successive elution with systems A and B to give the following compounds: α-picoline (bp 128-130°C; picrate mp 149-150°C), N-methylaniline (bp 195-196°C; picrate mp 144-145°C), N-methylmorpholine (bp 116-117°C; picrate mp 225-226°C), N-phenylmorpholine [mp 59-60°C (from hexane); picrate mp 162-164°C], N-methylpiperidine (bp 106-107°C; picrate mp 148°C), N-phenylpiperidine (bp 245-250°C; picrate mp 148°C), and N-methylpiperazine (bp 134-136°C; picrate mp 272-273°C). The purity of the α-picoline and amines obtained was monitored by chromatography. The compounds were identified by comparison of the bases and picrates with genuine samples.

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# REACTION OF N-PHENYLMALEINIMIDE WITH 2- AND 4-VINYLPYRIDINES

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The reaction of 2- and 4-vinylpyridines with N-phenylmaleinimide in acetic anhydride proceeds via the scheme of the diene synthesis and leads to pyrrolo[3,4-f]quinoline and pyrrolo[3,4-i]isoquinoline derivatives.

We have previously shown that the reaction of 2- and 4-vinylpyridines (I, II) with azadienophiles proceeds via a 1,4-cycloaddition scheme with the participation of a pseudodiene system (the vinyl group plus the $C_2$–$C_3$ multiple bond of the pyridine ring) [1, 2]. In addition, Wagner-Jauregg and co-workers have found that in neutral media (butanol and acetonitrile) the reaction of vinylpyridines I and II with N-substituted maleinimides proceeds via a 1,3-dipolar cycloaddition scheme with the participation of the pyridine nitrogen atom and leads to complex polycyclic compounds [3, 4].

We have established that they react with N-phenylmaleinimide via the usual scheme of the diene synthesis in acetic anhydride, in which the nucleophilic properties of vinylpyridines are markedly suppressed. Thus, we obtained diadducts IVa-d (Table 1), the formation of which can be explained by reaction of the initially formed adducts III with a second molecule of dienophile via the previously proposed scheme [1], when we refluxed mixtures of vinylpyridines Ia-d with N-phenylmaleinimide in acetic anhydride for many hours: (Scheme, top, following page.)

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*Deceased.

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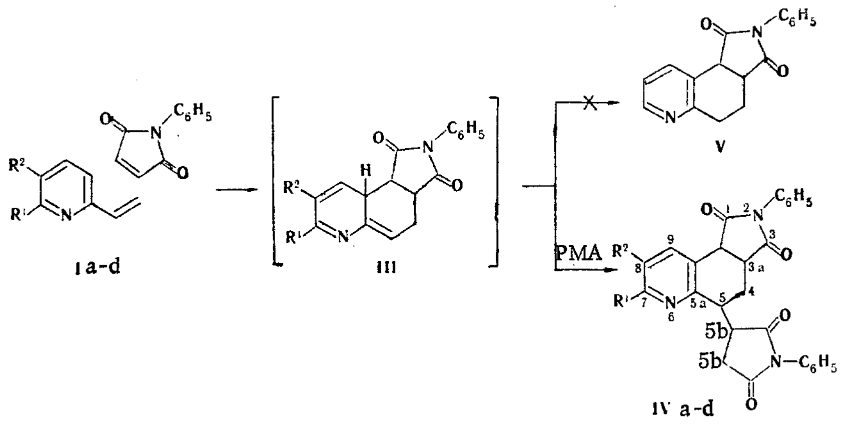


I, IV **a** $R^1=R^2=H$; **b** $R^1=CH_3$, $R^2=H$; **c** $R^1=H$, $R^2=CH_3$; **d** $R^1=H$, $R^2=C_2H_5$

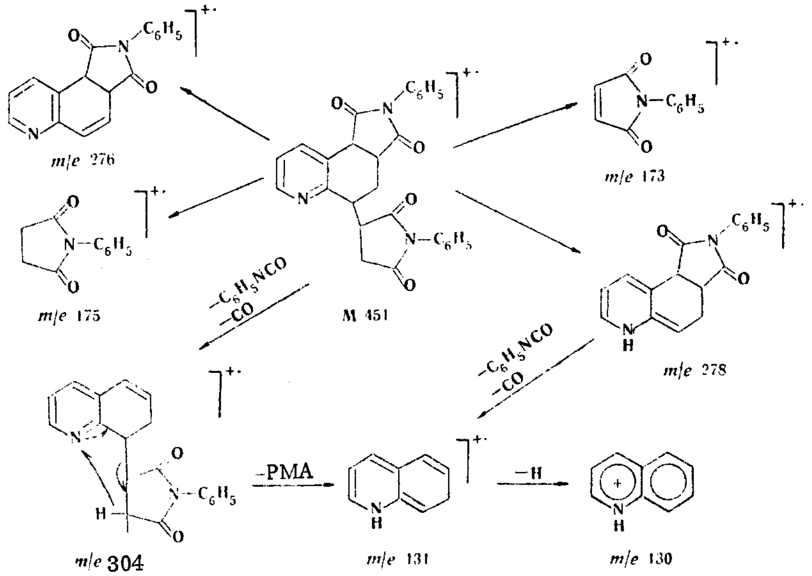
We were unable to detect monoadducts V in the reaction mixture. The structures of IVa-d follow unambiguously from an analysis of their spectral properties (Table 2).

