

SYNTHESIS AND STRUCTURE OF NITRO-SUBSTITUTED

6(5H)-PHENANTHRIDINONES

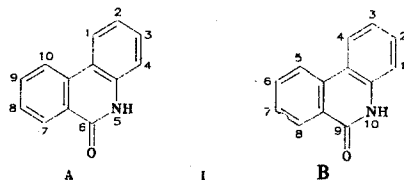
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Methods for the preparation of nitro-substituted 6(5h)-phenanthridinones were examined. The nitration of 6(5H)-phenanthridinone, 5-methyl-6-(5H)-phenanthridinone, and 2-bromo-6(5H)-phenanthridinone was studied, and 2-, 3-, 4-nitro-, 2,4-, 2,8-, 4,8-dinitro-, 2,4,8-trinitro-, and 2,4,8,10-tetranitro-6(5H)-phenanthridinones, 2,4,8-trinitro- and 2,4,8,10-tetranitro-6-(5H)-phenanthridinones, and 2-bromo-4,8-dinitro- and 2-bromo-4,8,10-trinitro-6-(5H)-phenanthridinones were obtained. Proton magnetic resonance spectroscopy was used to identify the structure and predict the orientation of substitution in the nitration of 6(5H)-phenanthridinone and its nitro-substituted derivatives. The distribution of the electron density in these compounds was evaluated from an analysis of the chemical shifts of the protons.

Nitro-substituted 6(5H)-phenanthridinones were synthesized for the first time in 1927 [1]. Subsequently, the interest in these compounds was associated with their use for the production of preparations that have good chemotherapeutic properties [2-7] and for the synthesis of pigments [8-10], heat-resistant polymers [11-13], biologically active compounds [14], and sensitizers for electrophotography [15].

Two systems of numbering of the atoms in the 6(5H)-phenanthridinone (I) molecule, which are represented by formulas A and B, have been used in the literature; this complicates the discussion of the material. In the present paper we used numbering system A, which corresponds to the IUPAC requirements.



A number of methods for the preparation of nitro-substituted 6(5H)-phenanthridinones are known: oxidation of the corresponding nitrophenanthridinones with potassium permanganate in sulfuric acid [16-18], oxidation of nitro-substituted 5-methyl-6-(5H)-phenanthridinones with sodium dichromate in acetic acid [2, 19, 20], from nitrophenanthrenequinones [18] or nitrofluorenones [3, 21-27] via the Schmidt reaction, from nitrofluorenone oximes via the Beckmann rearrangement [10, 20, 28, 29], from nitrodiphenic acid monoamides via the Hofmann reaction [1, 20, 29, 30], and from nitrodiphenic acid monohydrazides via the Curtius reaction [30, 31]. All of the possible mononitro-substituted 6(5H)-phenanthridinones and 3,8-dinitro-6(5H)-phenanthridinone have been synthesized by the enumerated methods. A method for the preparation of mononitro-6-(5H)-phenanthridinones by diazotization of amino-6(5H)-phenanthridinone or aminonitro-6(5H)-phenanthridinone with subsequent replacement of the diazo group by a nitro group or hydrogen was also described in [28, 32]. This method has limited application and is used, as a rule, in alternative synthesis to prove the location of the substituents. The multistep character, the difficulty involved in separating the isomeric compounds, and

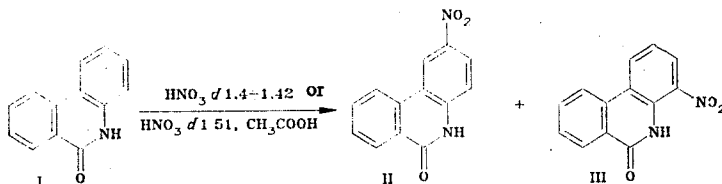
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the impossibility of obtaining nitrophenanthridinones with more than two nitro groups are among the drawbacks of all of the methods for the synthesis of nitro derivatives of I presented above.

