cation of which from petroleum ether yielded 0.6 g (53%) of acetoxydecahydroquinoline XXVII with mp 126-127°.

Esters XXII-XXVI were similarly synthesized (Table 2).

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OXIDATION OF STEREOISOMERIC N-AMINO-11,14-DICYANOPERHYDROACRIDINES

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UDC 547.835.2:541.63:542.943

The oxidation of trans–syn–trans–N-amino-11,14-dicyanoperhydroacridine with manganese dioxide or bromine gives two stereoisomeric 11,12-dicyanoperhydrofluorenes and two stereoisomeric 2-cyano-1-(2-cyanocyclohexylmethyl)-1-cyclohexenes. The oxidation of trans–anti–cis-N-amino-11,14-dicyanoperhydroacridines with manganese dioxide gives three other stereoisomers of 11,12-dicyanoperhydrofluorene.

It is known [1] that the oxidation of 1,1-disubstituted hydrazines may occur without nitrogen evolution (to give tetrazenes) or with nitrogen evolution. In particular, the oxidation of 2,6-dicyano-1-amino-2,6-dimethylpiperidines (I) with bromine is accompanied by nitrogen evolution and the formation of stereoisomeric 1,2-dicyano-1,2-dimethylcyclopentanes (the products of recombination of the intermediate diradical) and 2,6-dicyano-2-heptane (the product of disproportionation of the diradical) [2].

We carried out the oxidation of stereoisomeric N-amino-11,14-dicyanoperhydroacridines (IIa, b) [3] with active γ-manganese dioxide; the oxidation proceeds smoothly at room temperature and is accompanied by nitrogen evolution. The oxidation of trans–syn–trans isomer IIa leads to two stereoisomeric 11,12-dicyanoperhydrofluorenes (IIIa, b) and two stereoisomeric 2-cyano-1-(2-cyanocyclohexylmethyl)-1-cyclohexenes (IVa, b). The oxidation of trans–anti–cis-isomer IIb gives the three other stereoisomers of 11,12-dicyanoperhydrofluorene (IIIc-e); unsaturated cyanides of IV are not formed here.

Compounds IIIa-e are evidently recombination products, whereas IVa, b are products of disproportionation of the intermediate diradicals.

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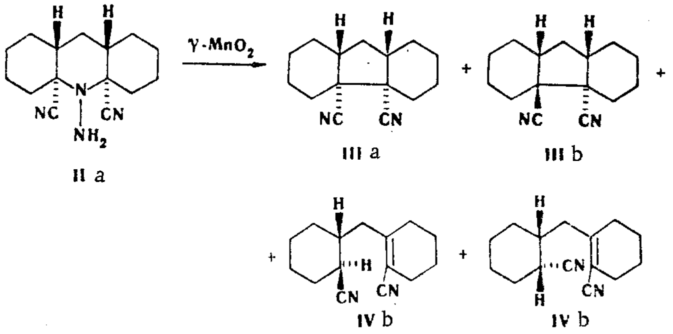
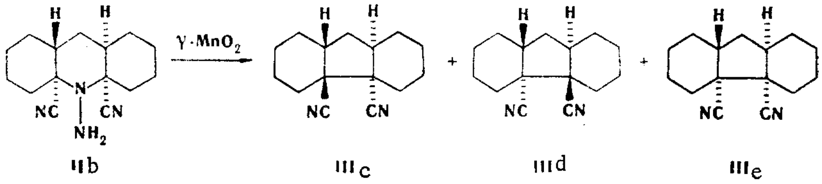
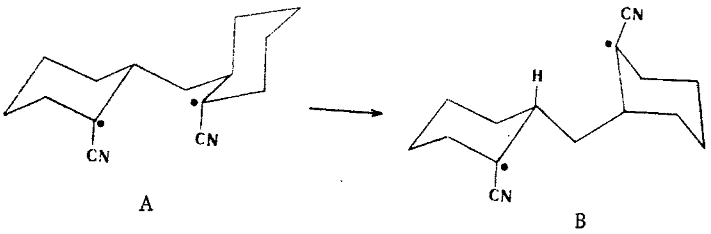


