4. A. E. Chichibabin and D. I. Orochko, Zh. Russk. Khim. Ova., 62, 1201 (1930).
5. P. B. Terent'ev, Mass Spectrometry in Organic Chemistry [in Russian], Vysshaya Shkola, Moscow (1979), pp. 123, 129.
6. N. S. Prostakov, A. T. Soldatenkov, and V. O. Fedorov, Zh. Org. Khim., 15, 1109 (1979).
7. A. T. Soldatenkov, V. O. Fedorov, R. Chandra, V. M. Polosin, A. I. Mikaya, and N. S. Prostakov, Zh. Org. Khim., 16, 188 (1980).
8. W. Treibs and J. Beger, Ann. Chem., 652, 192 (1962).
9. P. Ribereau, G. Nevers, G. Queguiner, and P. Pastour, Compt. Rend., Ser. C, 280, 293 (1975).

INVESTIGATION OF PHENANTHRIDONE AND DIOXOTETRAHYDRODIAZAPYRENE.

3.* INVESTIGATION OF THE NITRATION OF 5H-PHENANTHRIDIN-6-ONE AND ITS DERIVATIVES

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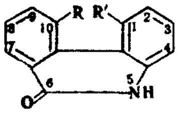
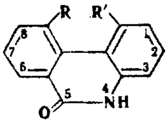
The nitration of 5H-phenanthridin-6-one (I), 5H-phenanthridin-6-one-10-carboxylic (II) and 5H-phenanthridin-6-one-1-carboxylic acids (III), 4H-cyclopenta[k,1,m]-phenanthridine-5,9-dione (IV), 4H-cyclopenta[k,1,m]phenanthridine-5-one (V), 5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (VI), and 5,9-dioxo-4,5,9,10-tetrahydro-4,10-diazapyrene (VII) with nitric acid (sp. gr. 1.42-1.51) and a nitrating mixture of 0-120°C was investigated. The orientation and sequence of incorporation of nitro groups in I-VII are determined by the presence of a phenanthridone structure in them. Mono-, di-, tri-, and tetranitro-substituted I-VII were obtained and characterized.

Continuing our study of phenanthridone and dioxotetrahydrodiazapyrene, we investigated the nitration of 5H-phenanthridin-6-one (I) [2], 5H-phenanthridon-6-one-10-carboxylic (II) [3] and 5H-phenanthridin-6-one-1-carboxylic (III) [4] acids, 4H-cyclopenta[k,1,m]phenanthridine-5,9-dione (IV) [5], 4H-cyclopenta[k,1,m]phenanthridine-5-one (V) [6], 5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (VI), and 5,9-dioxo-4,5,9,10-tetrahydro-4,10-diazapyrene (VII) [3]. All these comounds contain two benzene rings and one α-pyridone ring, which together form a phenanthridone structure.



I-III



IV-VII

I R=R'=H; II R=COOH, R'=H; III R=H, R'=COOH; IV R+R'=CO; V R+R'=CH_2;
VI R+R'=NH—CO; VII R+R'=CO—NH

Little study has been devoted to nitration of the phenanthridone structure [2]. We investigated the reaction of I-VII with HNO_3 (sp. gr. 1.42-1.51) and with a nitrating mixture at 0-120°C. We obtained mono-, di-, and trinitro-substituted derivatives of the heterocyclic systems. The orientation and sequence of incorporation of nitro groups in I-VII are determined by the presence in them of the phenanthridone structure. The presence of substituents or bridged groups in the 1 and 10 positions of the phenanthridone ring has a relatively small effect on them. Nitro-substituted I-VII, the conditions for their preparation, and their characteristics are presented in Table 1.

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*See [1] for Communication 2.

