REGIOORIENTATION IN THE REACTION OF SIDE CHAIN ACTIVATED ALKYLPYRIDINES WITH ELECTROPHILES

M. A. Yurovskaya, I. G. Khamlova, V. N. Nesterov, O. V. Shishkin, and Yu. T. Struchkov *

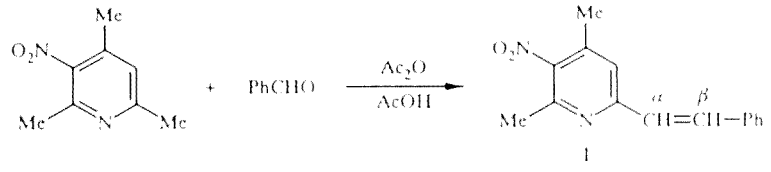
X-ray structural data has shown that condensation of sym-3-nitrocollidine with benzaldehyde occurs at the 6-methyl group. The presence of an acceptor group in the side chain of 2,6-dimethyl-4-cyanomethyl-3-nitropyridine causes condensation to occur at the activated methylene group in the 4-position.

α- and δ-Methylene groups in pyridine have quite a high CH-acidity and can condense with C-electrophiles like carbonyl compounds, under forcing conditions, in the presence of a catalyst. Data concerning the exchange constants for methylpyridines with and without a nitro group are given in a review [1] concerning the basic deuterium exchange of heteroaromatic compounds. The effect on CH-acidity changes in the order 4 > 2 > 3 and depends on the position of the heteroatom relative to the exchanging methyl group in the methylpyridines. Introduction of a nitro group at position 3 increases the CH-acidity of the α-methyl group by about 8 orders and the γ-methyl by 6-7 orders such that, for example, the methyl groups of 2,6-dimethyl-3-nitropyridine undergo H−D exchange under phase transfer catalytic conditions [2].

It has been shown that these mutual effects in the deuterium exchange of methyl groups in heteroaromatic compounds are similar in character to those in the condensation reactions of methyl groups with electrophiles.

The question of regioorientation is important in the reaction of polyalkylnitropyridines with electrophiles. Literature data on the condensation of dimethyl-3-nitropyridines with benzaldehyde in the presence of $ZnCl_2$ show that the reaction proceeds in low yield with little selectivity to form both mono- and di-styryl derivatives [3-5]. Thus condensation of 2,4-dimethyl-5-nitropyridine with benzaldehyde and $ZnCl_2$ gives 2,4-distyryl-5-nitropyridine in 6% yield. Use of acetic anhydride as catalyst increases the selectivity and a 30% yield of the condensation product at the α-methyl position is obtained [3]. On this basis it would be expected that condensation of 2,4,6-trimethyl-3-nitropyridine might occur similarly since reaction at the sterically hindered 2-CH_2 is less likely. However, the authors of [6] showed that use of $ZnCl_2$ gave only an 18% yield of a mono derivative, supposing it to result from condensation at position 6. We have carried out the condensation of 3-nitro-sym-collidine with benzaldehyde in the system $Ac_2O-AcOH$.

Chromatography of the reaction product gave a single compound which was 2-styryl-5-nitro-4,6-dimethylpyridine (I). The parameters for I agree with those of [6] which confirms the authors proposal. The given orientation of the process agrees with the values of the CH-acidities of the α- and γ-methyl groups.



I

*Deceased.

M. V. Lomonosov State University, Moscow 119899. A. N. Nesmeyanov Institute of Organoelemental Compounds, Moscow 117813. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1543-1550, November, 1995. Original article submitted June 10, 1995.

