heated to the boiling point. The precipitated MnO_2 was removed by filtration, and the filtrate was made alkaline and extracted with ether. The residue remaining after removal of the solvent consisted of starting XVI and sulfone VII (TLC). Several crystallizations from benzene yielded sulfone VII with mp 186-187.5°C, which was identical to an authentic sample according to the result of a mixed-melting-point determination and its chromatographic characteristics.

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CYCLOADDITION OF AZODICARBOXYLIC ACID ESTERS TO VINYLPYRIDINES

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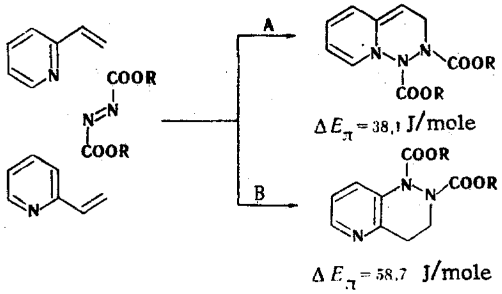
The reaction of methyl or ethyl esters of azodicarboxylic acid with 3-, 4-, 5-, or 6-alkyl-2-vinylpyridines proceeds via the scheme of the diene synthesis with the participation of the pseuodcarbodiene system of vinylpyridines and leads to the formation of 1,2,3,4-tetrahydro-5-azacinnoline derivatives. In addition to these "monoadducts," 4-[N,N'-bis(methoxycarbonyl)hydrazino] derivatives are formed in large amounts. The structures of all of the reaction products were proved by the IR, UV, PMR, and mass spectra. The possibility of the application of the computational methods of MO perturbation theory for the prediction of the probability of the formation of various regioisomers is demonstrated.

2-Vinylpyridines, like styrene [1, 2], are capable of undergoing 1,4-cycloaddition with N-phenyl-1,3,4-triazoline-2,5-dione to give the 5-azacinnoline system [3]. In experiments with 2-(1-alkoxyvinyl)pyridines [4] it was found that methyl and ethyl azodicarboxylates (Ia, b) give both cycloaddition products and vinyl substitution products; this is probably a consequence of the increased nucleophilicity of the terminal methylene carbon atom owing to the strong +M effect of the alkoxy group. We therefore investigated the reaction of esters Ia, b with unsubstituted 2-vinylpyridine (IIa) and with its isomeric alkyl(hetaryl)-substituted derivatives (IIb-i) and observed that the reaction proceeds only via a 1,4-cycloaddition scheme in all cases.

In the case of this reaction pathway one might have expected the addition of ester I to both the C=C—C=C— and —C=C—C=N— pseudodiene systems of vinyl pyridine:



M. V. Lomonosov Moscow State University, Moscow 117234. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 639-647, May, 1979. Original article submitted July 11, 1978.

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TABLE 1. Properties of 1,2-Bis(methoxycarbonyl)-1,2,3,4-tetrahydro-5-azacinnolines IVa, c-f, i

Compound	mp, °C	IR spectrum, cm^{-1}	UV spectrum, λmax, nm (log ε)	R_f	Found, %			Empirical formula	Calc., %			Yield, %
					C	H	N		C	H	N	
IVa	93—94	1590, 1685—1740	242 (3,99), 277 (3,67)	0,55—0,70	52,5	5,3	—	$C_{11}H_{13}N_3O_4$	52,6	5,2	—	10
IVc	119—120	1590, 1700—1740	232 (4,05), 282 (3,71)	0,60—0,70	54,2	5,7	—	$C_{12}H_{15}N_3O_4$	54,3	5,7	—	11
IVd	146—147	1600, 1725—1740	234 (3,96), 283 (3,68)	0,53—0,60	54,1	5,8	—	$C_{12}H_{15}N_3O_4$	54,3	5,7	—	10
IVe	106—108	1605, 1720—1740	232 (3,93), 283 (3,66)	0,56—0,63	55,8	6,0	15,1	$C_{13}H_{17}N_3O_4$	55,9	6,1	15,1	12
IVf	153* (dec.)	1595, 1720—1750	238 (3,92), 278 (3,65)	0,48—0,55	—	—	16,0	$C_{12}H_{15}N_3O_4$	—	—	15,8	8
IVi	56—58	1720	—	—	58,6	6,2	13,6	$C_{15}H_{19}N_3O_4$	58,8	6,2	13,8	30

*Methiodide.