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TABLE 1. Nitro-Substituted Phenanthridones and Their Derivatives (I-VII)

Com-pound	R	R′	Posit. of nitro group	Nitration conditions		mp,* °C	Found, %			Empirical formula	Calc., %			Yield,† %
	or a group formed by R and R′ together			nitrating agent	temp, °C		C	H	N		C	H	N	
I a	H	H	2	HNO$_3$ (sp.gr. = 1.42)	50	382—383	—	—	—	$C_{13}H_8N_2O_3$	—	—	—	93
I b	H	H	4	HNO$_3$ (sp.gr. = 1.42)	50	265—266	—	—	—	$C_{13}H_8N_2O_3$	—	—	—	93
I c	H	H	8		—	328—329	—	—	—	$C_{13}H_8N_2O_3$	—	—	—	—
I d	H	H	2, 8	HNO$_3$ (sp.gr. = 1.48)	25	306‡	54,8	2,7	14,8	$C_{13}H_7N_3O_5$	54,7	2,5	14,7	90
I e	H	H	4, 8	HNO$_3$ (sp.gr. = 1.48)	25	299,5	54,6	2,6	14,7	$C_{13}H_7N_3O_5$	54,7	2,5	14,7	90
I f	H	H	2, 4, 8	HNO$_3$/	110	222‡	47,5	1,9	16,9	$C_{13}H_6N_4O_7$	47,3	1,8	16,9	73
II a	COOH	H	2	HNO$_3$ (sp.gr. = 1.46)	20	>330	59,1	3,0	9,8	$C_{14}H_8N_2O_5$	59,1	2,8	9,9	83
II b	COOH	H	4	HNO$_3$ (sp.gr. = 1.46)	20	281‡	59,2	3,1	9,9	$C_{14}H_8N_2O_5$	59,1	2,8	9,9	83
III a	H	COOH	2	HNO$_3$ (sp.gr. = 1.46)	40	>330	59,3	2,8	9,8	$C_{14}H_8N_2O_5$	59,1	2,8	9,9	78
III b	H	COOH	4	HNO$_3$ (sp.gr. = 1.46)	40	284—285	59,0	2,9	9,9	$C_{14}H_8N_2O_5$	59,1	2,8	9,9	78
III c	H	COOH	8		—	>330	59,1	3,1	10,0	$C_{14}H_8N_2O_5$	59,1	2,8	9,9	—
IV a	—CO—		1	HNO$_3$ (sp.gr. = 1.42)	50	>330	63,2	2,4	10,4	$C_{14}H_6N_2O_4$	63,2	2,3	10,5	92
IV b	—CO—		3	HNO$_3$ (sp.gr. = 1.42)	50	343—344	63,3	2,6	10,7	$C_{14}H_6N_2O_4$	63,2	2,3	10,5	92
IV c	—CO—		7		—	>330	63,2	2,4	10,2	$C_{14}H_6N_2O_4$	63,2	2,3	10,5	—
IV d	—CO—		1, 7	HNO$_3$ (sp.gr. = 1.51)	0—5	>330	54,3	1,8	13,2	$C_{14}H_5N_3O_6$	54,1	1,6	13,5	81
IV e	—CO—		3, 7	HNO$_3$ (sp.gr. = 1.51)	0—5	335—336	54,1	1,7	13,3	$C_{14}H_5N_3O_6$	54,1	1,6	13,5	81
IV f	—CO—		1, 3, 7	HNO$_3$/	120	278—279	47,0	1,3	15,6	$C_{14}H_4N_4O_8$	47,2	1,1	15,7	83
V a	—CH$_2$—		1	HNO$_3$ (sp.gr. = 1.42)	40	>330	66,8	3,4	11,0	$C_{14}H_8N_2O_3$	66,7	3,2	11,1	90
V b	—CH$_2$—		3	HNO$_3$ (sp.gr. = 1.42)	40	305‡	66,9	3,4	11,2	$C_{14}H_8N_2O_3$	66,7	3,2	11,1	90
V c	—CH$_2$—		7		—	>330	66,7	3,4	11,2	$C_{14}H_8N_2O_3$	66,7	3,2	11,1	—
V d	—CH$_2$—		1, 7	HNO$_3$ (sp.gr. = 1.51)	0—5	>330	56,8	2,6	14,0	$C_{14}H_7N_3O_5$	56,6	2,4	14,1	84
V e	—CH$_2$—		3, 7	HNO$_3$ (sp.gr. = 1.51)	0—5	311‡	56,7	2,6	14,3	$C_{14}H_7N_3O_5$	56,6	2,4	14,1	84
V f	—CH$_2$—		1, 3, 7	HNO$_3$/	110	243‡	49,0	1,8	16,5	$C_{14}H_6N_4O_7$	49,1	1,7	16,4	72
VI a	—NH—CO—		1	HNO$_3$ (sp.gr. = 1.42)	45	>400	59,5	2,6	14,9	$C_{14}H_7N_3O_4$	59,8	2,5	14,9	86
VI b	—NH—CO—		3	HNO$_3$ (sp.gr. = 1.42)	45	>400	59,6	2,7	14,9	$C_{14}H_7N_3O_4$	59,8	2,5	14,9	86
VI c	—NH—CO—		7		—	>400	59,7	2,6	15,0	$C_{14}H_7N_3O_4$	59,8	2,5	14,9	—
VI d	—NH—CO—		1, 8	HNO$_3$ (sp.gr. = 1.42)	100	>400	51,5	1,9	17,3	$C_{14}H_6N_4O_6$	51,6	1,8	17,2	76
VI f	—NH—CO—		1, 3, 6	HNO$_3$ (sp.gr. = 1.50)	80	>400	45,5	1,4	19,0	$C_{14}H_5N_5O_8$	45,3	1,3	18,9	62
VI g	—NH—CO—		1, 3, 8	HNO$_3$ (sp.gr. = 1.50)	80	>400	45,4	1,3	19,0	$C_{14}H_5N_5O_8$	45,3	1,3	18,9	62
VI h	—NH—CO—		1, 3, 6, 8	HNO$_3$/	120	>400	40,2	1,1	20,0	$C_{14}H_4N_6O_{10}$	40,4	1,0	20,2	86
VII a	—CO—NH—		1	HNO$_3$ (sp.gr. = 1.42)	45	>330	59,7	2,6	15,0	$C_{14}H_7N_3O_4$	59,8	2,5	14,9	83
VII d	—CO—NH—		1, 3	HNO$_3$ (sp.gr. = 1.46)	50	332‡	51,5	1,8	17,1	$C_{14}H_6N_4O_6$	51,6	1,8	17,2	80
VII f	—CO—NH—		1, 3, 7	HNO$_3$ (sp.gr. = 1.51)	50	>330	45,1	1,4	19,0	$C_{14}H_5N_5O_8$	45,3	1,3	18,9	81