0009-3122/95/3111-1339$12.50

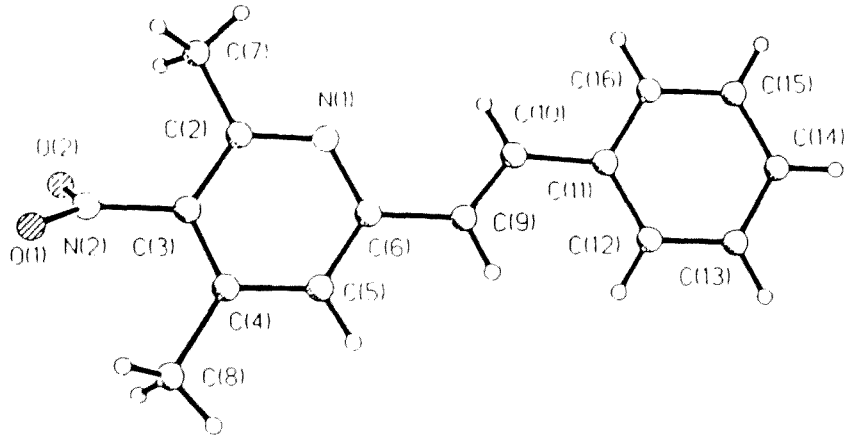


Fig. 1. General view of molecule I.

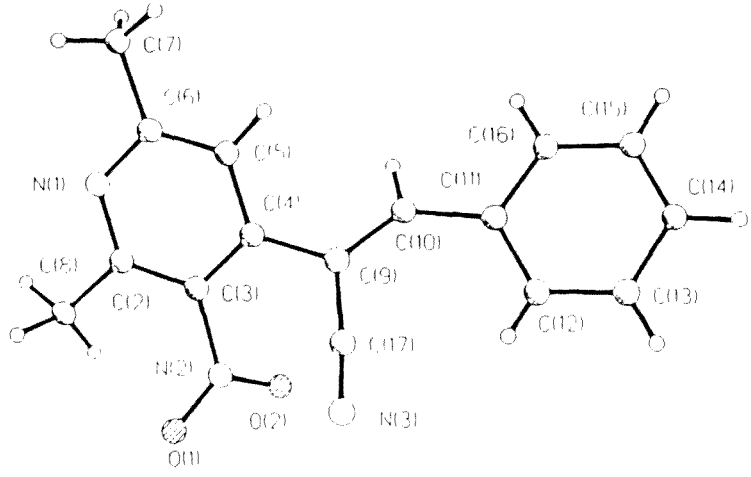
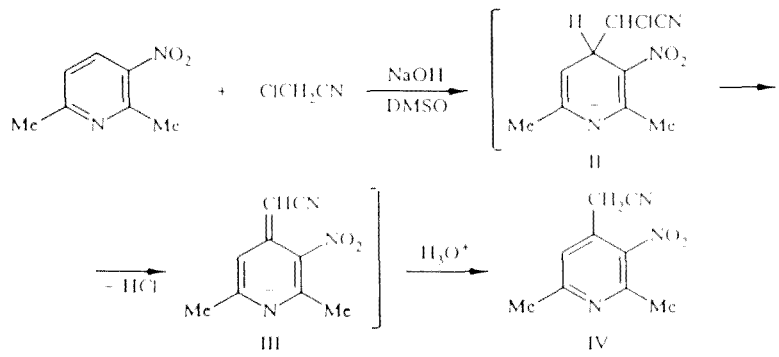


Fig. 2. General view of molecule Va.

A change in the regioorientation of the process can occur with a selective increase in the CH-acidity of one of the alkyl groups, e.g., by the introduction of an acceptor substituent in the side chain. Thus we chose 2,6-dimethyl-4-cyanomethyl-3-nitropyridine (IV) as the next model. In our view, the most logical method for obtaining such a structure may be vicarious nucleophilic substitution. In fact, we succeeded in introducing a cyanomethyl group in position 4 of 2,6-dimethyl-3-nitropyridine for the first time by the following scheme [7-8]:



In agreement with the overall scheme for vicarious nucleophilic substitution [7] it occurs via addition of a nucleophilic (NCCHCl) with a good leaving group (Cl^-) at position 4 of the pyridine ring to form the σ^H adduct II. Base initiated β-elimination of HCl then gives the intermediate III which is protonated to give the aromatic substitution product IV.