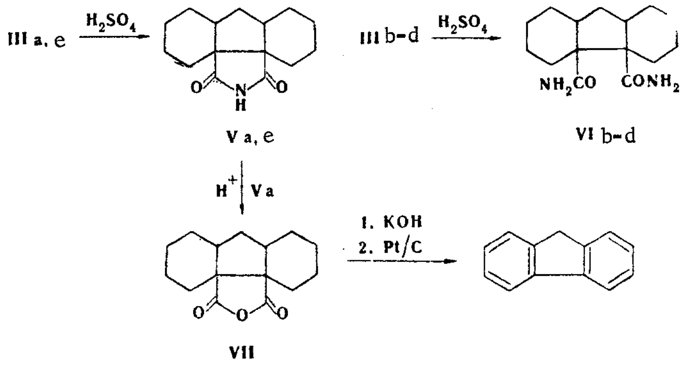


The fact that dinitriles IV are not formed in the oxidation of isomer IIb can be explained, in our opinion, by the fact that conversion of the appropriate diradical from starting conformation A, which is most convenient for recombination, to conformation B, which is most favorable for disproportionation, is more difficult than the analogous conversion in the case of oxidation of isomer IIa; this is confirmed by an examination of models.



All III and IV have an identical m/e value of 228. Absorption in the double-bond region is absent in the IR spectra of perhydrofluorenes IIIa-e, and the spectra contain the absorption of an unconjugated CN group at 2250 cm^{-1}. The spectra of all of the isomers of III are extremely similar.

Inasmuch as different III isomers are formed from IIa and IIb, it may be concluded that the configuration at the C$_{12}$ and C$_{13}$ atoms of starting dicyanides II is retained on oxidation; consequently, the hydrogen atoms attached to C$_{12}$ and C$_{13}$ in isomers IIIa, b are cis-oriented, whereas they are trans-oriented in isomers IIIc-e. The mutual orientation of the cyano groups in III was ascertained by their hydrolysis with concentrated H$_2$SO$_4$. In this case isomers IIIa and IIIe give imides of 11,12-perhydrofluorenedicarboxylic acids (Va, e), and consequently have a cis orientation of the cyano groups; isomers IIIb-d give diamides of the analogous acids (VIb-d), and this makes it possible to propose trans orientation of the cyano groups for them.



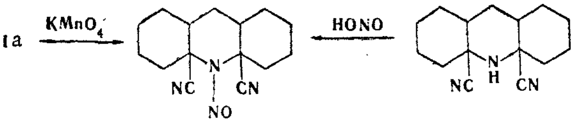
The structure of imides V is confirmed by their IR spectra, which contain absorption bands at 1720 and 1770 cm^{-1} ($C=O$ groups in five-membered imides); anhydride VII was obtained from imide Va by further hydrolysis, and its IR spectrum contains absorption at 1780 and 1830 cm^{-1} ($C=O$ in five-membered anhydrides). Successive treatment of anhydride VII with KOH and Pt/C brings about decarboxylation, dehydrogenation, and the formation of fluorene. The structure of diamides VI is confirmed by their IR spectra (the presence of an "amide I" band at 1670 cm^{-1}, an "amide II" band at 1590 cm^{-1}, and bands of primary amides at 3400 and 3500 cm^{-1}).

These results make it possible to unambiguously determine the configurations of isomers IIIb and IIIe as, respectively, cis–syn–trans and trans–anti–cis ("syn" and "anti" pertain to the hydrogen atoms attached to C_{10} and C_{13}). One can also assign a trans–syn–trans configuration with sufficient confidence to isomer IIIa; this configuration corresponds to the configuration of starting IIa. Isomer IIIa is formed in the greatest amount, whereas the other possible isomer with a cis orientation of the cyano groups is not formed at all. Isomers IIIc and IIId should have cis–anti–cis and trans–anti–trans configurations; the assignment can be made on the basis of the PMR spectral data. In this case we proceeded from the assumption that if the methylidyne proton and the electronegative cyano group closest to it are cis-oriented, the signal of this proton will be shifted to weak field. A similar example in the hydrofluorene series has been described for a carbethoxy derivative [4]. The spectrum of isomer IIIc contains a multiplet (2H) at 2.9 ppm, whereas all of the protons in the spectrum of isomer IIId resonate below 2.3 ppm. This makes it possible to assume that isomer IIIc contains two cis-fused rings, whereas fusion of this sort is absent in isomer IIId; consequently, isomer IIIc has a cis–anti–cis configuration, and isomer IIId has a trans–anti–trans configuration. The PMR spectra of the remaining isomers of III are in agreement with the configurations proposed for them. All of the protons in the spectrum of isomer IIIa (absence of cis fusions) give signals below 2.2 ppm, and the spectra of isomers IIIb and IIIe (one cis fusion) have signals (IH) at 2.5 and 2.9 ppm, respectively.