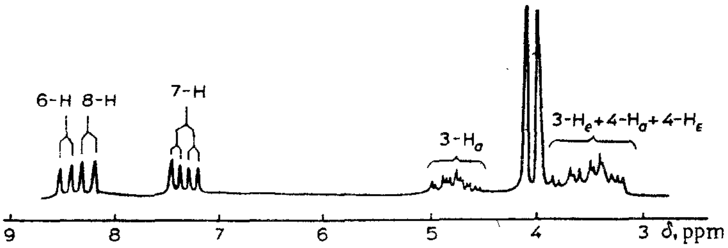

Fig. 1. PMR spectrum of IVa (CDCl$_3$).

We estimated the probability of realization of the process via pathways A and B using the concepts and computational methods of MO perturbation theory developed by Dewar [5] and Klopman [6] by calculating the ΔE_π values for both possible pathways by means of the equation*

$$\Delta E_\pi = 2\left[\frac{(C_a C'_c \beta_{ac} + C_b C'_d \beta_{bd})^2}{|E_R - E'_S|} + \frac{(C'_a C_c \beta_{ac} + C'_b C_d \beta_{bd})^2}{|E'_R - E_S|}\right],$$

where C_a, C_b, C_c, and C_d are the coefficients of the atomic orbitals of the interacting atoms of the upper occupied molecular orbitals (UOMO); C'_a, C'_b, C'_c, C'_d are the coefficients of the analogous atomic orbitals (AO) of the lower vacant molecular orbitals (LVMO); and E_R, E_S, E'_R, and E'_S are the energy levels of the diene and dienophile in the UOMO and LVMO, respectively. A comparison of the data obtained shows that pathway B is considerably more favorable (by 20.6 J/mole) from the point of view of energy considerations.

The reaction was carried out in refluxing hexane, benzene, or tetrahydrofuran (THF); no appreciable effect of the solvents was observed. The reaction was complete after 10 h (starting ester I was no longer present in the reaction medium), and crystalline monoadducts IVa, c-f, i (Table 1), together with powdery "diadducts" Va-h (Table 2, Scheme 1), were isolated after preparative chromatographic separation. Absorption bands of carbonyl groups at 1680-1740 cm^{-1} are observed in the IR specta of IV, but absorption bands of an N—H group are absent. An absorption maximum at 265-280 nm (log ε 3.4-3.8), which is characteristic for 3-acylaminopyridines [7], is observed in the UV spectra; this indicates retention of the aromatic character of the pyridine ring. The pattern characteristic for a 2,3-disubstituted pyridine is observed in the PMR spectra in the aromatic region (e.g., for IVa) (Fig. 1): a

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*The calculation was made by the MINDO/3 method with a BÉSM-6 computer. A. V. Gorelov participated in the calculations.

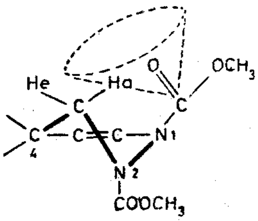


Fig. 2

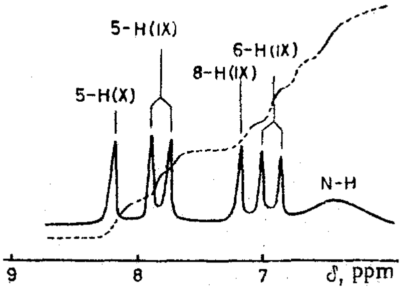
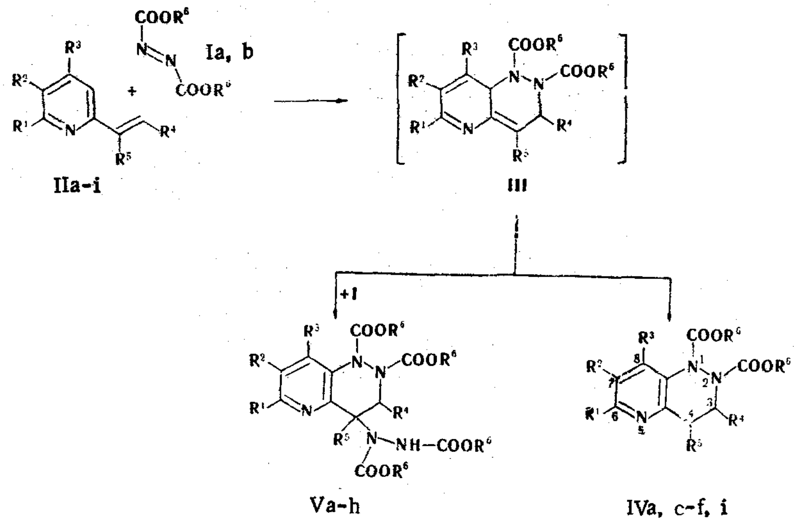


Fig. 3

Fig. 2. Effect of the anisotropy of the carbamoyl group on the 3-H_a proton in the PMR spectrum of IV and V.

