Chemistry of Heterocyclic Compounds, Vol. 37, No. 6, 2001

OXIDIZING REACTIONS OF AZINES. 7*. IMINATION OF 4-ARYL-1,2,3,6-TETRAHYDROPYRIDINES BY ARYLAMINES IN THE PRESENCE OF POTASSIUM PERMANGANATE. MOLECULAR STRUCTURE OF 1-METHYL-2-(4-NITROPHENYLIMINO)-4-PHENYL-1,2,5,6-TETRAHYDROPYRIDINE

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On treating 4-aryl substituted 1-methyl-1,2,3,6-tetrahydropyridines with potassium permanganate in the presence of arylamines a previously unknown intermolecular oxidative imination reaction occurs leading to the formation of 2-(arylimino)-1,2,5,6-tetrahydropyridines. The molecular structure of 1-methyl-2-(4-nitrophenylimino)-4-phenyl-1,2,5,6-tetrahydropyridine was studied by X-ray analysis and it was shown that the hydropyridine ring of the molecule has a sofa conformation and its amidine fragment is in the E-configuration.

Keywords: oxidative imination of 4-aryl-1,2,3,6-tetrahydropyridines.

The oxidation of 4-aryltetrahydropyridines by potassium permanganate in the presence of compounds containing reactive methylene groups occurs with the formation of products of C–C combination, such as the 2-acylmethylenetetrahydropyridines [2,3]. The joint oxidation of 4-aryl substituted 1,2,3,6-tetrahydropyridines with various arylamines has been studied in the present work with the aim of clarifying the possibilities of broadening the scope of this oxidative combination of a new type. The reaction was carried out at room temperature in acetonitrile solution in the presence of potassium permanganate. On oxidizing the 4-phenyltetrahydropyridine **1** in the presence of 4-nitroaniline a yellow amorphous powder (30% yield) was obtained by chromatographic separation of the reaction mixture and recrystallization from hexane. This product had mp 92-94°C and according to data of elemental analysis and spectral characteristics corresponded to the product, *viz*. imine **3,** of C–N coupling of the two substrates (see preliminary communication [4]). A second portion (3% yield) of precipitate was formed on extended storage of the mother liquor remaining after separation

* For part 6 see [1].

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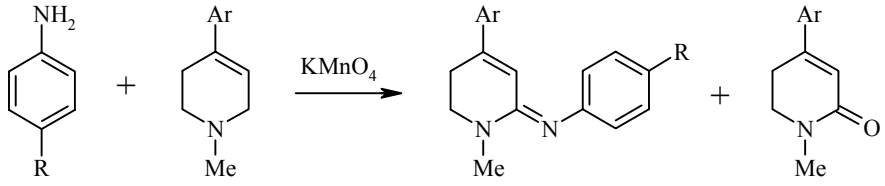
of the amorphous solid. This consisted of well-formed bright yellow monoclinic crystals, the melting point of which (118-120°C) differed significantly from that of the amorphous powder. Nonetheless the ^{1}H NMR, IR and mass spectra of both fractions proved to be identical. Carrying out an analogous oxidation in the cold (-10 to 0°C) or with slight heating (35-50°C) leads to a reduction in yield of the desired imine **3** to 20%, isolated as an amorphous fraction. An X-ray structural investigation was carried out for unambiguous proof of the structure of the synthesized amidine **3** and establishment of its spatial and molecular structure. In the crystalline state molecules of compound **3** occupy two systems of equivalent positions 1 and 2. The general form of one of the independent molecules is shown in Fig. 1.