TABLE 1. Bond Lengths (Å) in I

Bond	Å	Bond	Å	Bond	Å
$O_{(1)}—N_{(2)}$	1,221(7)	$C_{(3)}—C_{(4)}$	1,379(8)	$C_{(11)}—C_{(12)}$	1,379(8)
$O_{(2)}—N_{(2)}$	1,226(7)	$C_{(4)}—C_{(5)}$	1,380(8)	$C_{(11)}—C_{(16)}$	1,397(8)
$N_{(1)}—C_{(2)}$	1,319(7)	$C_{(4)}—C_{(8)}$	1,522(7)	$C_{(12)}—C_{(13)}$	1,383(8)
$N_{(1)}—C_{(6)}$	1,348(7)	$C_{(5)}—C_{(6)}$	1,394(7)	$C_{(13)}—C_{(14)}$	1,394(8)
$N_{(2)}—C_{(3)}$	1,474(8)	$C_{(6)}—C_{(9)}$	1,451(8)	$C_{(14)}—C_{(15)}$	1,373(8)
$C_{(2)}—C_{(3)}$	1,394(8)	$C_{(9)}—C_{(10)}$	1,343(8)	$C_{(15)}—C_{(16)}$	1,390(8)
$C_{(2)}—C_{(7)}$	1,502(8)	$C_{(10)}—C_{(11)}$	1,454(8)		

TABLE 2. Valence Angles ω (deg.) in I

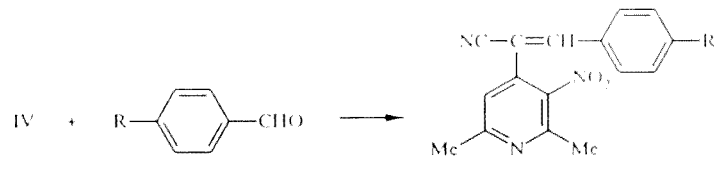
Angle	ω	Angle	ω
$C_{(2)}—N_{(1)}—C_{(6)}$	119,5(4)	$N_{(1)}—C_{(6)}—C_{(5)}$	121,2(5)
$O_{(1)}—N_{(2)}—O_{(2)}$	123,7(5)	$N_{(1)}—C_{(6)}—C_{(9)}$	119,2(5)
$O_{(1)}—N_{(2)}—C_{(3)}$	119,3(5)	$C_{(5)}—C_{(6)}—C_{(9)}$	119,6(5)
$O_{(2)}—N_{(2)}—C_{(3)}$	116,9(5)	$C_{(6)}—C_{(9)}—C_{(10)}$	126,2(5)
$N_{(1)}—C_{(2)}—C_{(3)}$	120,2(5)	$C_{(9)}—C_{(10)}—C_{(11)}$	125,7(5)
$N_{(1)}—C_{(2)}—C_{(7)}$	117,3(5)	$C_{(10)}—C_{(11)}—C_{(12)}$	123,1(5)
$C_{(3)}—C_{(2)}—C_{(7)}$	122,5(5)	$C_{(10)}—C_{(11)}—C_{(16)}$	118,8(5)
$N_{(2)}—C_{(3)}—C_{(2)}$	119,0(5)	$C_{(12)}—C_{(11)}—C_{(16)}$	118,0(5)
$N_{(2)}—C_{(3)}—C_{(4)}$	118,2(5)	$C_{(11)}—C_{(12)}—C_{(13)}$	121,4(5)
$C_{(2)}—C_{(3)}—C_{(4)}$	122,8(5)	$C_{(12)}—C_{(13)}—C_{(14)}$	119,9(5)
$C_{(3)}—C_{(4)}—C_{(5)}$	115,1(5)	$C_{(13)}—C_{(14)}—C_{(15)}$	119,5(5)
$C_{(3)}—C_{(4)}—C_{(8)}$	124,4(5)	$C_{(14)}—C_{(15)}—C_{(16)}$	120,2(5)
$C_{(5)}—C_{(4)}—C_{(8)}$	120,4(5)	$C_{(11)}—C_{(16)}—C_{(15)}$	120,8(5)
$C_{(4)}—C_{(5)}—C_{(6)}$	121,0(5)		