Fig. 3. Fragment of the PMR spectrum of a mixture of IX and X ($CDCl_3$).

quartet of the 6-H proton at weak field (8.48 ppm, $J_{6,7}$ = 4.5, $J_{6,8}$ = 1.5 Hz), a quartet of an 8-H proton (8.3 ppm, $J_{8,7}$ = 9, $J_{8,6}$ = 1.5 Hz), and quartet of a 7-H proton centered at 7.33 ppm ($J_{7,6}$ = 4.5, $J_{7,8}$ = 9 Hz). A multiplet of three aliphatic 3-H_e, 4-H_e, and 4-H_a protons at 3.2-3.8 ppm is observed at stronger field in addition to two singlets of six protons of methyl groups (3.95 and 4.05 ppm). The signal of the fourth proton of the saturated ring (3-H_a) is shifted to weaker field (4.8 ppm) owing to the deshielding effect on the axial proton of the carbonyl group in the 1 position (Fig. 2).



a $R^1=R^2=R^3=R^4=R^5=H$, $R^6=CH_3$; b $R^1=R^2=R^3=R^4=R^5=H$, $R^6=C_2H_5$; c $R^1=R^6=CH_3$, $R^2=R^3=R^4=R^5=H$; d $R^2=R^6=CH_3$, $R^1=R^3=R^4=R^5=H$; e $R^1=R^3=R^4=R^5=H$, $R^2=C_2H_5$, $R^6=CH_3$; f $R^1=R^2=R^4=R^5=H$, $R^3=R^6=CH_3$; g $R^1=R^2=R^3=R^5=H$, $R^4=R^6=CH_3$; h $R^1=R^2=R^3=R^5=H$, R^4= 2-pyridyl $R^6=C_2H_5$; i $R^1=R^2=R^3=H$, $R^4+R^5=-(CH_2)_4-$, $R^6=CH_3$

An intense molecular-ion peak is observed in the mass spectra of IV, and the character of its fragmentation corresponds to the proposed structure. All of these data constitute convincing evidence in favor of the 5-azacinnoline system (pathway B).

The UV spectra of V, which were obtained in higher yields, coincide almost completely with the UV spectra of IV. Intense absorption bands at 3280-3300 cm^{-1} (N−H vibrations) are observed in their IR spectra. A low-stability molecular ion, which readily loses a bis(methoxycarbonyl)hydrazine residue (147 amu), is noted in the mass spectra. The subsequent fragmentation of the resulting fragment is similar in many respects to the dissociative ionization of IV. The PMR spectra of V at weak field coincide with the spectra for the analogous IV, whereas four singlets (partially overlapped) of 12 protons of methyl groups (3.9-4.3 ppm) and multiplets of 3-H_e, 3-H_a, and 4-H_e protons, respectively, with centers at 3.9, 5.1, and 5.8 ppm are observed in the stronger-field region (e.g., in the PMR spectrum of Va).

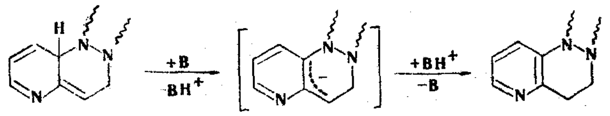
TABLE 2. Properties of 1,2,3,4-Tetrahydro-5-azacinnolines Va-g

Compound	R^1	R^2	R^3	R^4	R^6	mp, °C	IR spectrum, cm^{-1}	UV spectrum, λ_{max}, nm (log ε)	R_f	PMR spectrum, ppm, m, Hz			Found, %			Empirical formula	Calc., %			Yield, %
										6-H	7-H	8-H	C	H	N		C	H	N	
Va	H	H	H	H	CH_3	109—110	1590, 1720—1760, 3285	229 (3,95), 276 (3,55)	0,30—0,40	8,13, q, 4,5; 1,5	7,05, q, 9,0; 4,5	8,03, q, 9,0; 1,5	45,5	4,9	—	$C_{15}H_{19}N_5O_8$	45,4	4,8	—	52
Vb	H	H	H	H	C_2H_5	61—64	1590, 1720—1750, 3280	230 (3,91), 277 (3,51)	0,35—0,5	8,10, q, 4,5; 1,5	7,05, q, 9,0; 4,5	7,95, q, 9,0; 1,5	—	—	15,2	$C_{19}H_{27}N_5O_8$	—	—	15,4	50
Vc	CH_3	H	H	H	CH_3	104—107	1590, 1710—1750, 3285	233 (4,00), 283 (3,60)	0,31—0,38	—	6,97, d, 9,0	7,93, d, 9,0	46,6	5,0	—	$C_{16}H_{21}N_5O_8$	46,7	5,1	—	48
Vd	H	CH_3	H	H	CH_3	109—112	1610, 1720—1760, 3290	227 (3,95), 280 (3,64)	0,30—0,36	7,95, d, 1,5	—	7,90, d, 1,5	46,5	5,1	—	$C_{16}H_{21}N_5O_8$	46,7	5,1	—	56
Ve	H	C_2H_5	H	H	CH_3	114—116	1600, 1715—1760, 3290	227 (3,94), 281 (3,63)	0,31—0,36	8,05, d, 1,5	—	7,95, d, 1,5	47,8	5,3	—	$C_{17}H_{23}N_5O_8$	48,0	5,4	—	60
Vf	H	H	CH_3	H	CH_3	96—99	1720—1760, 3275	220* i (3,83), 265 (3,43)	0,29—0,35	8,05, d, 4,5	6,93, d, 4,5	—	46,6	5,1	—	$C_{16}H_{21}N_5O_8$	46,7	5,1	—	40
Vg	H	H	H	CH_3	CH_3	95—97	1600, 1730—1740, 3240	231 (3,91), 260* i (3,62), 273 (3,78)	0,4—0,6	8,12, q, 4,5; 1,5	7,18, q, 9,0; 4,5	7,93, q, 9,0; 1,5	46,7	5,0	17,2	$C_{16}H_{21}N_5O_8$	46,7	5,1	17,0	25