1, 3, 4, 6, 7 Ar = Ph; **2**, **5** Ar = [2,2]-paracyclophanyl-4; **3**, **5** R = NO_2;
6 R = Br; **7** R = N = NPh

The atomic coordinates are given in Tables 1 and 2, and the bond lengths and valence angles in Tables 3 and 4 (the bond lengths and values of the valence angles in the independent molecules differed insignificantly [5]). The tetrahydropyridine ring of the compound **3** molecules has a sofa conformation in both systems. The N1(N1'), C7(C7'), C8(C8'), C9(C9'), and C10(C10') atoms lie in one plane (the mean square deviation of the atoms from the plane was 0.028 Å in molecule *1* and 0.047 Å in molecule *2*). The C11(C11') atom deviates from this plane by 0.61 Å in molecule *1* and by 0.59 Å in molecule *2*. The N1(N1') atom has a flat trigonal configuration. The sum of the valence angles was 355° and 358° respectively. The phenyl ring is planar and is inclined to the mean plane of the heterocycle at 30.4° in molecule *1* and at 23° in molecule *2*. The nitrophenyl substituents in both independent molecules are in the *anti* position relative to the C=N bond of the amidine fragment. The plane of the nitrophenyl group makes an angle of 53.5° with the plane of the heterocycle in molecule *1* and 127.3° in molecule *2*. In both molecules the nitro group is turned slightly relative to the plane of the second phenyl ring (the angle is 5.4° in molecule *1* and 4.3° in molecule *2*). The packing of the molecules in the crystal is shown in Fig. 2.

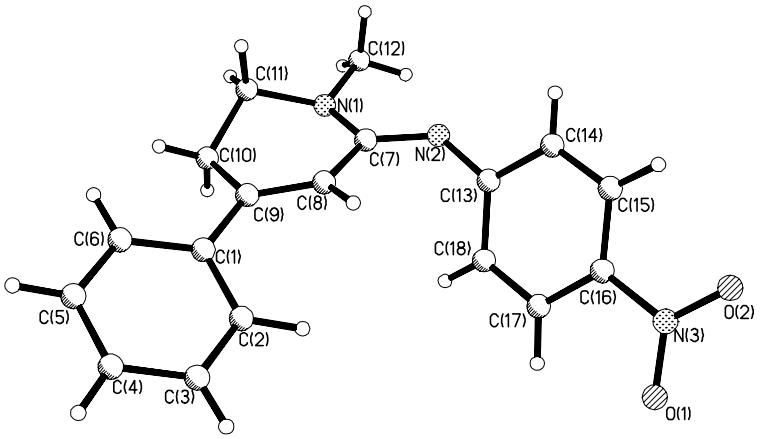


Fig. 1. General form of molecule of compound **3**.

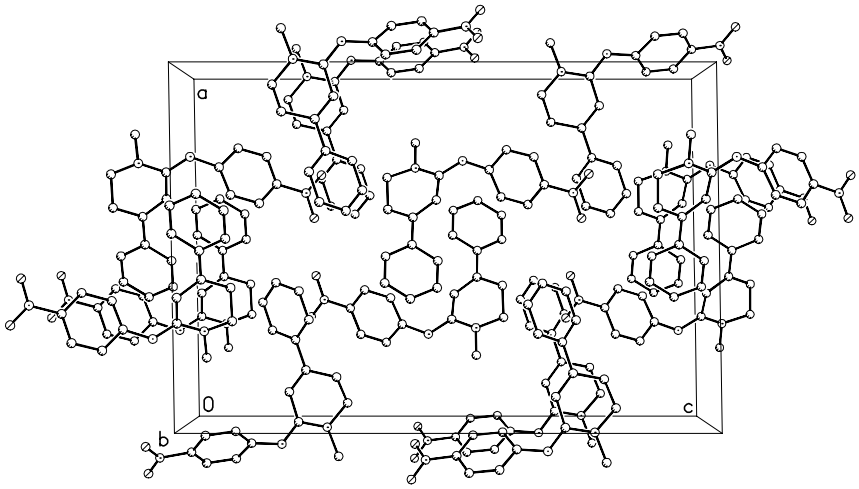


Fig. 2. Packing of the crystal structure of compound **3** along the OY axis (H atoms are not shown).