TABLE 3. Bond Lengths (Å) in Va

Bond	Å	Bond	Å	Bond	Å
$O_{(1)}—N_{(2)}$	1,228(6)	$C_{(3)}—C_{(4)}$	1,393(6)	$C_{(10)}—C_{(11)}$	1,463(6)
$O_{(2)}—N_{(2)}$	1,209(6)	$C_{(4)}—C_{(5)}$	1,394(6)	$C_{(11)}—C_{(12)}$	1,396(7)
$N_{(1)}—C_{(2)}$	1,346(6)	$C_{(4)}—C_{(9)}$	1,494(6)	$C_{(11)}—C_{(16)}$	1,403(6)
$N_{(1)}—C_{(6)}$	1,350(5)	$C_{(5)}—C_{(6)}$	1,378(6)	$C_{(12)}—C_{(13)}$	1,368(7)
$N_{(2)}—C_{(3)}$	1,487(6)	$C_{(6)}—C_{(7)}$	1,509(7)	$C_{(13)}—C_{(14)}$	1,380(8)
$N_{(3)}—C_{(17)}$	1,144(6)	$C_{(9)}—C_{(10)}$	1,347(6)	$C_{(14)}—C_{(15)}$	1,378(8)
$C_{(2)}—C_{(3)}$	1,380(6)	$C_{(9)}—C_{(17)}$	1,446(6)	$C_{(15)}—C_{(16)}$	1,375(7)
$C_{(2)}—C_{(8)}$	1,510(7)				

The IR spectrum of IV shows absorption bands for the nitro (1350 and 1540) and CN (2260 cm^{-1}) groups. The PMR spectrum shows a six proton singlet signal at 2.60 ppm for the 2- and 6-methyl groups, a singlet at 3.82 ppm for the methylene group and at 7.15 ppm for the aromatic 5-H proton.

As expected, condensation with benzaldehyde occurs exclusively at the methylene group and this is confirmed by an x-ray structural analysis of Va.



Va, b

Va R = H, b R = Br

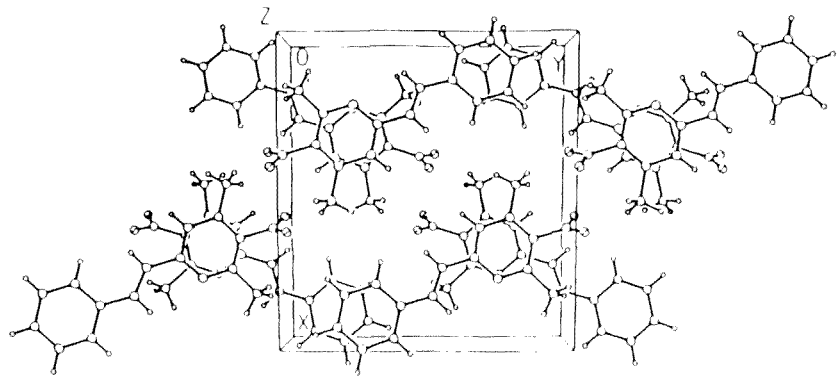


Fig. 3. ab Projection of crystalline structure I.

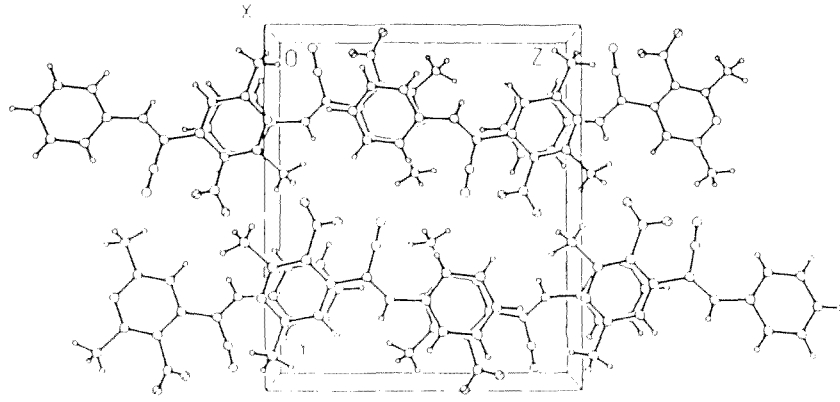


Fig. 4. bc Projection of crystalline structure Va.