*i stands for inflection.

We have previously [1] proposed a general scheme that explains the formation of diadducts of the V type. According to this scheme, when Vg is formed from trans-2-propenylpyridine with allowance for the [π4s + π2s] character of this electrocyclic reaction and the disrotatory direction of the orbitals, the methyl group in the 3 position should be axially oriented, while the bis(methoxycarbonyl)hydrazino group should be equatorially oriented. In this case the 3-H and 4-H atoms should have a cis-e—a configuration. In fact, in the PMR spectrum of the compound it is possible to isolate of doublet of the 4-H proton (4.1 ppm) with a spin—spin splitting constant of 3-4 Hz, which is characteristic for cis-e—a coupling [8].

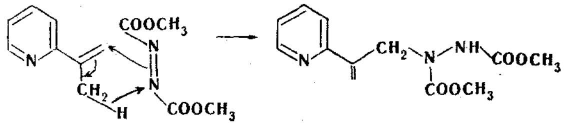
The proposed scheme of the reactions [1] excluded the possibility of the formation of monoadducts of the IV type. Their appearance in the reaction mixture is probably associated with the possibility of the isomerization of intermediate III under the influence of the base (vinylpyridine) that is present in the reaction mixture. This type of process has been described in the case of the reaction of styrene with dehydrobenzene [9]. We demonstrated by means of special experiments that even when monoadducts IV are heated with esters I in benzene for 20 h they do not form V, i.e., they are not intermediates in their synthesis.



An examination of the data in Table 2, in which the yields and properties of Va-c are presented, makes it possible to observe that the introduction of alkyl groups in the aromatic ring of 2-vinylpyridine has virtually no effect on the yield of the corresponding adduct V, while the presence of a methyl group in the β position of the vinyl group lowers the yield of adduct Vg appreciably (evidently due to steric hindrance during the diene synthesis). When an even bulkier pyridyl substituent is present in this position, it is found that 2,2-dipyridylethylene IIh reacts with Ib only upon heating in an autoclave (110°C) and that adduct Vh is nevertheless formed in low yield (17%).

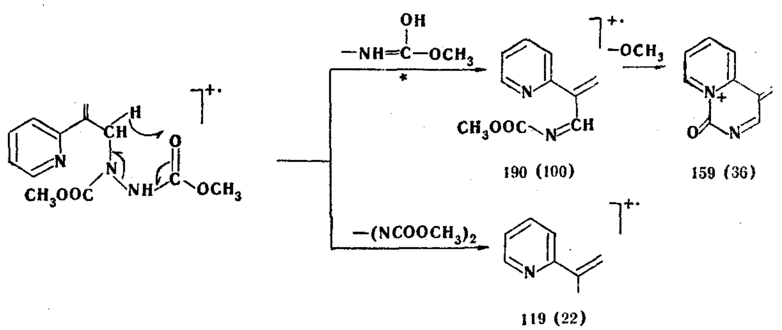
Compound Ia did not react with methyl trans-β-(2-pyridyl)acrylate even under severe conditions (in an autoclave at 140°C for 20 h). In the latter two cases, in addition to steric factors, the considerable decrease in the level of the UOMO of the pseudodiene system under the influence of the two electron-acceptor C=N and CO_2CH_3 groups probably also has an effect on the decrease in the reactivity.