TABLE 1. Coordinates of the Non-hydrogen Atoms ($\times 10^4$) and Equivalent Isotropic Parameters ($Å^2 \times 10^3$) in the Molecule of Compound **3**

Atom	*x*	*y*	*z*	U_{eq}
1	2	3	4	5
N(1)	2741(1)	9589(2)	556(1)	51(1)
N(2)	2550(1)	10230(2)	-356(1)	51(1)
N(3)	3488(1)	12758(2)	-2402(1)	63(1)
O(1)	4188(1)	12558(3)	-2552(1)	97(1)
O(2)	2982(1)	13511(2)	-2679(1)	91(1)
C(1)	4917(1)	12559(2)	623(1)	44(1)
C(2)	5364(1)	12822(3)	146(1)	57(1)
C(3)	6092(1)	13690(3)	167(1)	71(1)
C(4)	6386(2)	14320(3)	660(1)	75(1)
C(5)	5957(2)	14077(3)	1130(1)	72(1)
C(6)	5238(1)	13206(3)	1116(1)	56(1)
C(7)	2967(1)	10439(2)	99(1)	42(1)
C(8)	3670(1)	11544(3)	158(1)	45(1)
C(9)	4157(1)	11583(2)	604(1)	43(1)
C(10)	3925(1)	10509(4)	1087(1)	55(1)
C(11)	3024(1)	10195(4)	1094(1)	55(1)
C(12)	1998(2)	8615(4)	551(1)	71(1)
C(13)	2816(1)	10845(2)	-858(1)	42(1)
C(14)	2278(1)	11766(3)	-1181(1)	50(1)
C(15)	2492(1)	12393(3)	-1685(1)	53(1)
C(16)	3253(1)	12056(2)	-1876(1)	48(1)
C(17)	3795(1)	11087(3)	-1578(1)	56(1)
C(18)	3573(1)	10487(3)	-1074(1)	56(1)
N(1')	-26(1)	6028(2)	2701(1)	48(1)
N(2')	-518(1)	5668(2)	1824(1)	47(1)
N(3')	-830(1)	7046(3)	-432(1)	62(1)
O(1')	-457(1)	8222(3)	-630(1)	86(1)
O(2')	-1317(1)	6202(3)	-696(1)	97(1)
C(1')	2428(1)	6227(2)	2133(1)	42(1)
C(2')	2671(1)	5340(3)	1671(1)	52(1)
C(3')	3462(1)	5419(3)	1496(1)	62(1)
C(4')	4023(2)	6362(3)	1782(1)	67(1)

TABLE 1 (continued)

1	2	3	4	5
C(5')	3799(1)	7245(3)	2237(1)	67(1)
C(6')	3004(1)	7177(3)	2413(1)	56(1)
C(7')	113(1)	5839(2)	2155(1)	42(1)
C(8')	955(1)	5788(2)	1986(1)	43(1)
C(9')	1579(1)	6178(2)	2319(1)	40(1)
C(10')	1400(1)	6658(3)	2906(1)	48(1)
C(11')	644(1)	5783(3)	3091(1)	51(1)
C(12')	-847(1)	5996(4)	2908(1)	61(1)
C(13')	-482(1)	5918(2)	1258(1)	40(1)
C(14')	-976(1)	4894(3)	921(1)	48(1)
C(15')	-1079(1)	5250(3)	368(1)	52(1)
C(16')	-694(1)	6624(3)	147(1)	45(1)
C(17')	-182(1)	7633(3)	458(1)	45(1)
C(18')	-79(1)	7258(3)	1012(1)	43(1)

TABLE 2. Coordinates of Hydrogen Atoms ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) in the Molecule of Compound **3**