Figures 1 and 2 show general views of molecules I and Va and the bond lengths and valence angles are given in Tables 1, 2 and 3, 4 respectively.

Three planar fragments can be distinguished in I and Va: $N_1...C_6$ (A), $C_6...C_{11}$ in I or $C_4...C_{11}$ in Va (B), and $C_{11}...C_{16}$ (C). The dihedral angles A/B 5.1 (in I) and 40.0° (in Va), A/C 12.2 and 30.6°, and B/C 14.7 and 10.0° typify a not quite planar structure for the compounds studied (especially Va) and this is due to shortened intramolecular, non-valence contacts. In I 9-H...12-H is 2.17(1) Å; in Va $O_2...C_9$ 2.997(6), $O_2...C_{17}$ 2.933(6), $N_2...C_{17}$ 2.872(6), $C_{12}...C_{17}$ 3.078(6), and $C_{17}...H_{12}$ 2.52(1) Å (overall van der Waal radii [9] O and C 3.22, N and C 3.25, and C and H 2.90 Å; double the van der Waal radii being H 2.40 and C 3.40 Å). For this reason a marked increase of valence angles in the planar fragment B is observed (see Tables 3 and 4).

Molecules I and Va show a quite marked twist of the NO_2 group with respect to the heterocyclic ring plane (52.6 and 55.2° respectively) which can be explained in terms of steric interactions with neighboring atoms (see Figs. 1 and 2).

As a crystal, I shows a shortening of intermolecular contacts 2.60(1) and 2.79(1) Å (sum of van der Waal radii 2.90 Å) between 7-H of the reference molecule and atoms C_{10} and C_{11}, respectively, connected by the symmetrical transformation x, 0.5 − y, 0.5 + z. Molecules I and Va form layers along c and *a* respectively with an interplanar spacing of about 3.5 Å (Figs. 3 and 4).

The remaining geometrical parameters for crystalline I and Va have standard values [10].

The exact determination of the structure of I from x-ray data led to an unambiguous assignment of the PMR proton signals, in particular those of the methyl groups. The individual 2-CH_3 group appears as a singlet at 2.47 ppm whereas the 4-CH_3 group is a doublet at 2.27 ppm (J = 0.76 Hz) due to the neighboring ortho proton. Interaction with the 4-CH_3 gives a broadened singlet at 7.25 ppm. The protons signals for the vinyl group appear as a doublet with spin−spin coupling of 16.07