The diene synthesis does not take place in the reaction of ester Ia with 2-isopropenylpyridine (IIj), and the only reaction product is VI (in 30% yield), which is formed via the mechanism of the "ene synthesis." In 1943, Alder and co-workers [10] described the "ene" addition of ester Ib to α-methylstyrene, which leads to a structure similar to VI:



IIj VI

The reliability of structure VI was proved by the spectral data. Thus the molecular ion that is formed from it under electron impact energetically eliminates completely an azodicarboxylic ester molecule or a methyl carbamate molecule (due to a McLafferty rearrangement); this proves the noncyclic structure of VI:*



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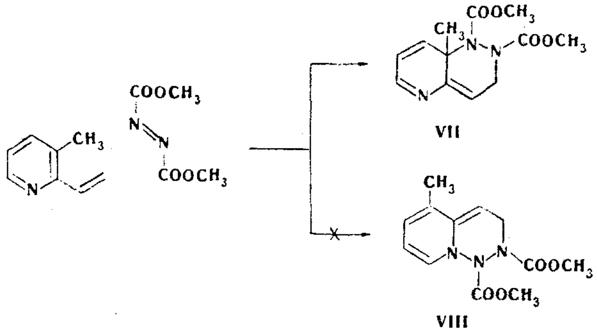
*Here and subsequently, the m/e values (and relative intensities in percent) are presented; the asterisk indicates the existence of a metastable ion.

In addition to the singlet of six protons of two methoxy groups and four signals of pyridine ring protons, the chemical shifts and multiplicities of which coincide with those observed in the PMR spectrum of starting IIj, the PMR spectrum of VI contains broad (due to allylic coupling) signals of olefin protons (5.45 and 5.88 ppm) and a broad singlet of protons of a methylene group (4.65 ppm).

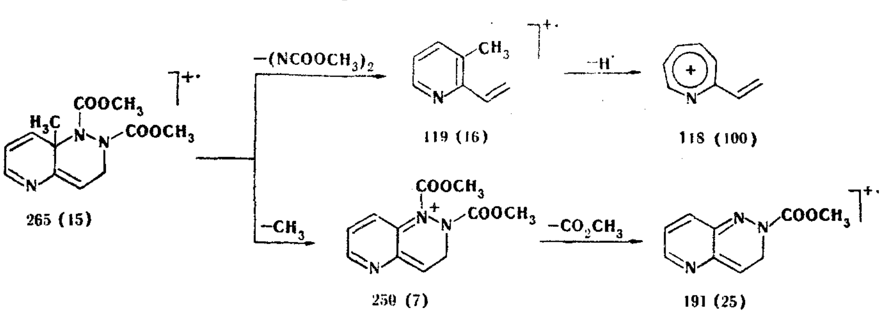
The presence of an amide group in hydrazide VI is also confirmed by the IR spectra, in which an intense absorption band of N—H vibrations at 3180 cm^{-1} and absorption bands of C=O groups at 1720-1760 cm^{-1} are observed.

However, if an α,β-disubstituted 2-vinylpyridine (IIi) is subjected to reaction with ester Ia, only IV can be isolated from the reaction mixture in 30% yield. Steric factors (the bent form of the cyclohexene ring), which also hinder conversion of intermediate III to a diadduct, evidently are also unfavorable for a process of the "ene" type in this case.

The reaction of ester Ia with 3-methyl-2-vinylpyridine (IIk), which under standard conditions (refluxing in benzene for 10 h) leads to a single reaction product, viz., VII (in 50% yield), is of particular interest. Its UV spectrum differs appreciably from the UV spectra of both IV and V (the long-wave absorption maximum is shifted hypsochromically 12-16 nm). The results of elementary analysis and the mass spectrum prove that it is the monoadduct. The PMR spectrum of this compound at strong field contains, in addition to singlets of two CH_3O groups (3.82 and 3.24 ppm), a singlet of three protons (2.40 ppm) of the geminal methyl group attached to C_9.