The IR spectra of IVa, b contain $C=C$ absorption at 1650 cm^{-1} and a double absorption peak of a CN group unconjugated at 2250 cm^{-1} (unconjugated) and 2220 cm^{-1} (conjugated). The PMR spectra of IVa, b do not contain the absorption of vinyl protons, and this determines the position of the double bond. The signal of the proton in the α position relative to the CN group in the spectrum of isomer IVb is found at weaker field (2.9 ppm) than in the spectrum of isomer IVa (it is overlapped at 2.3-2.5 ppm by signals of allyl protons); consequently, this proton is equatorially oriented in isomer IVb. Considering that a bulky substituent in the β position relative to the same CN group occupies the equatorial position, one can assign a trans configuration to isomer IVa and a cis configuration to IVb.

Oxidation with bromine (in the case of IIa) proceeds similarly to oxidation with manganese dioxide.

In contrast to the literature data on the oxidation of I [5], the oxidation of IIa with $KMnO_4$ in acetone does not give a tetrazene but rather N-nitroso-11,14-dicyanoperhydroacridine (VIII) and IIIa, b and IVa, b.



VIII

The IR spectrum of VIII contains the absorption of an N-nitroso group at 1540 cm^{-1}. It was obtained by alternative synthesis from the known 11,14-dicyanoperhydroacridine [6] by nitrosation.

EXPERIMENTAL

The IR spectra of $CHCl_3$ solutions of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of $CDCl_3$ solutions were recorded with a ZKR-60 spectrometer. The mass spectra were recorded with an MKh-1303 spectrometer.

Oxidation of N-Amino-11,14-dicyanoperhydroacridines (IIa, b) with γ-Manganese Dioxide. A) A mixture of 12.9 g (0.05 mole) of IIa and 20 g of MnO_2 [7] in 300 ml of benzene was

TABLE 1. Products of the Oxidation of N-Amino-11,14-dicyanoperhydroacridines

Compound	mp, °C	Empirical formula	Found, %			Calc., %		
			C	H	N	C	H	N
IIIa	250—252[a]	$C_{15}H_{20}N_2$	78,9	8,8	12,5	78,9	8,8	12,3
IIIb	70—71[b]	$C_{15}H_{20}N_2$	79,4	8,8	12,5	78,9	8.8	12,3
IIIc	155—157[c]	$C_{15}H_{20}N_2$	79.6	8,7	12,5	78,9	8,8	12,3
IIId	142—143[b]	$C_{15}H_{20}N_2$	79,0	8,7	12,4	78,9	8,8	12,3
IIIe	82—83[b]	$C_{15}H_{20}N_2$	79,5	9,1	12,3	78.9	8,8	12,3
IVa	92—93[b]	$C_{15}H_{20}N_2$	—	—	12,3	—	—	12,3
IVb	83—85[b]	$C_{15}H_{20}N_2$	—	—	12,5	—	—	12,3
Va	221—222[a]	$C_{15}H_{21}NO_2$	72,8	8,4	5,5	72,9	8,5	5,7
Ve	194—195[d]	$C_{15}H_{21}NO_2$	72,9	8,6	5,9	72,9	8,5	5,7
VIb	293—294[d]	$C_{15}H_{24}N_2O_2$	68,4	9,5	10,6	68,2	9,1	10.6
VIc	209—210[e]	$C_{15}H_{24}N_2O_2$	68,1	9,2	10,9	68,2	9,1	10,6
VId	348—349[d]	$C_{15}H_{24}N_2O_2$	67,8	9,1	10,8	68,2	9,1	10.6
VII	153—155[a]	$C_{15}H_{20}N_3$	71,6	8,0	—	72.6	8,0	—
VIII	181—182[e,f]	$C_{15}H_{20}N_4O$	65.6	7,5	20,6	66.2	7,4	20,6

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[a] From ethanol. [b] From hexane. [c] From hexane—benzene (1:1). [d] From n-propyl alcohol. [e] From dioxane. [f] With decomposition.

stirred at room temperature until nitrogen evolution ceased (1.5 h). The MnO_2 was removed by filtration and washed with 300 ml of $CHCl_3$, and the filtrate was evaporated to give 10.9 g (95%) of a mixture of oxidation products. The mixture was treated with ether, and the insoluble portion was removed by filtration to give 4.85 g (42%) of perhydrofluorene IIIa. The filtrate remaining after separation of IIIa was evaporated, and the residue was chromatographed with a column filled with 240 g of activity II Al_2O_3. Elution with petroleum ether—diethyl ether (9:1) yielded 1.1 g (10%) of isomer IIIb; elution with petroleum ether—diethyl ether (5:1) yielded, successively, 1.6 g (14%) of IVa and 1 g (9%) of IVb (the characteristics of the oxidation products and their derivatives are presented in Table 1).