TABLE 4. Valence Angles ω (deg.) in Va

Angle	ω	Angle	ω
$C_{(2)}$—$N_{(1)}$—$C_{(6)}$	118,5(4)	$N_{(1)}$—$C_{(6)}$—$C_{(7)}$	116,4(4)
$O_{(1)}$—$N_{(2)}$—$O_{(2)}$	125,0(4)	$C_{(5)}$—$C_{(6)}$—$C_{(7)}$	121,0(4)
$O_{(1)}$—$N_{(2)}$—$C_{(3)}$	116,9(4)	$C_{(4)}$—$C_{(9)}$—$C_{(10)}$	121,6(4)
$O_{(2)}$—$N_{(2)}$—$C_{(3)}$	118,2(4)	$C_{(4)}$—$C_{(9)}$—$C_{(17)}$	115,2(3)
$N_{(1)}$—$C_{(2)}$—$C_{(3)}$	120,8(4)	$C_{(10)}$—$C_{(9)}$—$C_{(17)}$	123,0(4)
$N_{(1)}$—$C_{(2)}$—$C_{(8)}$	115,0(4)	$C_{(9)}$—$C_{(10)}$—$C_{(11)}$	131,7(4)
$C_{(3)}$—$C_{(2)}$—$C_{(8)}$	124,2(4)	$C_{(10)}$—$C_{(11)}$—$C_{(12)}$	125,5(4)
$N_{(2)}$—$C_{(3)}$—$C_{(2)}$	118,7(4)	$C_{(10)}$—$C_{(11)}$—$C_{(16)}$	116,8(4)
$N_{(2)}$—$C_{(3)}$—$C_{(4)}$	119,2(4)	$C_{(12)}$—$C_{(11)}$—$C_{(16)}$	117,7(4)
$C_{(2)}$—$C_{(3)}$—$C_{(4)}$	122,0(4)	$C_{(11)}$—$C_{(12)}$—$C_{(13)}$	120,4(5)
$C_{(3)}$—$C_{(4)}$—$C_{(5)}$	115,8(4)	$C_{(12)}$—$C_{(13)}$—$C_{(14)}$	121,3(5)
$C_{(3)}$—$C_{(4)}$—$C_{(9)}$	124,9(4)	$C_{(13)}$—$C_{(14)}$—$C_{(15)}$	119,4(5)
$C_{(5)}$—$C_{(4)}$—$C_{(9)}$	119,2(4)	$C_{(14)}$—$C_{(15)}$—$C_{(16)}$	119,9(5)
$C_{(4)}$—$C_{(5)}$—$C_{(6)}$	120,3(4)	$C_{(11)}$—$C_{(16)}$—$C_{(15)}$	121,2(5)
$N_{(1)}$—$C_{(6)}$—$C_{(5)}$	122,6(4)	$N_{(3)}$—$C_{(17)}$—$C_{(9)}$	175,7(5)

TABLE 5. Atomic Coordinates ($\times 10^4$) in I

Atom	x	y	z
$O_{(1)}$	4232(3)	-92(3)	3038(6)
$O_{(2)}$	3751(3)	-294(3)	175(6)
$N_{(1)}$	2283(3)	2578(3)	346(6)
$N_{(2)}$	3860(4)	242(4)	1561(7)
$C_{(2)}$	2576(4)	1585(5)	583(8)
$C_{(3)}$	3538(4)	1358(4)	1386(8)
$C_{(4)}$	4202(4)	2133(5)	2059(7)
$C_{(5)}$	3870(4)	3161(5)	1764(8)
$C_{(6)}$	2924(4)	3370(4)	868(8)
$C_{(7)}$	1825(4)	735(4)	25(8)
$C_{(8)}$	5258(4)	1918(5)	2939(8)
$C_{(9)}$	2616(4)	4459(4)	500(8)
$C_{(10)}$	1753(4)	4778(4)	-433(7)
$C_{(11)}$	1470(4)	5871(4)	-857(7)
$C_{(12)}$	2137(4)	6698(5)	-703(9)
$C_{(13)}$	1831(5)	7734(5)	-1041(9)
$C_{(14)}$	838(4)	7951(5)	-1637(8)
$C_{(15)}$	170(4)	7132(5)	-1869(8)
$C_{(16)}$	480(4)	6096(5)	-1490(8)

Hz showing them to be trans orientated. The β-proton signal is at 6.88 ppm and that for the α-H proton undergoes a strong low field shift (7.66 ppm) due to the adjacent pyridine ring.

Assignment of the signals in the PMR spectrum of Va was made using double resonance experiments. The basic problem was the assignment of the signals for the vinyl and 5-H protons. Since the multiplicity of the signal at 7.166 ppm was altered by irradiation at the methyl group frequency, it was assigned as 5-H. Thus the signal at 7.284 ppm was due to the vinyl proton. The chemical shifts for the methyl groups are 2.533 (2-CH_3) and 2.586 ppm (6-CH_3). The spectral parameters for Vb corresponded with those of Va, bearing in mind the change in structure of the aryl substituent.

Hence we have confirmed experimentally that the regioorientation of the condensation of polyalkyl-3-nitropyridines with carbonyl compounds is regulated by the CH-acidity of the alkyl substituents.