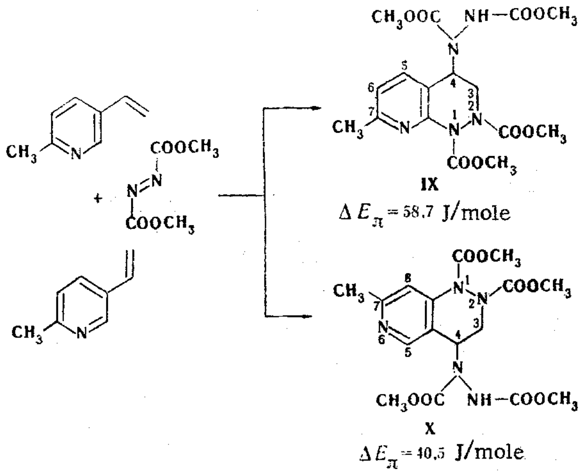
This unusual shift to weak field (one should have expected the chemical shift at 1.0-1.5 ppm) can probably be explained by the anisotropy of the close-lying carbonyl groups. Two quartets of protons attached to C_3 (3.72 and 4.53 ppm) and a quartet of an olefin proton attached to C_4 (5.62 ppm) are observed in the weaker-field region. Finally, the signals of pyridine 6-H, 7-H, and 8-H protons appear at, respectively, 8.5 (d), 7.40 (q), and 7.57 ppm (d). Thus the PMR spectrum makes it possible to assume tentatively structure VII rather than VIII, since in the case of the latter the signal of the protons of the methyl group attached to C_5 should have been observed (as in the case of Ii) at 2.1 ppm. The molecular ion of this substance undergoes fragmentation with the loss of 15 amu (the CH_3 group) (this is not observed in the spectra of either IV or V) or undergoes facile retrodiene fragmentation, which is also uncharacteristic for the mass spectra of mono- and diadducts.



Thus VII is the first example of a stable intermediate that is formed in the 1,4-cycloaddition of vinylhetarenes.

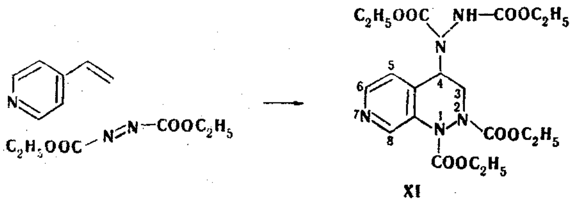
The reaction of ester Ia with 2-methyl-5-vinylpyridine may proceed by way of two carbodiene systems with the formation of derivatives of 8-aza- (IX) and 6-azacinnolines (X).

The calculation of the ΔE_π values of various regioisomers* gives results that favor IX:



A diadduct (according to the results of elementary analysis and the mass spectra), which, according to the PMR spectra, is a mixture of IX and X in a ratio of 2:1, is isolated in 24% yield when the reaction is carried out under the conditions described above (by refluxing the components in benzene for 6 h). Thus singlets of protons of 7-CH_3 groups at 2.41 ppm (IX) and 2.44 ppm (X) with an integral intensity ratio of 2:1 are observed at strong field. A similar ratio is retained with respect to the areas of the signals of the other protons, such as, for example, 5-H (Fig. 3), which gives a singlet at 8.05 ppm (X) and a doublet at 7.92 ppm with J_{56} = 8 Hz (X). Unfortunately, we were unable to separate this mixture into individual components using adsorption methods.

Finally, the reaction of 4-vinylpyridine with ester Ib gives diadduct XI (in 22% yield), which is a derivative of 7-azacinnoline; its PMR spectrum contains a singlet of the 8-H proton at weak field (8.5 ppm) and doublets of 5-H and 6-H protons (7.45 and 8.26 ppm) with characteristic constant J_{56} = 5 Hz. The mass-spectral behavior of this compound is similar to the fragmentation of Va.



EXPERIMENTAL

The UV spectra of methanol solutions of the compounds were recorded with a Cary-15 spectrophotometer. The IR spectra of mineral oil suspensions of the compound were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in deuterochloroform were obtained with Varian T-60 and Cameca-250 spectrometers with hexamethyldisiloxane as the internal standard. The mass spectra were obtained with MKh-1303 and MAT-111 (Varian) spectrometers with introduction of the compounds into the ionization region at ionizing-electron energies of 50 and 80 eV. Isolation of the compounds by preparative thin-layer chromatography (TLC) was carried out on plates in a 1.5-mm thick layer of aluminum oxide (activity II) in a benzene–methanol system (9:1). All of the vinylpyridines and azodicarboxylic acid esters were synthesized by known methods and were no less than 98% pure according to the results of GLC.

Reaction of 2-Vinylpyridines with Azodicarboxylic Acid Esters (General Method).† A solution of 0.04 mole of freshly distilled vinylpyridine II and 0.08 mole of ester I in 30 ml of dry benzene was refluxed for 10 h, after which the benzene was removed by distillation,

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*The calculation was made for the monoadducts.

†For vinylpyridines IIIa-f.

the unchanged starting compounds were extracted twice with a cold mixture of ether and pentane (1:1), and the residue was separated preparatively on aluminum oxide.

2-Bis(methoxycarbonyl)-4-[N,N'-bis(methoxycarbonyl)hydrazino]-1,2,3,4-tetrahydro-5-azacinnolines (V). These compounds were isolated from the bands with the R_f values indicated in Table 2. The yields of "diadducts" V and the results of elementary and physicochemical analysis are also presented in Table 2. The "monoadducts," i.e., 1,2-bis(methoxycarbonyl)-1,2,3,4-tetrahydro-5-azacinnolines (IV), were isolated from the UV-dark bands with the R_f values indicated in Table 1. The yields of IVa, c-f, i and the results of their elementary and physicochemical analysis are presented in Table 1.