Atom	*x*	*y*	*z*	U_{eq}
H(2)	5158(11)	12304(23)	-228(8)	63(6)
H(3)	6375(14)	13707(30)	-157(10)	86(8)
H(4)	6903(14)	14928(29)	654(9)	82(7)
H(5)	6145(14)	14536(29)	1479(10)	88(8)
H(6)	4947(12)	12972(25)	1456(8)	68(6)
H(8)	3781(10)	12252(21)	-137(7)	40(5)
H(10A)	4079(14)	11052(29)	1398(10)	84(8)
H(10B)	4171(13)	9376(28)	1071(8)	69(7)
H(11A)	2726(12)	11285(26)	1187(8)	60(6)
H(11B)	2892(12)	9283(26)	1339(8)	66(6)
H(12A)	1556(22)	9390(44)	631(14)	164(15)
H(12B)	2033(18)	7532(43)	714(13)	133(12)
H(12C)	1885(18)	8211(38)	199(14)	129(12)
H(14)	1782(12)	11931(23)	-1041(7)	56(6)
H(15)	2137(12)	13068(24)	-1912(8)	62(6)
H(17)	4316(14)	10818(27)	-1740(9)	85(7)
H(18)	3915(14)	9859(29)	-869(9)	86(8)
H(2')	2307(12)	4648(25)	1490(8)	63(7)
H(3')	3592(12)	4727(26)	1200(9)	68(7)
H(4')	4553(14)	6418(26)	1675(8)	70(7)
H(5')	4143(13)	7950(27)	2430(8)	68(7)
H(6')	2850(13)	7834(27)	2741(9)	76(7)
H(8')	1024(11)	5401(22)	1610(8)	56(5)
H(10C)	1888(12)	6345(23)	3156(8)	59(5)
H(10D)	1346(10)	7873(24)	2931(7)	43(5)
H(11C)	468(12)	6258(25)	3428(9)	69(6)
H(11D)	747(11)	4556(25)	3122(7)	52(6)
H(12D)	-825(16)	6275(33)	3267(12)	107(9)
H(12E)	-1043(17)	4823(38)	2888(11)	114(11)
H(12F)	-1201(16)	6692(33)	2713(10)	94(9)
H(14')	-1274(12)	3966(26)	1086(8)	68(6)
H(15')	-1429(12)	4532(25)	170(8)	64(6)
H(17')	63(11)	8717(24)	302(7)	52(5)
H(18')	237(11)	8046(22)	1217(7)	48(5)

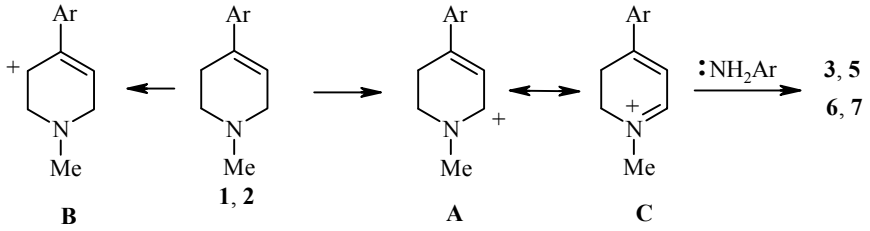
In the considered example of joint oxidation of tetrahydropyridine **1** with *p*-nitroaniline, 1-methyl-2-oxo-4-phenyltetrahydropyridine (**4**) (2%) was isolated from the reaction mixture by chromatography in addition to the *E*-geometric polymorphic isomer **3**. Compound **4** has been obtained [1,4] by the direct oxidation of the initial **1**. The formation of this cyclic amide **4** in the present case may be linked both with the direct oxidation of the initial compound **1** and with the possible hydrolysis of amidine **3** on treatment and chromatographic separation of the reaction mixture (many amidines have a low stability and may be hydrolyzed readily to amides [6,7]). The oxidative imination with *p*-nitroaniline was also carried out with tetrahydropyridine **2**, which has a paracyclophanyl substituent at $C_{(4)}$. The expected amidine **5** was isolated as a yellow amorphous powder in 30% yield. Two further examples of similar C–N coupling were obtained on joint oxidation of tetrahydropyridine **1** with *p*-bromoaniline and with *p*-aminoazobenzene. The corresponding amidines (**6** and **7**) were isolated as light-yellow and orange crystals in 17 and 20% yield respectively.