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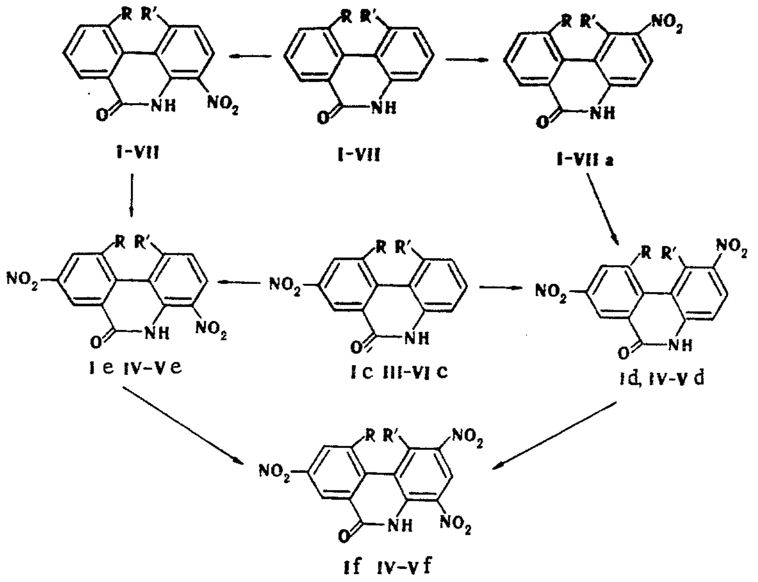
[a] According to the data in [2], Ia,b,c had mp 380-384, 265-267, and 329°C, respectively.