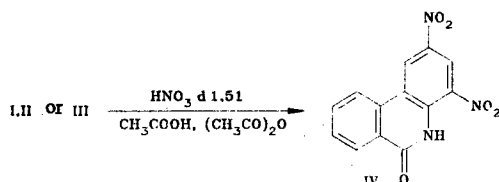
The direct nitration of 6(5H)-phenanthridinone (I) is the most convenient and promising method. A mixture of two mononitrophenanthridinones with unestablished structures was obtained by treatment of I with concentrated nitric acid at room temperature [1]. It was later shown [18, 20] that a mixture of 2-nitro- (II) and 4-nitro-6(5H)-phenanthridinone (III) in a ratio of 5:1 is formed under these conditions. Compounds II and III were subsequently synthesized in [15, 32-38] by the method in [1]. Nitro-substituted 6(5H)-phenanthridinones that contain two or more nitro groups and were obtained by the direct nitration of I were described in [15, 32]; however, in these papers due attention was not directed to the problems of the effect of the nitrating agent and the nitration conditions on the compositions of the reaction mixtures and the yields of the nitro compounds.

In the present research we studied the nitration of I in nitric acid with various concentrations, in a sulfuric acid-nitric acid (nitrating) mixture, and in a mixture of nitric acid with acetic acid and acetic anhydride.

Calculations of the electronic absorption spectra showed that charge transfer from the atoms of the lactam group to the atoms of the benzene ring bonded to the NH group occurs in the I molecule [39]; this charge transfer also determines the orientation of the substituents in electrophilic substitution. The first nitro group is incorporated in the 2 and 4 positions. Thus a mixture of nitrophenanthridinones II and III in a ratio of 6:1 was obtained in 96% yield when I was treated with nitric acid (d 1.40-1.42) at room temperature (under the conditions in [1]). Compounds with a higher degree of nitration begin to accumulate when the temperature is raised above 25°C and the density is increased to $d > 1.42$. This can be avoided by carrying out the nitration in a mixture of nitric (d 1.51) and acetic acids. A mixture of mononitro isomers II and III in a ratio of 5:1, which is virtually independent of the reaction temperature, is formed; this is a very convenient method for the preparation of the indicated compounds.

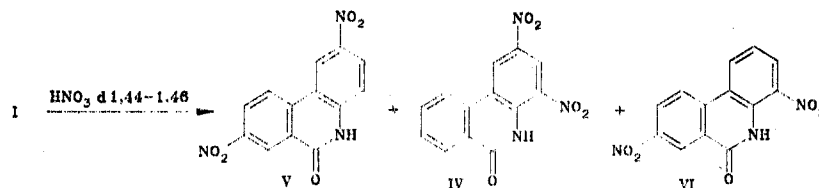


Dinitration is a special case. The orientation of the nitro groups depends on the nature of the nitrating agent. If the nitration of I is carried out with nitric acid (d 1.51) in a mixture of acetic acid and acetic anhydride, in which the nitrating agent is protonated acetyl nitrate, substitution takes place in one benzene ring, and 2,4-dinitro-6(5H)-phenanthridinone (IV) is formed in 85% yield. Compounds II and III are nitrated similarly under these conditions.



The use of concentrated nitric acid (d 1.44-1.46), in which the nitrating agent is the nitronium cation, which has low selectivity with respect to the substrate [40], leads to the formation of a mixture of 2,8-dinitro-6(5H)-phenanthridinone (V), 4,8-dinitro-6(5H)-phenanthridinone (VI), and IV. The ratio of dinitro isomers V and VI ranges from 5:1 to 7:1 and depends on the amount of nitrating agent; this is associated with the limited solubility of the intermediately formed 2-nitro-6(5H)-phenanthridinone (II) in the reaction medium. Dinitrophenanthridinones IV (20%), V (60%), and VI (12%) and mononitrophenanthridinone II (2%) were isolated from the reaction mixture when 40 ml of nitric acid (d 1.44-1.46) per 0.01 mole of I was used at room temperature. Only dinitration occurs when the volume of

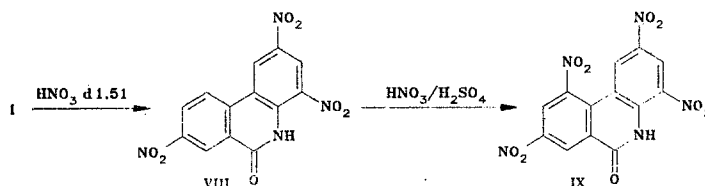
nitric acid is increased to 70 ml, and the yields of isomers IV, V, and VI, are respectively, 16%, 70%, and 9.4%.