The parameters of the ^{1}H NMR spectra for the proton signals of the tetrahydropyridine fragment were similar for all the amidines **3**, **5-7**. The singlet signal for the methyl group protons is displayed at 3.08-3.18 ppm undergoing a significant displacement (by 0.7 ppm) towards low field compared with the initial compound **1**. The protons of the two ring methylene groups at $C_{(5)}$ and $C_{(6)}$ resonate as two triplets at 2.71-2.88 and 3.44-3.53 ppm respectively with coupling constants of 6.4-6.8 Hz. The vinyl proton at $C_{(3)}$ is recorded as a somewhat broadened singlet (in the case of compound **3** as a triplet with CC J = 1.2 Hz) at 5.9-6.38 ppm. In the aromatic proton resonance region signals were observed for aryl group protons, the multiplicity and integrated intensity of which (see Experimental) also confirmed the introduction of arylimine fragments into the tetrahydropyridine ring. The parameters of the ^{1}H NMR spectra completely unambiguously (in view of the X-ray analysis data) indicate the regioselective imination of tetrahydropyridines **1** and **2** at one of the two allyl positions with the formation of

TABLE 3. Bond Lengths (*d*) in the Molecule of Compound **3**

Molecule *1*		Molecule *2*	
bond	*d*, Å	bond	*d*, Å
N(1)–C(7)	1.355(2)	N(1')–C(7')	1.358(2)
N(1)–C(12)	1.449(3)	N(1')–C(12')	1.452(3)
N(1)–C(11)	1.462(2)	N(1')–C(11')	1.457(2)
N(2)–C(7)	1.301(2)	N(2')–C(7')	1.310(2)
N(2)–C(13)	1.390(2)	N(2')–C(13')	1.391(2)
N(3)–O(2)	1.219(2)	N(3')–O(2')	1.221(2)
N(3)–O(1)	1.227(2)	N(3')–O(1')	1.221(2)
N(3)–C(16)	1.452(2)	N(3')–C(16')	1.458(2)
C(1)–C(6)	1.397(3)	C(1')–C(6')	1.383(3)
C(1)–C(2)	1.397(3)	C(1')–C(2')	1.390(3)
C(1)–C(9)	1.474(3)	C(1')–C(9')	1.479(2)
C(2)–C(3)	1.384(3)	C(2')–C(3')	1.380(3)
C(3)–C(4)	1.379(3)	C(3')–C(4')	1.370(3)
C(4)–C(5)	1.364(4)	C(4')–C(5')	1.364(3)
C(5)–C(6)	1.373(3)	C(5')–C(6')	1.387(3)
C(7)–C(8)	1.460(3)	C(7')–C(8')	1.456(2)
C(8)–C(9)	1.338(2)	C(8')–C(9')	1.336(2)
C(9)–C(10)	1.504(3)	C(9')–C(10')	1.509(2)
C(10)–C(11)	1.507(3)	C(10')–C(11')	1.502(3)
C(13)–C(14)	1.383(3)	C(13')–C(14')	1.403(3)
C(13)–C(18)	1.391(3)	C(13')–C(18')	1.393(3)
C(14)–C(15)	1.371(3)	C(14')–C(15')	1.381(3)
C(15)–C(16)	1.372(3)	C(15')–C(16')	1.374(3)
C(16)–C(17)	1.375(3)	C(16')–C(17')	1.379(3)
C(17)–C(18)	1.368(3)	C(17')–C(18')	1.385(2)

amidines **3** and **5**-**7**. The formation of the latter probably occurs through the previous fission of hydride ion by permanganate anion [8] from the allyl (methylene) groups of the tetrahydropyridine ring. However the selectivity of the subsequent nucleophilic attack of carbocations A and B by arylamine is determined by the possibility of stabilizing carbocation A as the iminium ion C, in which the ring nitrogen atom serves as an internal nucleophile.