Thus, one intense maximum at 260-265 nm, which is characteristic for pyridine derivatives, is observed in the UV spectra of IVa-d, while the IR spectra contain absorption bands at 1680-1700 $cm^{-1}$ of four amide carbonyl groups [5].

Well-resolved signals of three protons (7-H, 8-H, and 9-H), which are characteristic for a 2,3-disubstituted pyridine ring, are noted in the PMR spectrum of IVa at weak field.

A doublet of one 9b-H proton at 4.70 ppm, a multiplet of two 5e-H protons at 3.65 ppm, and a multiplet of five protons (3a-H, 4-H, 5-H, and 5b-H) at 2.3-3.3 ppm are observed in the stronger-field region. A similar pattern in the strong-field region is noted in the PMR spectra of IVb-d.

Finally, the mass spectrum of IVa contains an intense molecular-ion peak ($M^+$) with m/e 451,* the fragmentation of which (see the scheme given below) proceeds either with the simultaneous elimination of phenyl isocyanate and CO fragments (304) or, more likely, with splitting out of a molecule of N-phenylmaleinimide (278) and the N-phenylsuccinimide radical or molecule (the 277 and 276 ions, respectively). The presence of an intense ion peak with 278, which subsequently eliminates phenyl isocyanate and CO molecules (131), proves the presence of an N-phenylsuccinyl residue precisely in the 5 position rather than in the 9b position, as was previously assumed [6]. The formation of similar fragments is also characteristic for the mass spectra of IVb-d.



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*The m/e values of the ions are given here and subsequently.

TABLE 1. Properties of Pyrrolo[3,4-f]quinolines IVa-d

| Compound | mp, °C | Found, % |  | Empirical formula | Calc., % |  | Yield, % |
|---|---|---|---|---|---|---|---|
|  |  | C | H |  | C | H |  |
| IVa | 272—273 | 71,6 | 4,8 | $C_{27}H_{21}N_3O_4$* | 71,8 | 4,7 | 37 |
| IVb | 280—281 | 72,1 | 4,9 | $C_{28}H_{23}N_3O_4$ | 72,3 | 5,0 | 25 |
| IVc | 242—243 | 72,2 | 4,9 | $C_{28}H_{23}N_3O_4$ | 72,3 | 5,0 | 33 |
| IVd | 234—235 | 72,5 | 5,1 | $C_{29}H_{25}N_3O_4$ | 72,7 | 5,2 | 30 |

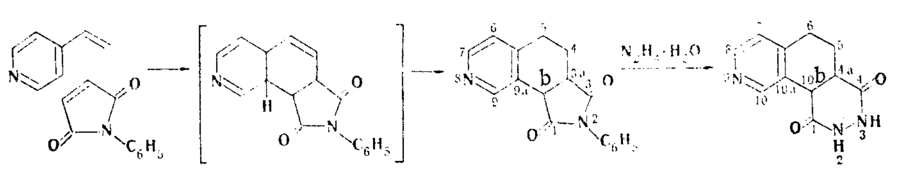
*Found: N 9.2%. Calculated: N 9.3%.

TABLE 2. Spectral Properties of Pyrrolo[3,4-f]quinolines IVa-d

| Compound | PMR spectra, δ, ppm, multiplicity, J, Hz, in $CF_3COOH$ |  |  |  | UV spectra $\lambda_{max}$, nm (log ε) | IR spectra, $cm^{-1}$ | mass spectrum,* m/e (relative intensity, %) |
|---|---|---|---|---|---|---|---|
|  | 7-H | 8-H | 9-H | $CH_3$ |  |  |  |
| IVa | 8,2 q, $J_{7,8}=5$, $J_{7,9}=2$ | 7,5 q, $J_{8,7}=5$, $J_{8,9}=8$ | 8,5 q, $J_{9,8}=8$, $J_{9,7}=2$ | — | 260 (2,80) | 1580, 1590, 1600, 1690—1730, 1780 | 451 (75), 304 (21), 278 (76), 277 (37), 276 (12), 175 (34), 173 (41), 157 (32), 155 (27), 131 (74), 130 (100) |
| IVb | — | 7,4 d, $J_{8,9}=8$ | 8,5 d, $J_{9,8}=8$ | 2,8 s | 262 (2,80) | 1590, 1605, 1700—1730, 1785 | 465 (63), 318 (32), 292 (85), 291 (42), 290 (35), 175 (37), 173 (25), 171 (25), 145 (87), 144 (100, 129 (18) |
| IVc | 8.0 d, $J_{7,9}=2$ | — | 8,4 d, $J_{9,7}=2$ | 2,2s | 265 (2,85) | 1600, 1700—1730, 1780 | 465 (58), 318 (40), 292 (88), 291 (56), 290 (65), 175 (30), 173 (26), 171 (35), 145 (80), 144 (100), 143 (35) |
| IVd | 8,0 d, $J_{7,9}=2$ | — | 8,4 d, $J_{9,7}=2$ | —$CH_2$—, 2.9 q, | 265 (2,90) | 1600, 1710—1740, 1780 | 479 (45), 332 (15), 306 (75), 305 (28), 304 (10), 291 (35), 289 (25), 175 (25), 173 (20), 158 (100), 143 (80) |

*The molecular peak and the 10 most intense peaks are presented.