A mixture of dinitro compounds V and VI in a ratio of (4-5):1 is formed in the nitration of 8-nitro-6(5H)-phenanthridinone (VII) in nitric acid (d 1.44) at room temperature.

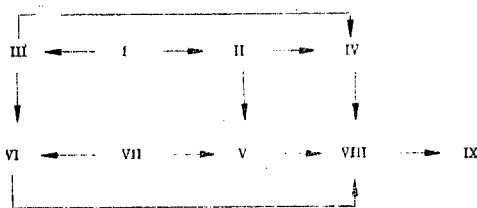
2,4,8-Trinitro-6(5H)-phenanthridinone (VIII) begins to accumulate in the reaction mixture when the nitric acid concentration or the temperature is increased. The best yield of VII (85%) was obtained when 6(5H)-phenanthridinone was refluxed in nitric acid (d 1.51) or when it was treated with a mixture of nitric acid (d 1.51) and acetic anhydride at 0-5°C.

More severe conditions are necessary for the introduction of four nitro groups. 2,4,8,10-Tetranitro-6(5H)-phenanthridinone (IX) is formed in 92% yield when I is heated in a mixture of nitric (d 1.51) and sulfuric (d 1.83) acids at 120°C for 2 h.



We tested a wide range of nitric acid concentrations, temperature conditions, and reagent ratios, and we also checked the nitration conditions [32]. We found that the principal reaction product when I is treated with nitric acid (d 1.48-1.51) at 0-25°C is X admixed with dinitro compounds IV-VI. Nitro-substituted IX and VIII in a ratio of 5:1 are formed when I is heated in the nitrating mixture at 110-120°C for 20-30 min.

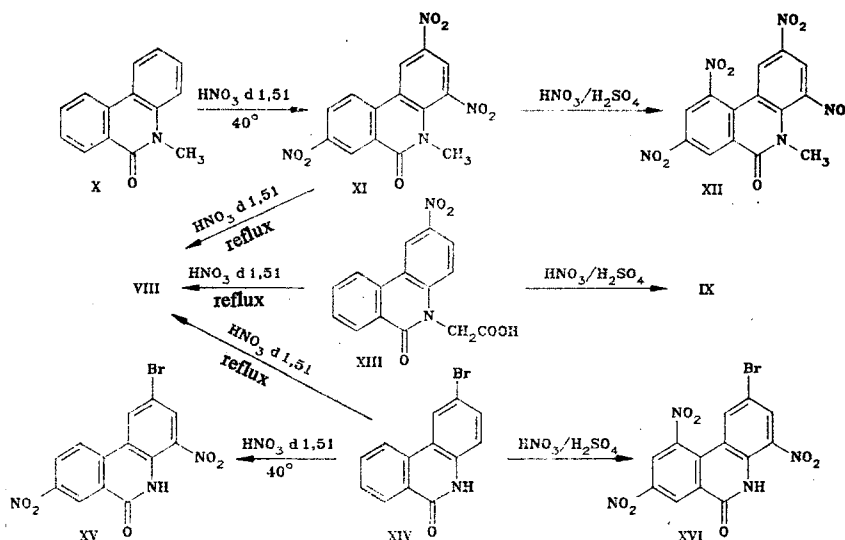
The general scheme of the nitration of 6(5H)-phenanthridinone is presented below:



In developing our research on the synthesis of electron acceptors for electrophotography we investigated the nitration of some derivatives of I. 2,4,8-Trinitro-5-methyl-6(5H)-phenanthridinone (XI) was obtained from 5-methyl-6-(5H)-phenanthridinone (X) [41] in nitric acid at 40°C, and 2,4,8,10-tetranitro-5-methyl-6-(5H)-phenanthridinone (XII) was obtained in the nitrating mixture at 20°C. Replacement of the methyl group by hydrogen to give trinitro-substituted VIII occurs when XI is refluxed in nitric acid (d 1.51).

Attempts to introduce three or four nitro groups into ethyl 2-nitro-6-(5H)-phenanthridinone-5-acetate (XIII) [37] were unsuccessful. Compounds VIII and IX, respectively, are formed when the reaction is carried out in nitric acid or the nitrating mixture.