The possibility of intermolecular oxidative imination of tetrahydropyridines by arylamines has been established by the formation of a new group of amidines.

TABLE 4. Valence Angles (ω) in the Molecule of Compound **3**

Molecule *1*		Molecule *2*	
Angle	ω, deg.	Angle	ω, Angle.
C(7)–N(1)–C(12)	120.2(2)	C(7')–N(1')–C(12')	120.5(2)
C(7)–N(1)–C(11)	118.6(2)	C(7')–N(1')–C(11')	118.8(2)
C(12)–N(1)–C(11)	116.2(2)	C(12')–N(1')–C(11')	118.4(2)
C(7)–N(2)–C(13)	121.9(2)	C(7')–N(2')–C(13')	123.0(2)
O(1)–N(3)–O(2)	122.6(2)	O(1')–N(3')–O(2')	122.9(2)
O(1)–N(3)–C(16)	118.4(2)	O(1')–N(3')–C(16')	119.1(2)
O(2)–N(3)–C(16)	118.9(2)	O(2')–N(3')–C(16')	118.1(2)
C(6)–C(1)–C(2)	117.1(2)	C(6')–C(1')–C(2')	117.9(2)
C(6)–C(1)–C(9)	122.0(2)	C(6')–C(1')–C(9')	120.7(2)
C(2)–C(1)–C(9)	120.8(2)	C(2')–C(1')–C(9')	121.4(2)
C(3)–C(2)–C(1)	120.9(2)	C(3')–C(2')–C(1')	120.8(2)
C(4)–C(3)–C(2)	120.3(2)	C(4')–C(3')–C(2')	120.2(2)
C(5)–C(4)–C(3)	119.6(2)	C(5')–C(4')–C(3')	120.1(2)
C(4)–C(5)–C(6)	120.7(2)	C(4')–C(5')–C(6')	119.9(2)
C(1)–C(6)–C(5)	121.4(2)	C(1')–C(6')–C(5')	121.0(2)
N(2)–C(7)–N(1)	118.8(2)	N(2')–C(7')–N(1')	117.7(2)
N(2)–C(7)–C(8)	124.6(2)	N(2')–C(7')–C(8')	125.2(2)
N(1)–C(7)–C(8)	116.6(2)	N(1')–C(7')–C(8')	117.0(2)
C(9)–C(8)–C(7)	124.0(2)	C(9')–C(8')–C(7')	123.6(2)
C(8)–C(9)–C(1)	122.5(2)	C(8')–C(9')–C(1')	123.1(2)
C(8)–C(9)–C(10)	117.5(2)	C(8')–C(9')–C(10')	118.0(2)
C(1)–C(9)–C(10)	120.0(2)	C(1')–C(9')–C(10')	118.9(2)
C(9)–C(10)–C(11)	111.4(2)	C(9')–C(10')–C(11')	110.0(2)
N(1)–C(11)–C(10)	110.3(2)	N(1')–C(11')–C(10')	111.6(2)
N(2)–C(13)–C(18)	123.8(2)	N(2')–C(13')–C(18')	124.0(2)
N(2)–C(13)–C(14)	118.3(2)	N(2')–C(13')–C(14')	117.4(2)
C(14)–C(13)–C(18)	117.8(2)	C(14')–C(13')–C(18')	117.9(2)
C(15)–C(14)–C(13)	121.7(2)	C(15')–C(14')–C(13')	120.6(2)
C(14)–C(15)–C(16)	118.8(2)	C(14')–C(15')–C(16')	119.4(2)
C(15)–C(16)–C(17)	121.4(2)	C(15')–C(16')–C(17')	122.0(2)
C(15)–C(16)–N(3)	118.8(2)	C(15')–C(16')–N(3')	119.5(2)
C(17)–C(16)–N(3)	119.8(2)	C(17')–C(16')–N(3')	118.5(2)
C(16)–C(17)–C(18)	118.9(2)	C(16')–C(17')–C(18')	118.1(2)
C(17)–C(18)–C(13)	121.4(2)	C(17')–C(18')–C(13')	121.8(2)

