7; N 6.1%.

2-Methyloxazoloanthra-N-methylpyridinium Sulfate (Va). This compound was obtained by the method used to prepare Vb sulfate. In air, Va was rapidly transformed to VIa.

1-Acetamido- and 1-Benzamidoanthrapyridones (IIIa,b). A. A 1-g sample of IIa,b was dissolved by refluxing in 60 ml of aqueous dioxane (1:1), and 2 ml of 40% sodium hydroxide solution was added to the solution. The mixture was cooled, neutralized with sulfuric acid, and filtered. The solid was washed with water and alcohol.

B. The compounds were hydrolyzed under the conditions in method A using 1 ml of 35% hydrochloric acid in place of sodium hydroxide.

1-Acetamido-N-methylanthrapyridone (VIa). A. This compound was obtained in the same way as Va with acetic anhydride–acetic acid (1:1) in place of acetic anhydride. The reaction mixture was poured into water, and the precipitate was removed by filtration and washed with water.

B. The sulfate of Va was dissolved in water, and VIa immediately began to precipitate from the solution.

1-Benzamido-N-methylanthrapyridone (VIb). This compound was obtained by brief heating of a solution of Vb sulfate in water or aqueous alcohol; in the latter case, VIb precipitated in the form of needles.

N-(1-Anthrapyridonyl)acetamidine and N-(1-Anthrapyridonyl)benzamidines (VIIa-e). A 1-g (0.003 mole) sample of IIa,b was dissolved by heating in 50 ml of dioxane, after which 0.004-0.006 mole of ammonia or amine was added, and the solution immediately took on a bright-yellow fluorescent color and a crystalline precipitate began to form. The mixture was stirred without heating for 20-30 min, after which it was filtered, and the solid material was washed with water, alcohol, or ether. The reaction can be carried out in a suspension at room temperature.

N-(1-Anthrapyridonyl)-N',N'-dimethylacetamidine (VIIb). A. This compound was obtained from IIa by the action of aqueous dimethylamine via the method presented above. The product was crystallized from aqueous dioxane (needles).

B. A mixture of 1 g (0.003 mole) of imino ester IXa in 20 ml of methanol was heated to 30°, and 0.9 ml (0.004 mole) of 20% aqueous dimethylamine solution was added. The precipitated needles were removed by filtration and washed with water to give 0.099 g (95%) of VIIb.

N-(1-Anthrapyridonyl)-N',N'-dimethylformamidinium Chloride (VIIf). A 1-g (0.004 mole) sample of aminoanthrapyridone was dissolved at 130° in 40 ml (0.5 mole) of dimethylformamide, and the solution was cooled to 80°. A 1-ml (0.01 mole) sample of $POCl_3$ was added, and the mixture was stirred at this temperature for 30 min until a precipitate formed. The mixture was then cooled and filtered to give 1.08 g (80%) of needles of VIIf with mp 263° (dec.). Found: C 63.9; H 4.5; Cl 10.0; N 11.9%. $C_{10}H_{16}ClN_3O_2$. Calculated: C 64.4; H 4.6; Cl 10.0; N 11.9%.

N-(N-Methyl-1-anthrapyridonyl)acetamidines and -benzamidines (VIIIa-e). A suspension of 0.5 g of Va,b in 5 ml of amine or amine solution was stirred without heating for 20-30 min, after which it was filtered and the solid was washed with alcohol.

N-(N-Methyl-1-anthrapyridonyl)-N',N'-dimethylacetamidine (VIIIa). A 1-ml (0.01 mole) sample of $POCl_3$ was added with cooling to a solution of 1 g (0.003 mole) of IV in 30 ml (0.41 mole) of dimethylacetamide, and the mixture was stirred for 1 h and then poured into water. The mixture was made alkaline with sodium hydroxide solution, and the resulting precipitate was removed by filtration, washed with water and crystallized from aqueous dioxane to give a product in 60% yield.

Methyl N-(1-Anthrapyridonyl)iminoacetate (IXa). A 0.5-ml (0.002 mole) sample of 20% solution of sodium methoxide in methanol was added to 0.3 g (0.001 mole) of IIa in 20 ml of methanol, and the mixture was stirred for 20-30 min, cooled, and filtered to give 0.27 g (80%) of IXa.

Methyl N-(N-Methyl-1-anthrapyridonyl)iminoacetate and -iminobenzoate (XIIa,b). A. A suspension of 0.5 g of Va,b in 10 ml of absolute methanol was heated to the boiling point, cooled, and filtered to give Xa,b.

B. Compound Xa was similarly obtained, but the reaction was carried out at room temperature for 2 h.

C. Compounds Va,b were converted instantaneously to Xa,b by the action of sodium methoxide in the cold.

Dioxazoloanthra[1,9:4,10]- and Dioxazoloanthra[1,9:5,10]dipyridines (XI, XII). These compounds were obtained, respectively, from 1,8-diaminoanthra[1,9:4,10]- and 1,7-diaminoanthra[1,9:5,10]dipyridones via the general method as for II. Compound XI, which melted above 350° (from dimethylformamide), was obtained in 96% yield. Found: C 72.6; H 3.5; N 15.5%. Compound XII melted above 350° (from dimethylacetamide). Found: C 72.4; H 3.4; N 15.6%. $C_{22}H_{12}N_4O_2$. Calculated %: C 72.5; H 3.3; N 15.4%.

1,8-Di(N-n-butylacetamidino)anthra[1,9:4,10]- and 1,7-Di(N-n-butylacetamidino)anthra[1,9:5,10]dipyridones (XIII, XIV). A mixture of 0.1 g of XI or XII and 4 ml of n-butylamine was stirred at room tem-

perature, during which the solid gradually dissolved. After this, a precipitate began to form. The precipitate was removed by filtration and washed with alcohol to give 0.13 g (94%) of XIII, XIV. Both compounds were converted (without melting) to XI and XII, respectively, on heating in a capillary at ~ 250°. XIII. Found: C 70.2; H 6.6; N 16.1%. Compound XIV. Found: C 70.3; H 6.8; N 16.3%. $C_{30}H_{34}N_6O_2$. Calculated: C 70.5; H 6.7; N 16.4%.

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