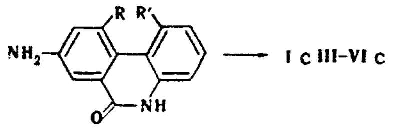
† In those cases in which nitro isomers were formed their overall yields are presented.

‡ With decomposition.

In I-III the first nitro group is incorportated in the 2 or 4 position of the benzene ring that contains an acylated amino group (the A ring), while in IV-VII the nitro group is incorporated in the 1 or 3 position. Thus a mixture of 2-nitro and 4-nitro isomers (Ia,b) in a ratio of 5:1 was obtained in the reaction of I with concentrated HNO_3. Consequently, the nitration of I give primarily the 2-nitro isomer. The ratio of mononitro isomers IVa,b in the nitration of IV, which differs from I with respect to the bridged CO group, under the same conditions does not exceed 1:12, i.e., nitration takes place almost exclusively in the 3 position.

A second nitro group is incorporated in the B ring in the 8 position in I and, respectively, in the 7 position of IV and V when they are treated with HNO_3 (sp. gr. 1.48-1.51). Thus 2,8-dinitro and 4,8-dinitro isomers (Id,e) were obtained from I. The position of the nitro groups in 2,8-dinitro derivative Id was shown by independent syntheses of this compound from 2-nitrophenanthridone and 8-nitrophenanthridone (Ic). The position of the nitro groups in 4,8-dinitro isomer Ie was demonstrated by independent syntheses from mononitro-substituted Ib,c. The position of the substituents in dinitro-substituted IVd,e and Vd,e was similarly proved. Compounds Ic and IIIc-VIc were previously synthesized from, respectively, 8-amino-5H-phenanthridin-6-one (VII) [7], 8-amino-5H-phenanthridin-6-one-1-carboxylic acid (IX) [4], 7-amino-4H-cyclopenta[k,l,m]phenanthridine-5,9-dione (X) [9], 7-amino-4H-cyclopenta[k,l,m]phenanthridin-5-one (XI) [6], and 7-amino-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (XII) [8] by diazotization of these compounds and subsequent exchange of the diazo group for a nitro group.



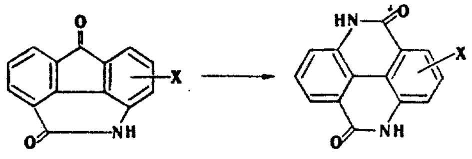


VIII-XII

VIII R=R'=H; IX R=H, R'=COOH; X R+R'=CO; XI R+R'=CH_2; XII R+R'=NH—CO

In the case of more profound nitration of I, IV, and V a third nitro group is incorporated in the unsubstituted 4 or 2 position of the A ring in the case of Id,e and in the 3 or 1 position in the case of IVd, Vd, and IVe and Ve. Trinitro-substituted If, IVf, and Vf were obtained by treatment of I, IV, and V with a nitrating mixture at 110-120°C. The same compounds can be obtained by treatment of dinitro-substituted Id, IVd, and Vd or Ie, IVe, and Ve at 110-120°C with a nitrating mixture.