B) Compound IIb was similarly oxidized. A 16-g sample of IIb yielded 12.8 g (91%) of a mixture of oxidation products. The mixture was treated with ether, and 7.4 g (52%) of IIIc was removed by filtration. The remaining reaction products were separated with a column filled with 200 g of activity II Al_2O_3; elution with petroleum ether—diethyl ether (19:1) yielded, successively, 0.52 g (3%) of IIId, 1 g (6%) of IIIc, and 2.1 g (13%) of IIIe.

Hydrolysis of 11,12-Dicyanoperhydrofluorenes. A solution of 2.3 g (0.01 mole) of IIIa-e in 20 ml of concentrated H_2SO_4 was allowed to stand at room temperature for 24 h, after which it was heated at 100° for 6 h. It was then cooled and diluted with water, and the resulting precipitate was removed by filtration, washed with water, and dried. Imides Va (96%) and Ve (84%) were obtained, respectively, from dinitriles IIIa and IIIe. Diamides VIb (73%), VIc (33%), and VId (95%) were obtained, respectively, from dinitriles IIIb-d.

11,12-Perhydrofluorenedicarboxylic Acid Anhydride (VII). A solution of 1.25 g of imide Va in a mixture of 7 ml of concentrated H_2SO_4 and 7 ml of 98% CH_3COOH was refluxed for 10 h, after which it was cooled, and the resulting precipitate was removed by filtration and washed with water to give 0.5 g (40%) of anhydride VII.

A 0.16-g sample of KOH was added to a solution of 0.4 g of anhydride VII in 75 ml of absolute ethanol, after which the mixture was refluxed for 30 min. The solvent was then evaporated, 0.2 g of Pt/C was added to the residue, and the mixture was heated at 320° (70 ml of H_2 was collected). It was then cooled, treated with 10 ml of ether, and filtered. The ether was evaporated to give 40 mg of fluorene (identical to an authentic sample with respect to its IR spectrum and a mixed-melting-point determination).

Oxidation of N-Amino-11,14-dicyanoperhydroacridine (IIa) with $KMnO_4$ in Acetone. A mixture of 5.2 g (0.02 mole) of IIa and 6 g (0.038 mole) of $KMnO_4$ in 150 ml of acetone was stirred at room temperature for 1 h. A total of 0.32 liter of N_2 was evolved, after which 4 g of oxalic acid was added to decompose the excess $KMnO_4$. The MnO_2 was removed by filtration and washed with 200 ml of acetone, the filtrate was evaporated, and the residue was treated with ether. The ether-insoluble portion (2.5 g), which was a mixture of VIII and IIIa, was removed by filtration. Crystallization from dioxane gave 1.6 g (29%) of pure nitrosamine VIII. The filtrate from the separation of the mixture of VIII and IIIa was evaporated, and the residue was separated with a column as described above to give 0.16 g (3.5%) of IIIb, 0.23 g (5%) of IIIa, and 0.25 g (5.5%) of IVb.

N-Nitroso-11,14-dicyanoperhydroacridine (VIII). A solution of 2.8 g (0.04 mole) of $NaNO_2$ in 10 ml of water was added with stirring and cooling (to 15°) in the course of 15 min to a suspension Of 2.43 g (0.01 mole) of 11,14-dicyanoperhydroacridine in 40 ml of CH_3COOH, after which the mixture was stirred for another 3 h. The solid material was removed by filtration, washed with water, and dried to give 2.4 g (88%) of nitrosamine VIII (identical to a sample obtained by oxidation of IIa with respect to a mixed-melting-point determination and its IR spectrum).

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AZOMETHINES OF NITROGEN-CONTAINING HETEROCYCLES.

I. SYNTHESIS AND STUDY OF THE STRUCTURES OF SCHIFF BASES FROM 3-METHYL-2-AZAFLUORENONE AND ARYLAMINES

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In an investigation of the conditions for the formation of Schiff bases from 3-methyl-2-azafluorenone and arylamines it was shown that the use of boron trifluoride etherate as the catalyst insures the highest yields. The fundamental possibility of the preparation of Schiff bases by condensation of 3-methyl-2-azafluorene with p-nitrosodimethylaniline and subsequent reduction of the resulting oxazirane structure is demonstrated. The ratio of the cis and trans isomers of the resulting azomethines was established on the basis of PMR spectral data.

At present there are no data available on the synthesis of Schiff bases with the participation of azafluorene systems, and this has been responsible for the inaccessibility of the latter. Continuing our research on the chemistry of azomethines that we have used in the syntheses of complex heterocyclic systems (azaphenanthrenes and naphthyridines) [1], we turned to the preparation of Schiff bases from 3-methyl-2-azafluorenone (I) and 3-methyl-2-azafluorene (II) [2]).

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