EXPERIMENTAL

The IR spectra were recorded on a UR 20 spectrometer in KBr disks, mass spectra were obtained on a MX 1303 instrument. The ^{1}H NMR spectra were recorded on Bruker W 80 (80 MHz) and Bruker WM 250 (250 MHz) instruments in $CDCl_3$ solution, internal standard was TMS. A check on the progress of reactions and the homogeneity of the compounds obtained was effected by TLC on Silufol UV-254 plates, visualization was with iodine vapor. Separation and purification of substances was effected by column chromatography on silica gel L-60 (40/100).

1-Methyl-2-(4-nitrophenylimino)-4-phenyl-1,2,5,6-tetrahydropyridine (3). Finely powdered potassium permanganate (0.91 g, 5.8 mmol) was added at room temperature during 20 min to a mixture consisting of 1-methyl-4-phenyltetrahydropyridine 1 (1 g, 5.8 mmol) and *p*-nitroaniline (0.95 g, 6.8 mmol) in acetonitrile (50 ml). The mixture was stirred for 2 h, then the manganese dioxide was separated, and washed with acetonitrile (3 × 10 ml). The filtrates were combined, and the solvent distilled off under reduced pressure. The residue was separated on a column of silica gel (eluent hexane–ether, 2 : 1). On crystallization of the fraction with R_f 0.49 (acetone) amidine **3** (0.54 g, 30%) was obtained for the first time as a yellow amorphous powder; mp 92-94°C. After storing the mother liquor for a month further amidine **3** (50 mg, 3%) was obtained as transparent monoclinic bright yellow crystals of mp 118-120°C. Both portions of substance had identical IR and ^{1}H NMR spectra and chromatographic mobility. The structure of the crystalline sample was studied by X-ray analysis. A fraction with R_f 0.17 (2% yield) was separated chromatographically and proved to be identical by mp (78-80°C) and spectral data to the previously obtained 1-methyl-2-oxo-4-phenyltetrahydropyridine **4** [1,4]. On carrying out this reaction in the cold (0°C) or with slight heating (35-50°C) the desired amidine **3** was obtained in less than 20% yield. IR spectrum, ν, cm^{-1}: 1339 and 1550 (NO_2), 1624 and 1640 (C=C–C=N). Mass spectrum, *m/z* (I_{rel}, %): 307 (100) (M^+), 306 (44), 259 (27), 250 (33), 230 (6), 187 (35), 166 (37), 149 (60). ^{1}H NMR spectrum of amidine **3**, δ, ppm, *J* (Hz): 2.88 (2H, tt, $^2J = {}^3J = 6.8$, $^4J = 1.2$, 5-CH_2); 3.15 (3H, s, Me); 3.53 (2H, t, $^2J = {}^3J = 6.8$, 6-CH_2); 6.28 (1H, t, $^4J = 1.2$, 3-H); 6.9 and 8.16 (2H each, AA'BB' system of nitrophenyl fragment, $^2J = 9.0$, $^3J = 2.0$); 7.36 (5H, s, Ph). Found, %: C 70.49; H 5.42; N 13.31. $C_{18}H_{17}N_3O_2$. Calculated, %: C 70.36; H 5.54; N 13.68.

1-Methyl-2-(4-nitrophenylimino)-4-([2.2]-paracyclophan-4-yl)-1,2,5,6-tetrahydropyridine (5) was obtained analogously on oxidative imination of 1-methyl-4-(paracyclophan-4-yl)tetrahydropyridine **2** (1.0 g, 3.3 mmol) with *p*-nitroaniline (4.3 mmol). Compound **5** (0.42 g, 29%) was isolated as a yellow amorphous powder; mp 114-117°C. R_f 0.37 (acetone). IR spectrum, ν, cm^{-1}: 1335 and 1556, 1627. Mass spectrum: 437 (M^+). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 2.71 and 3.44 (2H each, both t, $J = 6.4$, 5-CH_2 and 6-CH_2); 2.7-3.2 (m, CH_2 of paracyclophane); 3.13 (3H, s, Me); 5.9 (1H, s, 3-H); 6.0-6.6 (m, H_{arom} paracyclophane portion); 6.88 and 8.1 (2H each, both d, $J = 8.6$, AA'BB' system of nitrophenyl fragment). Found, %: C 76.70; H 6.11; N 9.87. $C_{28}H_{27}N_3O_2$. Calculated, %: C 76.89; H 6.18; N 9.61.