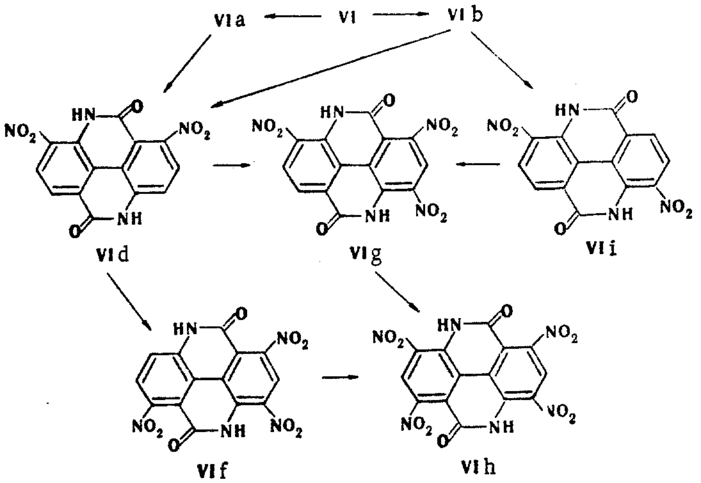
As in the case of compounds of the phenanthridone series, the first nitro group in the nitration of 5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (VI), which contains two α-pyridone rings, is incorporated in the 1 or 3 position. The structures of the isolated 1-nitro- and 3-nitro-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrenes (VIa,b) were proved by independent synthesis via the Schmidt reaction from IVa,b, in which the position of the nitro groups with respect to the amino group in the A ring is known. The Schmidt reaction in the case of IV proceeds with expansion of the five-membered ring that contains a keto group, and VI is formed. Mononitro isomers VIa,b were similarly obtained by treatment of solutions of IVa,b in sulfuric acid with sodium azide.



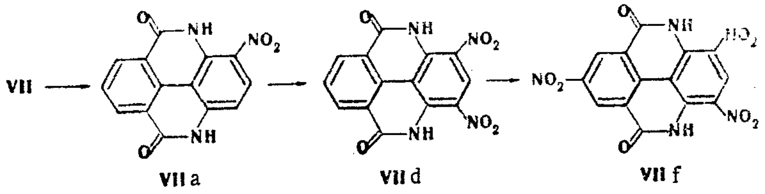
IV, IVa,b VI, VIa,b

IV, VI X=H; IVa, VIa X=1-NO_2; IVb VIb X=3-NO_2

In contrast to IV and V, a bridged CONH group affects the orientation of the substituents in the case of incorporation of a second and subsequent nitro groups in VI. Treatment of dioxotetrahydrodiazapyrene VI with HNO_3 (sp. gr. 1.42) at 100°C gave a difficult-to-separate mixture of nitro-substituted compounds, from which we isolated 1,8-dinitro-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (VId). The same compound can be obtained by nitration under the same conditions of mononitro-substituted VIa and VIb. A multiplet signal centered at 8.02 ppm is observed in the PMR spectrum of VId. 1,3,6-Trinitro- and 1,3,8-trinitro-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrenes (VIf,g) were obtained by reaction of dioxotetrahydrodiazapyrene VI with HNO_3 (sp. gr. 1.50) at 80°C, while 1,3,6,8-tetranitro-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (VIh) was obtained with a nitrating mixture at 120°C. The PMR spectrum of tetranitrodiazapyrene VIh contains one singlet at 8.02 ppm, which corresponds to two protons in the 2 and 7 positions of the tetrahydrodiazapyrene ring. Tetranitrodiazapyrene VIh can be obtained by treatment of trinitro-substituted VIf and VIg with fuming nitric acid. The presence in the mixture of products of nitration of VI of an intermediate, viz., 3,8-dinitro-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (VIi), may be proposed on the basis of the structures of the isolated mono- and trinitro-substituted derivatives of dioxotetrahydrodiazapyrenes VI. However, we were unable to isolate this intermediate. In this case the nitration of VI to a tetranitro-substituted compound can be described by the scheme:



1-Nitro-5,9-dioxo-4,5,9,10-tetrahydro-4,10-diazapyrene (VIIa) was obtained by nitration of 5,9-dioxo-4,5,9,10-tetrahydro-4,10-diazapyrene (VII) with HNO_3 (sp. gr. 1.42). The IR spectrum of a dilute solution of VIIa in chloroform contains absorption bands at 3280 and 3100 cm^{-1}, which are characteristic for an associated NH group. This makes it possible to assume the existence of an intramolecular NH...ON bond between the NH group and the adjacent nitro group. Compounds IVb, Vb, VIb,h, and VIId,f, in which there is an NO_2 group that is capable of forming an intramolecular hydrogen bond, have similar absorption that is characteristic for an associated NH group. 1,3-Dinitro-5,9-dioxo-4,5,9,10-tetrahydro-4,10-diazapyrene (VIId) was obtained by treatment of diazapyrene VII with HNO_3 (sp. gr. 1.46), while 1,3,7-trinitro-5,9-dioxo-4,5,9,10-tetrahydro-4,10-diazapyrene (VIIf) was obtained by treatment of VII with HNO_3 (sp. gr. 1.51).



EXPERIMENTAL

The reaction was monitored by TLC on Silufol UV-254 plates. Analytical samples of the nitro compounds were obtained by chromatography of the reaction mixtures with columns filled with L 100/160 μ silica gel and crystallization from aqueous DMF. A mixture of 25% ammonium hydroxide and dioxane was used as the mobile phase for TLC and for column chromatography. The PMR spectra of solutions of the compounds in d_6-DMSO were recorded with a Bruker WH-90 spectrometer. The IR spectra were recorded with a UR-20 spectrometer.

General Method for the Preparation of Ia-VIIa and Ib-VIIb. A 0.01-mole sample of I-VII was added to 30 ml of concentrated HNO_3 (sp. gr) 1.42), and the mixture was stirred at 40-50°C for 30 min. It was then cooled and poured over ice, and the mixture of mononitro isomers was removed by filtration, washed with water, and separated chromatographically with a column filled with silica gel. The constants of the substances are presented in Table 1.

Compounds Ia, IIa, Ib, and IIb can be obtained by treatment of I and II with nitric acid (sp. gr. 1.46) at 20-40°C. The reaction products were isolated in the same way.

General Method for the Preparation of Ic and IIIc-VIc. A 0.01-mole sample of amino compound VIII-XII was dissolved in 10 ml of concentrated H_2SO_4, and the solution was poured over 40 g of ice. The amine sulfate was diazotized with 2.3 ml (0.01 mole) of a 30% solution of sodium nitrite at 0-10°C by stirring at this temperature for 2 h. The diazo compound was added with stirring to a solution of 18 g (0.26 mole) of sodium nitrite and 14 g (0.17 mole) of sodium bicarbonate in 150 ml of water at 60°, and the mixture was stirred for 2 h. The precipitate was isolated and washed. Nitro compounds Ic and IIIc-VIc were obtained in 60-65% yields and were recrystallized from aqueous DMF. The constants of the substances are presented in Table 1.

General Method for the Preparation of Id, IVd, Vd, Ie, IVe, and Ve. A) A 0.01-mole sample of I, IV, or V was added to 40 ml of nitric acid (sp. gr) 1.48-1.51), and the mixture was stirred at 0-25°C for 30 min. It was then poured over ice, and the precipitated mixture of dinitro isomers was washed with water, dried, and separated chromatographically with a column filled with silica gel. The constants of the substances are presented in Table 1.

B) A 0.005-mole sample of mononitro compound Ia, IVa, or Va was added to 20 ml of HNO_3 (sp. gr. 1.51), and the mixture was stirred at 20°C for 30 min. It was then poured over ice, and the precipitate was removed by filtration and washed with water. Compounds Id, IVd, and Vd were obtained in 86-89% yields.

C) A 0.005-mole sample of mononitro compound Ib, IVb, or Vb was treated with fuming nitric acid under the conditions of the preceding experiment. This procedure gave Ie, IVe, and Ve in 85-88% yields.

