CONDENSED HETEROCYCLIC SYSTEMS WITH A QUATERNARY NITROGEN ATOM.

IV.* SYNTHESIS OF PYRIDO[1,2-f]PHENANTHRIDINIUM PERCHLORATES

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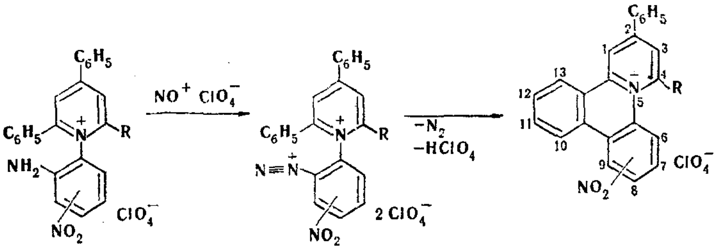
Nitro and amino derivatives of pyrido[1,2-f]phenanthridinium perchlorate were synthesized by the Pschorr method and by photocyclodehydrogenation from N-(nitrophenyl)- or N-(aminophenyl)pyridinium perchlorates. The mechanism of the photoconversion was investigated.

Pyrido[1,2-f]phenanthridinium salts (dibenzoquinolizinium salts) can be synthesized [2] by the Pschorr method and are luminophores with rather high quantum yields [3].

In order to synthesize amines of this series we obtained nitro derivatives of N-(2-aminophenyl)pyridinium salts (I) by condensation of nitro-1,2-phenylenediamines with pyrylium salts in dimethylformamide (DMF).



Ia-d IIa-d IIIa-d

It should be noted that pyrylium salts react selectively with the amino groups of 3- and 4-nitro-1,2-phenylenediamines. Thus 3-nitro-1,2-phenylenediamine undergoes condensation with pyrylium salts at the amino group in the meta position relative to the nitro group, whereas 4-nitro-1,2-phenylenediamine undergoes condensation with the amino group in the para position. This was established by elimination of the amino group in I and by comparison of the salts obtained with genuine samples of N-nitrophenylpyridinium perchlorates.

We carried out the intramolecular cyclization of the synthesized pyridinium perchlorates I by the methods in [3, 4], which were proposed for the synthesis of benzo[c]phenanthridine and its derivatives. However, the diazotization of pyridinium salts I was carried out under more severe conditions because of their low solubilities in dilute mineral acids. Nitrosyl perchlorate, which makes it possible to avoid the formation of a mixture of salts with different anions, was selected as the diazotizing agent. Cyclization of the diazonium dications of II leads to 8- and 9-nitropyrido[1,2-f]phenanthridinium perchlorates (III).

The reduction of the nitro group in III with zinc dust, iron, or stannous chloride in hydrochloric acid leads to the formation of stable complexes of aminopyrido[1,2-f]phenanthridinium perchlorates (IV) with the salts of the corresponding metals. The catalytic hydrogenation of III with hydrogen over palladium-coated carbon proceeds most smoothly and gives the amines in quantitative yields; moreover, hydrogenation of the heteroring is not observed.

We were unable to synthesize 7-aminopyrido[1,2-f]phenanthridinium perchlorate (IV) by this method, since the starting N-(2-amino-5-nitrophenyl)pyridinium perchlorate is not formed by condensation of the pyrylium salt with the corresponding nitro derivative of o-phenylenediamine. We were also unable to carry out the nitration of N-(2-aminophenyl)-2,4,6-tri-

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*See [1] for communication III.

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TABLE 1. N-[2-Amino-3(4)-nitrophenyl]pyridinium Perchlorates (I)

Compound	R	Position of the NO_2 group	mp, °C	Found, %				Empirical formula	Calc., %				Yield, %
				C	H	Cl	N		C	H	Cl	N	
Ia	C_6H_5	4′	264—265[a]	64,2	4,2	6.9	7,5	$C_{29}H_{22}ClN_3O_6$	64,0	4,0	6.5	7,7	93
Ib	C_6H_5	3′	260—261[b]	64,1	4.4	6,7	7.6	$C_{29}H_{22}ClN_3O_6$	64,0	4,0	6.5	7,7	88
Ic	CH_3	4′	210—211[b]	60,1	4.6	7,4	8.9	$C_{24}H_{20}ClN_3O_6$	59,8	4,2	7.3	8,7	83
Id	CH_3	3′	147—148[b]	60,3	4,0	7,0	8,5	$C_{24}H_{20}ClN_3O_6$	59,8	4,2	7,3	8,7	97

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[a] From nitromethane. [b] From methanol.

TABLE 2. Nitropyrido[1,2-f]phenanthridinium Perchlorates (III)

Compound	R	Position of the NO_2 group	mp, °C	Found, %				Empirical formula	Calc., %				Yield, %
				C	H	Cl	N		C	H	Cl	N	
IIIa	C_6H_5	8	307—308[a]	65,4	4,0	6,7	5,0	$C_{29}H_{19}ClN_2O_6$	66,1	3,6	6,7	5.3	60
IIIb	C_6H_5	9	277—278[b]	65,9	3,9	6.7	5,2	$C_{29}H_{19}ClN_2O_6$	66,1	3,6	6,7	5,3	91
IIIc	CH_3	8	195—196[b]	61,9	3.7	7,4	5,8	$C_{24}H_{17}ClN_2O_6$	61,2	3,6	7,6	6,0	76
IIId	CH_3	9	290(dec.)[b]	61,0	4,0	7,8	5,8	$C_{24}H_{17}ClN_2O_6$	61,2	3,6	7,6	6,0	77

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[a] From nitromethane. [b] From glacial acetic acid.