The reaction of 4-vinylpyridine with N-phenylmaleinimide proceeds with the formation of only "monoadduct" VI. An intense absorption band at 1700 $cm^{-1}$ is observed in its IR spectra, and its PMR spectrum in the weak-field region contains, in addition to a broad signal of five protons of the benzene ring, a singlet of one 9-H proton at 8.95 ppm and doublets of 7-H and 6-H protons at 8.45 and 7.85 ppm, respectively, with an additional spin—spin coupling constant (SSCC) of 5 Hz, which confirms the presence of a 3,4-disubstituted pyridine ring. At stronger field one observes a doublet of a 9b-H proton at 4.50 ppm, a multiplet of one 3a-H proton at 3.85 ppm, a quartet of two 5-H protons at 3.05 ppm, and a multiplet of two 4-H protons at 2.15 ppm. Finally, the mass spectrum of VI contains, in addition to an intense $M^+$ peak with 278, a maximum peak of a 131 ion, which is formed by simultaneous elimination of phenyl isocyanate and CO from the $M^+$ fragment. Thus, the mass-spectral fragmentation completely confirms the VI structure. Its reaction with hydrazine hydrate proceeds via the usual scheme and leads to pyrazine derivative VII.



II V VI VII

## EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The UV spectra of solutions of the compounds in methanol were recorded with a Pye–Unicam SP-8000 spectrophotometer. The PMR spectra of solutions in trifluoroacetic acid were obtained with a Varian T-60 spectrometer with hexamethyldisiloxane as the external standard. The mass spectra were recorded with a Varian MAT-111 mass spectrometer with introduction of the substances in the ionization region at an ionizing-electron energy of 80 eV.

The substances were isolated by means of preparative thin-layer chromatography (TLC) on plates with a 1.5-mm-thick layer of aluminum oxide (activity II) in a benzene–methanol system (9:1).

2-Phenyl-5-(1'-phenyl-2',5'-dioxo-2',3',4',5'-tetrahydro-3-pyrrolyl)-1,3-dioxo-2,3,3a,9b,4,5-hexahydropyrrolo[3,4-f]quinolines (IVa-d). These compounds were obtained by a general method. A solution of 0.1 mole of N-phenylmaleinimide and 0.05 mole of freshly distilled vinylpyridine Ia-d in 100 ml of distilled (over $P_2O_5$) acetic anhydride was refluxed for 15 h, after which the acetic anhydride was removed by distillation, and the residue was washed repeatedly with methanol and recrystallized from chloroform. The yields and constants of the products, the results of elementary analysis, and the data from spectral analysis of the compounds are presented in Tables 1 and 2.

2-Phenyl-1,3-dioxo-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[3,4-i]isoquinoline (VI). A solution of 1.05 g (10 mmole) of II and 1.73 g (10 mmole) of N-phenylmaleinimide in 5 ml of acetic anhydride was refluxed for 10 h, after which the anhydride was evaporated, and the residue was extracted three times with methanol. The methanol was removed by distillation, and the residual brown oil was separated preparatively. Compound VI was isolated from the band with $R_f$ 0.48-0.52 and recrystallized from benzene to give 50 mg (18%) of a product with mp 132-133°C. Found: C 73.2; H 4.9%. $C_{27}H_{14}N_2O_2$. Calculated: C 73.4; H 5.0%. Mass spectrum (relative intensity, %): 278 (44), 131 (100), 130 (71), 129 (10), 119 (6), 104 (12), 103 (11), 91 (6), 78 (8), 77 (19), 51 (12).

1,4-Dioxo-1,2,3,4,4a,10a,5,6-octahydropyridazo[4,5-i]isoquinoline (VII). A 1-ml sample of hydrazine hydrate was added to a solution of 280 mg (1 mmole) of VI in 5 ml of ethanol, and the mixture was maintained at 20°C for 20 h. The colorless acicular crystals were removed by filtration, washed with ethanol, and dried to give 206 mg (97%) of a product with mp 147-149°C. Found: C 61.0; H 5.0%. $C_{11}H_{11}N_3O_2$. Calculated: C 60.8; H 5.1%. IR spectrum: 1580-1600, 1620-1640, and 3200 $cm^{-1}$. Mass spectrum (relative intensity, %): 217 (39), 189 (11), 132 (15), 131 (100), 130 (71), 117 (4), 104 (11), 103 (16), 102 (6), 78 (6), 77 (16).

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