TABLE 6. Atomic Coordinates ($\times 10^4$; $\times 10^3$ for H) in Va

Atom	x	y	z
O(1)	1783(7)	4861(2)	1343(3)
O(2)	3830(6)	5367(3)	2413(3)
N(1)	2011(5)	7442(2)	15(3)
N(2)	2662(6)	5471(3)	1754(3)
N(3)	-89(7)	5399(3)	3672(3)
C(2)	2359(7)	6605(3)	365(3)
C(3)	2245(6)	6403(3)	1405(3)
C(4)	1808(6)	7053(3)	2138(3)
C(5)	1440(6)	7911(3)	1752(3)
C(6)	1559(6)	8082(3)	707(3)
C(7)	1128(10)	9002(3)	271(4)
C(8)	2903(10)	5937(4)	-456(4)
C(9)	1618(6)	6878(3)	3271(3)
C(10)	2188(6)	7478(3)	3988(3)
C(11)	2024(6)	7495(3)	5116(3)
C(12)	1473(8)	6773(4)	5728(4)
C(13)	1340(8)	6871(4)	6777(4)
C(14)	1732(7)	7680(4)	7257(4)
C(15)	2280(7)	8402(4)	6669(4)
C(16)	2472(7)	8305(3)	5617(4)
C(17)	685(7)	6054(3)	3530(3)
H(5)	109(5)	839(3)	223(3)
H(7.1)	41(8)	932(4)	84(5)
H(7.2)	61(8)	894(4)	-38(5)
H(7.3)	225(9)	932(4)	6(5)
H(8.1)	326(7)	622(3)	-109(4)
H(8.2)	379(7)	550(4)	-18(4)
H(8.3)	176(8)	568(4)	-82(5)
H(10)	284(6)	796(3)	374(3)
H(12)	113(6)	630(3)	545(3)
H(13)	92(7)	640(3)	717(4)
H(14)	151(5)	772(3)	800(4)
H(15)	266(6)	896(3)	696(4)
H(16)	282(6)	878(3)	520(3)

EXPERIMENTAL

IR Spectra were recorded on a UR-20 instrument in Vaseline mull. PMR Spectra were taken on a Varian VXR-400 instrument for $CDCl_3$ solutions with HMDS internal standard. Assignment of the PMR signals for Va,b was made using double resonance experiments.

Unit cell parameters and intensities of 1546 (I) and 2608 (Va) independent reflections were measured on a Siemens P3/PC four circle automatic diffractometer (λ MoKα, graphite monochromator, $\theta/2\theta$ scanning to θ_{max} = 30 and 28°).

The structure was solved by a direct method revealing all of the nonhydrogen atoms and refined by full matrix least squares analysis in the anisotropic approximation for nonhydrogen atoms for 743 and 1424 reflections with $I > 3\sigma$ (I). In I, the position of the hydrogen atoms was calculated geometrically and refined by the "riding" method with fixed U_{iso} = 0.08 Å [10]. In Va all the hydrogen atoms were directly revealed by difference synthesis and included in the refinement in the isotropic approximation. The final values of the difference factors were R = 0.058 and R_w = 0.052 in I and R = 0.057 and R_w = 0.057 in Va. All of the calculations were carried out using the SHELXTL PLUS program (version PC) [11]. Atomic coordinates are given in Tables 5 and 6 (thermal parameters can be obtained from the authors).

Crystalline I is monoclinic; at 20°C a = 13.652(5), b = 12.610(5), c = 7.453(5) Å, β = 98.05(1)°, V = 1270(2) Å^3, d_{calc} = 1.434 g/cm^3, space group $P2_1/C$, Z = 4.

Crystalline Va is monoclinic; at 20°C a = 7.365(2), b = 14.853(3), c = 12.911(4) Å, β = 91.02(2)°, V = 1412(1) Å^3, d_{calc} = 1.389 g/cm^3, space group $P2_1/n$, Z = 4.