Simultaneous replacement of the halogen atoms by a nitro group to give VIII occurs when 2-bromo- (XIV) and 2-iodo-6(5H)-phenanthridinone are refluxed in nitric acid (d 1.51). In contrast to the iodo derivative, two or three nitro groups can be introduced into XIV by treatment with nitric acid (d 1.51) at 40°C or with the nitrating mixture to give, respectively, 2-bromo-4,8-dinitro-6(5H)-phenanthridinone (XV) and 2-bromo-4,8,10-trinitro-6(5H)-phenanthridinone (XVI).



We used PMR spectroscopy to establish the structures of the synthesized compounds and to predict the orientation of substitution in the nitration of 6(5H)-phenanthridinone and its nitro-substituted derivatives. The number of nitro groups in all of the investigated compounds was determined by means of integration (Table 1). The assignments were made on the basis of the multiplicities of the signals by using the principles of the effect of nitro groups on aromatic protons [42]. A slight effect of substitution in one aromatic ring on the chemical shifts of the protons of the other ring was demonstrated in the analysis of the spectra. We made a comparison of the spectral information in series of mononitro-substituted II, III, and 3-nitro-6(5H)-phenanthridinone, traces of which are formed in the nitration of I in nitric acid. As a result, we were able to interpret the PMR spectrum of the starting 6(5H)-phenanthridinone.

Replacement of the protons by a nitro group simplifies the form of the spectrum of the aromatic protons. Whereas in the case of unsubstituted phenanthridinone the spectrum is a complex, second-order, multiplet pattern, the introduction of an NO₂ group into the 2,3, and 8 positions leads to separation of the signals with a doublet structure from the protons in the 1, 4, and 7 positions with meta spin-spin coupling constants (SSCC). When NO₂ groups are introduced into the 2 and 4 position, the signals from the protons in the 1 and 3 position show up in the spectrum in the form of two doublets with a meta constant. The SSCC of the protons in the spectra of the investigated nitrophenanthridinones are characteristic for aromatic compounds [42]: The ortho constant is ~8 Hz, and the meta constant is ~2 Hz. The chemical shifts of the protons of the NH group are found at 11-12 ppm. This constitutes evidence for a strong hydrogen bond between the deuterated solvent (d₆-DMSO) and the

TABLE 1. Chemical Shifts of the Protons in the PMR Spectra of 6(5H)-Phenanthridinone and Its Nitro-Substituted Derivatives II-VI, VIII, and IX and 3-Nitro-6(5H)-phenanthridinone

Compound	Position of the nitro grp.	Signals of the protons, δ , ppm (d ₆ -DMSO)								
		1-H	2-H	3-H	4-H	7-H	8-H	9-H	10-H	NH
I	—	8,30	7,30	7,80	7,50	8,40	7,70	8,00	8,50	11,70
II	2-	9,20	—	8,30	7,50	8,30	7,70	8,00	8,60	12,20
— ^a	3-	8,40	8,00	—	8,20	8,30	7,70	8,00	8,60	12,00
III	4-	8,80	7,40	8,30	—	8,30	7,70	8,00	8,50	11,00
IV	2,4-	9,50	—	9,00	—	8,40	7,70	8,00	8,80	11,40
V	2,8-	9,20	—	8,30	7,50	8,80	—	8,50	8,90	—
VI	4,8-	8,80	7,40	8,30	—	8,80	—	8,50	8,90	—
VIII	2,4,8-	9,40	—	8,90	—	8,80	—	8,50	8,90	11,50
IX	2,4,8,10-	9,30	—	9,10	—	8,70	—	9,10	—	—

^a3-Nitro-6(5H)-phenanthridinone.