TABLE 3. Aminopyrido[1,2-f]phenanthridinium Perchlorates (IV)

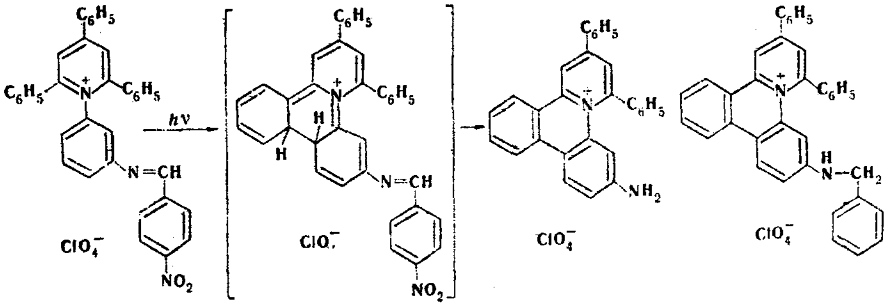
Compound	R	Position of the NO_2 group	mp, °C	Found, %				Empirical formula	Calc., %				Yield, %
				C	H	Cl	N		C	H	Cl	N	
IVa	C_6H_5	8	323—324	69,8	4,5	7,4	5,3	$C_{29}H_{21}ClN_2O_4$	70,0	4,2	7,1	5,6	Quant.
IVb	CH_3	8	230—231	65,9	4,4	8,3	6,0	$C_{24}H_{19}ClN_2O_4$	66,2	4,4	8,1	6,4	Quant.
IVc	C_6H_5	9	295—296	70.1	4,6	6,9	5,3	$C_{29}H_{21}ClN_2O_4$	70,0	4,2	7,1	5,6	Quant.
IVd	CH_3	9	>300	65,8	4,2	8,1	6,0	$C_{24}H_{19}ClN_2O_4$	66,2	4,4	8,1	6,4	Quant.
IVe	C_6H_5	7	267—268	70,2	4,7	6,9	5,7	$C_{29}H_{21}ClN_2O_4$	70,0	4,2	7,1	5,6	30

phenylpyridinium perchlorate by the method proposed for the nitration of other heteroaromatic cations [5], despite the suitable orientation of substituents.

It is known [6] that unsubstituted N-phenylpyridinium perchlorates readily undergo photocyclodehydrogenation to give cyclic pyrido[1,2-f]phenanthridinium perchlorates. However, phototransformations of this sort are not observed for N-(aminophenyl)pyridinium perchlorates. Spectral-luminescence studies provide evidence for the development in this case of nonphotoactive low-lying states of intramolecular charge transfer from the N-phenyl group to the pyridinium ring. The existence of such states determines the development of the long-wave band (λ 400-410 nm) in the absorption spectra and the intense fluorescence (λ_{max} 470 nm) of solutions of these compounds at room temperature. Similar competition between the photochemical transformations and fluorescence was observed during a study of the photocyclodehydrogenation of stilbenes [7]. On the basis of these data, the direct photochemical synthesis of IV is impossible.

The results of a study of the effect of oxidizing agents on the rate of photocyclization of N-phenylpyridinium perchlorates showed that the addition of a catalytic amount of iodine to the solution substantially increases the rate of formation of the final photoproducts and that removal of oxygen from the solutions slows down the phototransformations markedly. These experimental data are characteristic for photocyclodehydrogenation reactions that pass through a step involving the formation of dihydro intermediate VI, which is oxidized by the dissolved oxygen to the final cyclic compound.

The above-described mechanism of the phototransformations made it possible to accomplish the photochemical synthesis of IVe using N-[3-(p-nitrobenzalamino)phenyl]-2,4,6-triphenylpyridinium perchlorate (V). A solution of V was irradiated in an argon atmosphere. Under these conditions, the benzylidene grouping is a hydrogen acceptor.



V VI IVe

In addition to amines IVe and VII, compounds with unestablished structures, which are possibly a mixture of starting azomethine V and products of the decomposition of the benzylidene derivative of perchlorate IV, were isolated from the reaction mixture.

The amino group in perchlorates IV is inert with respect to diazotizing and acylating reagents. The low basicities do not make it possible to measure the pK values of these amines by means of potentiometric titration in acetonitrile [9].