D) A 0.005-mole sample of mononitro compound Ic, IVc, or Vc was treated with fuming nitric acid under the conditions of experiment B. This procedure gave a mixture of Id, IVd, Vd, Ie, IVe, and Ve, which were separated chromatographically. The IR spectra of the isolated compounds and the compounds obtained in experiments B and C were identical.

General Method for the Preparation of If, IVf, and Vf. A) A 0.01-mole sample of I, IV, or V was added to a mixture of 4 ml of HNO_3 (sp. gr. 1.51) and 20 ml of H_2SO_4 (sp. gr. 1.84), and the mixture was stirred at 60°C for 30 min. The temperature was then raised to 110-120°C, and the mixture was stirred for 20-30 min. It was cooled and poured into ice, and the precipitated If, IVf, or Vf was removed by filtration, washed with water, and purified by chromatography. The constants are presented in Table 1.

B). A 0.005-mole sample of dinitro compound Id, IVd, or Vd was treated with a nitrating mixture under the conditions of the preceding experiment. Compounds If, IVf, and Vf were obtained in 82-85% yields. The IR spectra of the isolated compounds and the compound obtained in experiment A were identical.

C) A 0.005-mole sample of dinitro compound Ie, IVe, and Ve was treated with a nitrating mixture under the conditions of experiment A. Compounds If, IVf, and Vf were obtained in 80-86% yields. The IR spectra of the isolated compounds and the compounds obtained in experiment A were identical.

5,10-Dioxo-4,5,9,10-tetrahydro-4,9-diazapyrene (VI). A 1.2-g (0.005 mole) sample of IV was dissolved in 20 ml of concentrated H_2SO_4, and 0.65 g (0.01 mole) of sodium azide was added gradually to the solution at 50°C in the course of 3 h. The mixture was stirred for another hour, after which it was poured over ice. The white precipitate was removed by filtration, washed, and dried to give 1.15 g (86%) of VI with mp > 400°C (from DMF) (mp > 400°C [1]), R_f 0.34 [25% ammonium hydroxide—dioxane (3:5)] and 0.83 [25% ammonium hydroxide—dioxane (1:4)], and greenish-yellow luminescence upon UV irradiation. IR spectrum (KBr): 3200, 3040, 2990, 2910, 1665, 1625, 1585, 1505, 1460, 1440, 1370, 1335, 1280, 1250, 875, 820, 800, 745 cm^{-1}.

Compounds VIa,b were similarly obtained from IVa,b, respectively. The IR spectra of these compounds and the compounds obtained by nitration of dioxotetrahydrodiazapyrene VI were identical.

LITERATURE CITED

1. G. I. Migachev, A. M. Terent'ev, and V. I. Lisoded, Khim. Geterotsikl. Soedin., No. 12, 1672 (1979).
2. A. G. Caldwell and L. P. Walls, J. Chem. Soc., No. 6, 2156 (1952).
3. G. I. Migachev, L. V. Eremenko, Ya. G. Urman, A. Kh. Bulai, and K. M. Dyumaev, Zh. Org. Khim., 15, 1491 (1979).
4. G. I. Migachev, A. M. Andrievskii, and N. S. Dokunikhin, Zh. Vses. Khim. Obshchestva, 21, 237 (1976).
5. N. S. Dokunikhin, G. I. Migachev, and N. G. Grekhova, Khim. Geterotsikl. Soedin., No. 9, 1287 (1976).
6. G. I. Migachev, Zh. Vses. Khim. Obshchestva, 24, 395 (1979).
7. G. I. Migachev, Zh. Org. Khim., 15, 567 (1979).
8. G. I. Migachev, A. M. Andrievskii, and N. S. Dokunikhin, Zh. Org. Khim., 15, 2508 (1979).
9. G. I. Migachev, N. G. Grekhova, and N. S. Dokunikhin, Zh. Org. Khim., 14, 2384 (1978).