TABLE 2. Characteristics of Nitro-Substituted II-IX, XI, XII, XV, XVI, and 3-Nitro- and 3,8-Dinitro-6(5H)-phenanthridinones

Compound	mp, deg C	R _F (system)	IR spectrum, cm ⁻¹ (KCl)			Found, %			Empirical formula	Calculated, %		
			νC=O	νNO ₂	νNH	C	H	N		C	H	N
II	382—383 [33]	0,25 (A)	1690	1345, 1545	3130, 3160	65,0	3,2	11,6	C ₁₃ H ₈ N ₂ O ₃	65,0	3,3	11,7
— ^a	348,5—349 [18]	0,38 (A)	1690	1340, 1520	3215	64,9	3,3	11,6	C ₁₃ H ₈ N ₂ O ₃	65,0	3,3	11,7
III	264—265 [33]	0,62 (A)	1668	1355, 1540	3300	65,0	3,3	11,7	C ₁₃ H ₈ N ₂ O ₃	65,0	3,3	11,7
IV	303— 303,5	0,75 (A)	1680	1340, 1515	3260, 3300	54,7	2,5	14,6	C ₁₃ H ₇ N ₃ O ₅	54,7	2,5	14,4
V	>400	0,27 (A)	1675	1355, 1540	3090, 3400	54,7	2,4	14,5	C ₁₃ H ₇ N ₃ O ₅	54,7	2,5	14,4
VI	278—279	0,45 (B)	1685	1345, 1520	3100, 3250, 3400	54,7	2,4	14,4	C ₁₃ H ₇ N ₃ O ₅	54,7	2,5	14,4
— ^b	380 [3]	0,42 (A)	1670	1340, 1520	3400	54,8	2,4	14,4	C ₁₃ H ₇ N ₃ O ₅	54,7	2,5	14,4
VII	328—329	0,32 (A)	1670	1335, 1525	3180	65,0	3,3	1,6	C ₁₃ H ₈ N ₂ O ₃	65,0	3,3	11,7
VIII	224,5—225	0,60 (D)	1700	1345, 1540	3090, 3250	47,2	1,8	16,9	C ₁₃ H ₆ N ₄ O ₇	47,3	1,8	17,0
IX	236—237	0,53 (D)	1712	1355, 1545	3090, 3290	41,8	1,4	18,7	C ₁₃ H ₅ N ₅ O ₉	41,7	1,3	18,7
XI	221— 222,5	0,60 (C)	1685	1350, 1540	3095, 3400	48,9	2,5	16,2	C ₁₄ H ₈ N ₄ O ₇	48,8	2,3	16,3
XII	208—209	0,67 (C)	1680	1350, 1540	3095, 3400	43,2	1,7	17,8	C ₁₄ H ₇ N ₅ O ₉	43,2	1,8	18,0
XV	233,5— 234,5	0,63 (B)	1690	1340, 1535	3240	42,8	1,8	11,4 (22,1)	C ₁₃ H ₆ BrN ₃ O ₅	42,9	1,7	11,3 (22,0)
XVI	226—228	0,56 (B)	1700	1350, 1540	3100, 3260	38,3	1,2	13,5 (19,4)	C ₁₃ H ₅ BrN ₄ O ₇	38,1	1,2	13,7 (19,6)

^a3-Nitro-6(5H)-phenanthridinone.

^b3,8-Dinitro-6(5H)-phenanthridinone.

investigated compound; this is evidently associated with the high acidity of this proton. It is interesting to note that the NH group undergoes 50% deuteration in d₆-DMSO. When the number of substitutions is increased, the signal of the NH group becomes broader because of facilitation of exchange with the protons of the water that is present in solution.

An analysis of the chemical shifts of the protons of I and its nitro-substituted derivatives makes it possible to evaluate the distribution of the electron density in these compounds. In unsubstituted 6(5H)-phenanthridinone I, mononitro isomers II and III, and dinitro isomers V and VI the maximum electron density is found in the ring bonded to the NH group (the numbers of the compounds and the positions with the maximum electron density are presented): I, 2 and 4; II, 4 and 8; III, 2 and 8; V, 4; VI, 2. In IV the maximum electron density is found in the second benzene ring in the 8 position. These data are in agreement with the results of orientation of the substituents in the nitration of the indicated compounds. On the other hand, they can be used in the study of various electrophilic substitution reactions in the 6(5H)-phenanthridinone molecule.

The structures of tri- (VIII) and tetranitro-substituted (IX) 6(5H)-phenanthridinones were proved by alternative synthesis from II-VII and data from the PMR spectra (Table 1). The structure of IX was previously investigated by x-ray diffraction analysis [43].