2-Styryl-3-nitro-4,6-dimethylpyridine (I, $C_{15}H_{14}N_2O_2$). A mixture of 2,4,6-trimethyl-3-nitropyridine (1.2 g), benzaldehyde (1 ml), acetic acid (1 ml), and anhydrous acetic anhydride (1 ml) was heated at 130-140°C for 22 h. The product was column chromatographed on silica gel using benzene eluant to give a yellow crystalline product (280 mg, 17%) with mp 97°C. PMR Spectrum ($CDCl_3$): 2.270 (3H, d, J = 0.76 Hz, 4-CH_3), 2.466 (3H, s, 2-CH_3), 6.88 (1H, d, J = 16.07 Hz, β-H), 7.25 (1H, br.s, 5-H), 7.30-7.57 (m, Ph, 5-H), 7.66 ppm (1H, d, J = 16.07 Hz, α-H).

4-Cyanomethyl-2,6-dimethyl-3-nitropyridine (IV, $C_9H_9N_3O_2$). A solution of chloroacetonitrile (0.76 g, 0.01 mole) and 3-nitro-2,6-lutidine (1.5 g, 0.01 mole) in DMSO 10 ml was added dropwise to a vigorously stirred suspension of NaOH in DMSO such that the temperature did not exceed 20°C. The product was stirred at room temperature for 1 h, poured into cold 5% HCl, extracted with chloroform, and dried over Na_2SO_4. The solvent was evaporated and the residue purified by column chromatography using silica gel (40 × 100 mk) using benzene–ethyl acetate as eluant (10:1) to give product (0.8 g, 42%). IR Spectrum (film): 1350 (ν_s NO_2), 1540 (ν_{as} NO_2), 2260 cm^{-1} (ν CN). PMR Spectrum ($CDCl_3$): 2.60 (6H, s, 2-CH_3, 6-CH_3), 3.82 (2H, s, $-CH_2CN$), 7.15 ppm (1H, s, 5-H).

4-(α-Cyano-β-phenylvinyl)-2,6-dimethyl-3-nitropyridine (Va, $C_{16}H_{13}N_3O_2$). A solution of 4-cyanomethyl-2,6-dimethyl-3-nitropyridine (0.025 mole), benzaldehyde (0.03 ml), and piperidine (0.005 mole) in ethanol (10 ml) was refluxed using a condenser until precipitation began, cooled, and the residue filtered and recrystallized from ethanol to give yellow crystals (83%) with mp 175-178°C. PMR Spectrum ($CDCl_3$): 2.533 (3H, s, 2-CH_3), 2.586 (3H, s, 6-CH_3), 7.166 (1H, s, 5-H), 7.284 (1H, s, β-H), 7.46-7.80 ppm (5H, m, Ph).

Compound Vb was synthesized similarly as yellow crystals with mp 185-187°C in 64% yield.

The authors express their thanks to the Russian fund for fundamental research (grants 93-03-4593 and 94-03-08338) for support of this work and also ISF (grant NBD 300) and GK, RF with VO, NTP "Fine organic synthesis" (grant FT-28).

REFERENCES

1. N. N. Zatsepina and I. F. Tupitsyn, Khim. Geterotsikl. Soedin., No. 12, 1587 (1974).
2. W. J. Spillone, P. Kavanagah, and F. Young, J. Chem. Soc. Perkin Trans. I, No. 6, 1763 (1981).
3. L. Achremovicz and Z. Skrowaczewska, Roczn. Chem., **39**, 1417 (1965).
4. L. Achremovicz and Z. Skrowaczewska, Roczn. Chem., **41**, 1555 (1967).
5. T. Bonas and Z. Skrowaczewska, Roczn. Chem., **43**, 739 (1969).
6. F. Kogl, C. M. van der Want, and C. A. Salemnik, Rec. Trav. Chim., **67**, 29 (1948).
7. M. Makosza, Synthesis, No. 2, 103 (1991).
8. M. Makosza, J. Golinski, and J. Baran, J. Org. Chem., **49**, 1488 (1984).
9. A. Bondi, J. Phys. Chem., **170**, 3006 (1966).
10. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, J. Chem. Soc. Perkin Trans. II, 1 (1987).
11. W. Robinson and G. M. Sheldick, Crystallographic Computing Techniques and New Technologies, Oxford Univ. Press, Oxford (1988), p. 366.