1,2-Bis(ethoxycarbonyl)-3-(2-pyridyl)-4-[N,N'-bis(ethoxycarbonyl)hydrazino]-1,2,3,4-tetrahydro-5-azacinnoline (Vh). A mixture of 1.82 g (10 mmole) of vinylpyridine IIh and 3.5 g (20 mmole) of ester Ib was heated in vacuo at 110°C for days, after which it was worked up as in the preceding experiment to give 0.94 g (17%) of a product with mp 93-96°C. Found: N 15.7%; M 530. $C_{24}H_{30}N_6O_8$. Calculated: N 15.9%; M 530. PMR spectrum (CCl_4): 1.4-1.8 (12H, m, CH_3CH_2O), 4.0-4.8 (8H, m, CH_3CH_2O), 6.2 (1H, d, 3-H_e, J_{34} = 4 Hz), 6.5 (1H, d, 4-H_e, J_{43} = 4 Hz), 7.2-8.2 (6H, m, pyridine ring β- and γ-H), and 8.8 ppm (2H, d, pyridine ring α-H, $J_{\alpha\beta}$ = 5 Hz). IR spectrum: 3250, 1750, 1730, 1720, 1590, 1570 cm^{-1}.

Reaction of 2-Isopropenylpyridine (IIg) with Ester Ia. A mixture of 400 mg (3.4 mmole) of IIg with 970 mg (6.7 mmole) of ester Ia in 10 ml of benzene was refluxed for 20 h, after which the benzene was removed by distillation, and the residue was separated preparatively on aluminum oxide. Workup of the band with R_f 0.20-0.36 gave the adduct of the "ene" synthesis, viz., VI. The yield of product with mp 92°C (from heptane was 264 mg (30%). Found: C 54.3; H 5.8; N 16.0%. $C_{12}H_{15}N_3O_4$. Calculated: C 54.3; H 5.6; N 15.9%. PMR spectrum ($CDCl_3$): 3.8 (6H, s, CH_3O), 4.65 (2H, s, CH_2), 5.45, (1H, s, $=CH_2$), 5.88 (1H, s, $=CH_2$), 7.0-7.25 (1H, broad s, N—H), 7.23 (1H, q, 5-H, J_{54} = 9, J_{56} = 5 Hz), 7.46 (1H, q, 4-H, J_{45} = 9 Hz, J_{46} = 1.5 Hz), 7.53 (1H, d, 3-H, J_{34} = 9 Hz), and 8.5 ppm (1H, q, 6-H, J_{65} = 5, J_{64} = 1.5 Hz). IR spectrum: 3290, 1720-1760, 1595 cm^{-1}, UV spectrum, λ_{max} (log ε): 253 (1.77), 280 i (4.2), 286 nm (4.12).

1,4-Bis(methoxycarbonyl)-9-methyl-1,2,3,9-tetrahydro-5-azacinnoline (VII). A mixture of 4.76 g (40 mmole) of freshly distilled vinylpyridine IIk, 11.8 g (80 mmole) of ester Ia, and 30 ml of benzene was refluxed for 10 h, after which the benzene was removed and the residue was extracted with a cold mixture of ether and pentane (1:1). The residue was chromatographed on aluminum oxide with isolation of the substance from the band with R_f 0.4-0.6 to give 5.3 g (50%) of a product with mp 164-167°C. Found: C 52.7; H 5.8; N 16.0%. $C_{12}H_{15}N_3O_4$. Calculated: C 52.4; H 5.7; N 15.9%. UV spectrum, λ_{max} (log ε): 266 nm (3.57). IR spectrum: 1680-1710, 1580 cm^{-1}.

Reaction of 2-Methyl-5-vinylpyridine with Ester Ia. A solution of 1.19 g (10 mmole) of 2-methyl-5-vinylpyridine and 2.85 g (20 mmole) of ester Ia in benzene was refluxed for 6 h, after which the benzene was removed by evaporation, and the residue was separated preparatively on aluminum oxide. Workup of the band with R_f 0.22-0.46 gave 0.97 g (24%) of a mixture of IX and X with mp 36-42°C. Found: C 47.0; H 4.5%; M 411. $C_{16}H_{21}N_5O_8$. Calculated: C 46.7; H 4.5%; M 411. PMR spectrum: 2.41 (6H, s, 7-CH_3 IX), 2.44 (3H, s, 7-CH_3 X), 3.6-3.9 (36H, m, CH_3O), 4.2-5.7 (9H, m, 3-H and 4-H), 7.0 (2H, d, 6-H IX, $J_{6,5}$ = 9 Hz), 7.11 (1H, s, 8-H X), 7.92 (2H, d, 5-H IX, $J_{5,6}$ = 9 Hz), 8.05 ppm (1H, s, 5-H X).