EXPERIMENTAL

The IR spectra of KCl pellets of the compounds were recorded with a Perkin-Elmer 580 spectrometer. The PMR spectra of saturated solutions of the nitrophenanthridinones in d₆-DMSO (containing 99.3% of the isotope) were obtained with a Bruker HX-90 spectrometer under pulse-accumulation conditions at 100°C with tetramethylsilane as the internal standard. The accuracy in the measurement of the chemical shifts was +0.01 ppm. The purity of the products was monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates in systems A [acetone-benzene (1:5)], B [acetone-benzene (1:7)], C [acetone-benzene (1:20)], and D [25% ammonium hydroxide-dioxane (1:7)].

The following compounds were synthesized by known methods: I [44], II [3], VII [1], 3-nitro-6(5H)-phenanthridinone [23], X [41], XIII [37], and XIV [33].

The characteristics of the synthesized compounds are presented in Tables 1 and 2.

2-Nitro-6(5H)-phenanthridinone (II) and 4-Nitro-6(5H)-phenanthridinone (III). A 1.95-g (10 mmole) sample of I was added to a mixture of 3 ml of acetic acid and 1.2 ml of nitric acid (d 1.51), after which the mixture was refluxed for 2 h and cooled. The precipitate was removed by filtration and recrystallized from DMF to give 1.81 g (75.5%) of cream-colored crystals of II. Water (40 ml) was added to the filtrate, and the resulting precipitate was removed by filtration and recrystallized from acetic acid to give 0.3 g (12.5%) of yellow needles of III.

2,4-Dinitro-6(5H)-phenanthridinone (IV). A) A 2-ml sample of nitric acid (d 1.51) was added dropwise to a mixture of 70 ml of acetic acid, 10 ml of acetic anhydride, and 5 g (26 mmole) of I, and the resulting mixture was refluxed for 2 h, cooled, and poured over ice. The precipitate was removed by filtration and recrystallized from acetic acid to give 5.75 g (78.8%) of yellow needles of IV. Compound IV was also obtained by this method from II and III.

B) A 50-ml sample of sulfuric acid (d 1.83) was added to a suspension of 2.55 g (10 mmole) of 2-amino-4-nitro-6(5H)-phenanthridinone [28], after which the mixture was cooled to 0-5°C, diazotized at this temperature with 2 ml of 40% sodium nitrite solution, and stirred for 0.5 h. The diazo solution was filtered, and the filtrate was added to a solution of a mixture of 40 g of sodium nitrite and 20 g of sodium bicarbonate in 200 ml of water at 50-60°C. The mixture was stirred for 3 h, and the precipitate was removed by filtration, washed with water, and recrystallized from acetic acid to give 3.1 g (71%) of IV, which, according to the IR spectral data and the melting point, was identical to the sample from the preceding experiment.

2,8-Dinitro-6(5H)-phenanthridinone (V), 2,4-Dinitro-6(5H)-phenanthridinone (IV), 4,8-Dinitro-6(5H)-phenanthridinone (VI), and 2-Nitro-6(5H)-phenanthridinone (II). A) A 3.9-g (20 mmole) sample of I was added to 80 ml of nitric acid (d 1.44), after which the mixture was stirred at room temperature for 6 h and poured over ice. The precipitate was removed by filtration, washed with water, and dried to give 5.42 g of a mixture of nitro compounds. The precipitate was extracted with acetic acid (two 100-ml portions). The residue was washed with water and recrystallized from DMF to give 3.14 g (55%) of cream-colored crystals of V. The extract was diluted with 400 ml of water, and the precipitate was removed by filtration, washed with water, and dried. A 2.26-g sample of the substance was dissolved in 80 ml of DMF, the solution was mixed with 50 g of Silicagel L 100/160, the solvent was removed, and the residue was applied to a column (3 by 80 cm) packed with 350 g of silica gel and eluted with benzene-acetone (10:1). Evaporation of the first fraction and recrystallization of the residue from acetic acid gave 1.14 g (20%) of IV, which was identical to the sample obtained from the preceding experiment. Workup of the second fraction in a similar manner gave 0.7 g (12%) of yellow needles (from acetic acid) of VI. Workup of the third fraction gave 0.28 g (5%) of V (from an overall yield of 60%), and workup of the fourth fraction gave 0.12 g (2%) of II.