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The UV spectra were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of solutions of the compounds in d_6-DMSO were recorded with a Tesla BS-476 spectrometer with hexamethyldisiloxane as the internal standard. The photochemical synthesis was carried out in a reactor with a 1 kW mercury lamp.*

N-[2-Amino-3(4)-nitrophenyl]pyridinium Perchlorates (I). A mixture of 10 mmole of the pyrylium salt, 10 mmole of nitro-1,2-phenylenediamine, and 30 ml of dimethylformamide (DMF) was heated for 2 h, after which it was cooled and diluted with water. The resulting yellow precipitate was removed by filtration. The characteristics of the compounds obtained are presented in Table 1. IR spectrum: 1520 (NO_2); 1570, 1640, 3300, and 3450 cm^{-1} (NH_2).

Replacement of the Amino Group in Salts I by Hydrogen. A diazonium solution prepared from 5 mmole of perchlorate I by the method in [2] was diluted with 30 ml of absolute ether, the diazonium compound was removed by filtration and added to 10 ml of ethanol, and the mixture was treated with a catalytic amount of copper powder. The mixture was allowed to stand for 10 h, after which it was filtered, and 20 ml of ether was added to the filtrate. The precipitated corresponding N-[3(4)-nitrophenyl]pyridinium perchlorate was removed by filtration.

Nitropyrido[1,2-f]phenanthridinium Perchlorates (III). A 0.33-g (2.5 mmole) sample of nitrosyl perchlorate was added to a solution of 2.5 mmole of N-[2-amino-3(4)-nitrophenyl]-pyridinium perchlorate I in 30 ml of glacial acetic acid heated to 50°C, and the mixture was stirred for 3-5 min.

The mixture was cooled, and 50 ml of absolute ether was added. The colorless cyrstalline precipitate of diazonium salt II was removed by filtration, washed with water, and added to 20 ml of acetone. Nitrogen evolution was observed after the addition of copper powder to the solution. The solution was allowed to stand for 12 h, after which the solvent was removed by distillation. The compounds were obtained as yellow crystalline substances, data on which are presented in Table 2. IR spectrum: 1540 (NO_2) and 1630 cm^{-1}.

Aminopyrido[1,2-f]phenanthridinium Perchlorates (IV). A 10 mmole sample of perchlorate III was dissolved in 10 ml of DMF, 0.01 g of 5% Pd/C was added, and the compound was hydrogenated until hydrogen absorption ceased (2-3 h). The catalyst was removed by filtration, 20 ml of water was added to the filtrate, and the red precipitate was crystallized from nitromethane. Data on the compounds obtained are presented in Table 3. IR spectrum: 3450 m (NH_2) and 1650 cm^{-1}.

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*The reactor was designed and manufactured in the Lensovet Leningrad Technological Institute.

7-Amino-2,4-diphenylpyrido[1,2-f]phenanthridinium Perchlorate (IVe). A 2 g sample of perchlorate V [8] was dissolved in 1 liter of absolute methylene chloride, and the solution was irradiated in a photoreactor in an argon atmosphere for 3 h. The solvent was then removed by distillation. The resulting dark-red crystalline residue was identified as a mixture of starting azomethine V (10%), with R_f 1, a compound with unestablished structure (10%, with R_f 0.85, 7-(p-nitrobenzylamino)-2,4-diphenylpyrido[1,2-f]phenanthridinium perchlorate (VII) (35%) with R_f 0.27, and perchlorate IV (30%) with R_f 0.78 [Al_2O_3, chloroform—acetone—nitromethane (4:1:1)]. Data on perchlorate IV are presented in Table 3. IR spectrum: 3390 cm^{-1} (NH_2).

7-(p-Nitrobenzylamino)-2,4-diphenylpyrido[1,2-f]phenanthridinium Perchlorate (VII). This compound was obtained as yellow prisms with mp 110°C (from ethanol). IR spectrum: 3330 (NH) and 1545 cm^{-1} (NO_2). PMR spectrum: 2.22 (s, NH) and 4.2 ppm (s, CH_2). Found: C 68.1; H 5.0; Cl 5.8%. $C_{36}H_{26}ClN_3O_6$. Calculated: C 68.4; H 4.9; Cl 5.7%.

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CONFORMATIONAL STUDY OF CHIRAL HETEROCYCLIC ENAMINO KETONES*

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An assumption regarding the existence of a homoconjugation effect involving enaminoketo and phenyl groups as a result of the drawing together in space of their π orbitals was made on the basis of circular dichroism (CD) data and an examination of the preferred conformations of two-ring enamino ketones with α-phenylethyl and α-benzylethyl substituents. A study of enamino ketones with a chiral alkyl substituent attached to the nitrogen atom made it possible to confirm this assumption.

A study of the chiral-optical properties of two-ring cisoid enamino ketones I and II, which have α-phenylethyl or α-benzylethyl substituents attached to the nitrogen atom, by optical rotatory dispersion (ORD) and circular dichroism (CD) has made it possible to make an assumption regarding the drawing together in space of the π orbitals of the phenyl and enaminoketo chromophores separated by two and three σ bonds, i.e., manifestation of a homoconjugation effect [2, 3].

For a further study of the nature of the enaminoketo chromophore, which has a cis-s-trans configuration, and its geometry for an evaluation of the contribution of homoconjugation to optical rotation we investigated model compounds — cisoid two-ring enamino ketones III with

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