1,2-Bis(ethoxycarbonyl)-4-[N,N'-bis(ethoxycarbonyl)hydrazino]-1,2,3,4-tetrahydro-7-azacinnoline (XI). A solution of 0.8 g (8 mmole) of 4-vinylpyridine and 2.8 g (16 mmole) of ester Ib in THF was refluxed for 14 h, after which the solvent was removed by evaporation, and the residue was chromatographed preparatively. Workup of the band with R_f 0.25-0.30 yielded 0.8 g (22%) of 7-azacinnoline XI with mp 72-73°C. Found: C 50.1; H 5.8%; M 453. $C_{19}H_{27}N_5O_8$. Calculated: C 50.3; H 5.9%; M 453. UV spectrum, λ_{max} (log ε): 230 (3.68), 275 nm (3.35). IR spectrum: 3300, 1720-1760 cm^{-1}. PMR spectrum (deuteroacetone): 1.4-1.8 (12H, m, CH_3CH_2O), 4.2-4.6 (10H, m, CH_3CH_2O and 3-H), 5.5 (1H, m, 4-H), 7.45 (1H, d, 5-H, $J_{5,6}$ = 5 Hz), 8.26 (1H, d, 6-H, $J_{6,5}$ = 5 Hz), 8.50 (1H, s, 8-H), 8.7 ppm (1H, br s, N—H).

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SYNTHESIS OF SUBSTITUTED BENZO[g]ISOQUINOLINES AND 8-AZABENZO[a]FLUORANTHENES

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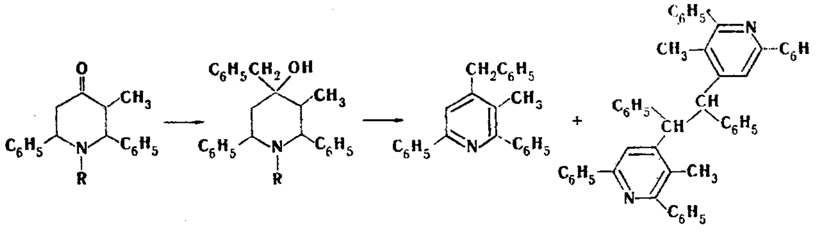
UDC 547.833'838.07

The conversion of 1,3-dimethyl-2,6-diphenyl-4-benzyl-4-piperidol and its N-unsubstituted analog by means of pyridine N-oxide to 3-methyl-2,6-diphenyl-4-benzylpyridine (I) is accompanied by the formation of 1,2-diphenyl-1,2-bis(3'-methyl-2',6'-diphenyl-4'-pyridyl)ethane, which was obtained under the same conditions directly from γ-benzyl-substituted pyridine I. The initial product in the catalytic dehydrocyclization of pyridine base I is 1,3-diphenylbenzo[g]isoquinoline, which is subsequently partially converted to 7-phenyl-8-azabenzo[a]fluoranthene. Spectral data for these heterocyclic compounds and the characteristics of the substances obtained by oxidation of them are presented.

Little study has been devoted to heterocyclic system of the benzoisoquinoline and benzoazafluoranthene heterocyclic systems because of the lack of methods for their synthesis. The possibility of the conversion of substituted aryl-γ-pyridylmethanes to benzoisoquinolines by dehydrocyclization was demonstrated in [1, 2]. The present research is a continuation of our studies in this area. 1,3-Dimethyl-2,6-diphenyl-4-benzyl-4-piperidol (I) and its N-unsubstituted analog (II) were obtained for the synthesis of the corresponding pyridine base from 1,3-dimethyl- and 3-methyl-2,6-diphenyl-4-piperidones. The conversion of these piperidols to 3-methyl-2,6-diphenyl-4-benzylpyridine (III) was accomplished by means of pyridine N-oxide, as described in [3]. A peculiarity of this reaction in this case is the fact that, in addition to pyridine base III, approximately the same amount of 1,2-diphenyl-1,2-bis(3'-methyl-2',6'-diphenyl-4'-pyridyl)ethane (IV) is formed; the latter is evidently the product of oxidative condensation at the methylene groups of molecules of pyridine base III. This assumption is confirmed by the synthesis of IV from substituted pyridine III when it is treated with pyridine N-oxide under the same conditions.



I, II   III   IV

I R=CH_3; II R=H

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