B) Compound II was nitrated under the conditions of the preceding experiment to give a mixture of dinitro isomers, from which V and IV were isolated in a ratio of 3.5:1 (92% yield).

C) Compound VII was nitrated under the same conditions. Workup gave a mixture of V and VI in a ratio of 5:1 (85% yield).

D) Compound III was nitrated similarly to give a mixture of IV and VI in a ratio of 2:1 (87% yield).

E) Compound VII was nitrated under the conditions used for the preparation of IV (in acetic acid with acetic anhydride). A mixture of V and VI in a ratio of 4:1 was obtained (81% yield).

2,4,8-Trinitro-6(5H)-phenanthridinone (VIII). A) A 1.95-g (10 mmole) sample of I was added at 0-5°C to a mixture of 50 ml of nitric acid (d 1.51) and 10 ml of acetic anhydride, and the resulting mixture was stirred at this temperature for 2 h and poured over ice. The precipitate was removed by filtration, washed with 50 ml of water, and recrystallized from acetic acid to give 2.8 g (85%) of VIII in the form of pale-yellow crystals.

B) A 5.85-g (30 mmole) sample of I was refluxed in 50 ml of nitric acid (d 1.51) for 2 h, after which the mixture was cooled and poured over ice, and the precipitate was removed by filtration, washed with water, and dried to give 8.42 g (85%) of VIII, which was identical to the sample from the preceding experiment.

Compound VIII was obtained via this method from II-VII, X, XI, XIII, XIV, and 2-iodo-6(5H)-phenanthridinone.

2,4,8,10-Tetranitro-6(5H)-phenanthridinone (IX). A 1.95-g (10 mmole) sample of I was added to a mixture of 4 ml of nitric acid (d 1.51) and 32 ml of sulfuric acid (d 1.83), and the resulting mixture was stirred at 120°C for 2 h. It was then cooled and poured over ice, and the precipitate was removed by filtration, washed with 50 ml of water, and dried to give 3.44 g (92%) of IX in the form of yellow needles from acetic acid.

Compound IX was obtained via this method from VIII and X-XVI.

2,4,8-Trinitro-5-methyl-6(5H)-phenanthridinone (XI). A 1-g (5 mmole) sample of X was added to 20 ml of nitric acid (d 1.51), and the mixture was stirred at 40°C for 1 h, after which the solution was poured over ice. The precipitate was removed by filtration, washed with 30 ml of water, and dried to give 0.82 g (70%) of XI in the form of yellow crystals from acetic acid.

2,4,8,10-Tetranitro-5-methyl-6(5H)-phenanthridinone (XII). A 1-g (5 mmole) sample of X was added to a mixture of 10 ml of nitric acid (d 1.51) and 30 ml of sulfuric acid (d 1.83), and the mixture was stirred at room temperature for 1 h, after which it was worked up as in the preceding experiment to give 1.21 g (65%) of XII in the form of light-yellow crystals from acetic acid.

Compound XII was obtained in 70% yield via this method from XI.

2-Bromo-4,8-dinitro-6(5H)-phenanthridinone (XV). A 5.48-g (20 mmole) sample of XIV was added to 100 ml of nitric acid (d 1.51), and the mixture was stirred at 40°C for 1.5 h. The solution was cooled and poured over ice, and the precipitate was removed by filtration, washed with 50 ml of water, dried, and recrystallized twice from acetic acid to give 4.73 g (65%) of XV in the form of pale-yellow crystals.

2-Bromo-4,8,10-trinitro-6(5H)-phenanthridinone (XVI). A 5.48-g (20 mmole) sample of XIV was added to a mixture of 8 ml of nitric acid (d 1.51) and 64 ml of sulfuric acid (d 1.83), and the resulting mixture was heated to 90°C and stirred at this temperature for 3 h. The solution was cooled and poured over ice, and the precipitate was removed by filtration, washed with 50 ml of water, and dried to give 7.32 g of the nitration product. A 2-g sample of the substance was dissolved in 40 ml of benzene, and the solution was applied to a column (3 by 50 cm) packed with 200 ml of Silicagel L 100/160 and eluted with benzene. Workup of the first fraction gave 1.56 g (78%) of XVI. Workup of the second fraction gave 0.24 g (12%) of IX.

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