2-(4-Bromophenylimino)-1-methyl-4-phenyl-1,2,5,6-tetrahydropyridine (6) was obtained analogously from a mixture of tetrahydropyridine **1** (1.0 g, 5.8 mmol) and *p*-bromoaniline (2.2 g, 12.8 mmol). The yield of imine **6** was 0.34 g (17%) of needle-like light yellow crystals of mp 100-103°C. R_f 0.58 (ether). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 2.78 and 3.50 (2H each, both t, $J = 6.4$, 5-CH_2 and 6-CH_2); 3.08 (3H, s, Me); 6.27 (1H, br. s, 3-H); 6.64 and 7.25 (2H each, both d, $J = 8.3$, AA'BB' system in *p*-bromophenyl fragment); 7.3 (5H, m, Ph). Found, %: C 62.81; H 5.17; N 8.36. $C_{18}H_{17}BrN_2$. Calculated, %: C 63.34; H 4.99; N 8.21.

1-Methyl-4-phenyl-2-[4-(phenylazo)phenyl]-1,2,5,6-tetrahydropyridine (7) was obtained analogously from a mixture of tetrahydropyridine **1** (0.5 g, 2.9 mmol) and 4-aminoazobenzene (0.57 g, 2.9 mmol). Imine **7** (0.21 g, 20%) of mp 156-159°C was isolated chromatographically as orange prismatic crystals, R_f 0.52 (acetone). IR spectrum: 1629 cm^{-1} (C=C–C=N). Mass spectrum: 366 (M^+). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 2.82 and 3.49 (2H each, both t, $J = 6.4$, 5- and 6-CH_2); 3.18 (3H, s, Me); 6.38 (1H, br. s, 3-H); 6.89 and 7.83 (2H each, both d, $J = 8.6$, AA'BB' system); 7.2-7.5 (8H, m, 5H from C-Ph and 3H from N-Ph); 7.83 (2H, m, N-Ph). Found, %: C 78.81; H 6.34; N 15.01. $C_{24}H_{22}N_4$. Calculated, %: C 78.69; H 6.01; 15.30.

X-ray Structural Analysis of Compound 3. Crystals of amidine **3** of composition $C_{18}H_{17}N_3O_2$ grown in ether were monoclinic and had the following crystallographic parameters: space group $P2_1/c$, a = 16.498(4), b = 7.930(2), c = 24.270(5) Å; β = 90.92°; V = 3174(1) Å^3; Z = 8; d_{calc} = 1.286 g/cm^3; M = 307.35. The parameters of the unit cell and the intensities of 7644 reflections were measured on a Siemens P3/PC automatic four-circle diffractometer (T = 20°C, λMo$K\alpha$ radiation, graphite monochromator, $\theta/2\theta$ scanning , θ_{max} = 28°). The structure was solved by the direct method and refined by a full matrix least squares method in an anisotropic approach for the nonhydrogen atoms. The hydrogen atoms were localized objectively in a Fourier difference synthesis and were refined isotropically. The final values of the divergence factors were R_1 = 0.0462 for 2858 independent reflections with $I > 2\sigma$ and wR_2 = 0.1518 for each of 7709 reflections. All calculations were carried out with the SHELXTL PLUS set of programs (PC version 5.0) [9]. The numbering of atoms is given in Fig. 1.

The work was carried out with the support of the Russian Fund for Fundamental Investigations (project No. 99-03-32940a).

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