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The reaction of 2-aminopyridine as well as 2-benzylaminopyridine hydrochloride with benzyl chlorides used in molar ratio of 1:2 and 1:1 respectively and carried out at 250° leads *via* 2-benzylamino-5-benzylpyridines to 2-amino-5-benzylpyridines as the final products. The formation of 2-benzylamino-5-benzylpyridines did not occur in the direct *C*-benzylation reaction of the 2-benzylaminopyridine ring with the use of benzyl chloride. Its formation takes place *via* the intermediate state of 2-(*N,N*-dibenzylamino)pyridinium and 1-benzyl-2-benzylaminopyridinium chlorides for which the solvent separated ion-molecule form is proposed. Interaction of the ingredients of the intermediate state *i.e.*, benzyl cation and 2-benzylaminopyridine, leads in an electrophilic mechanism to the formation of 2-benzylamino-5-benzylpyridine hydrochlorides. Thermolysis of the aminomethylene bond in 2-benzylamino-5-benzylpyridine hydrochlorides leads to the final 2-amino-5-benzylpyridines.

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Electrophilic benzylation and pyridylmethylation of the 2,6-diaminopyridine ring leads to 3-substituted or 3,5-disubstituted 2,6-diaminopyridines. It was found that *C*-benzylation of the 2,6-diaminopyridine ring occurs by an intermolecular rearrangement process, catalyzed by Lewis acid [1,2]. In contrast to *N*-benzyl and *N*-(2- and 4-picolyl)-2,6-diaminopyridines, *N*-benzyl and *N*-(2-picolyl)-2-aminopyridines do not rearrange to *C*-substituted products [1,3,4].

Previous papers presented the results of the reaction of 2-aminopyridines with benzyl chloride used in a molar ratio of 1:2 and carried out at 250 ± 5°, where benzylation of the pyridine ring takes place to give 3- (when the 5-position is blocked) or 5-benzyl derivatives of 2-aminopyridine [3,4].

This paper presents the results of the reaction of 2-amino and 2-benzylaminopyridine with substituted benzyl chlorides, where benzylation of the ring also takes place. Reaction mixtures were analyzed by high resolution chromatography and the products were rationalized by means of the quantum chemical calculations.

Reaction of 2-Aminopyridine with Substituted Benzyl Chlorides.

The reactions of 2-aminopyridine (**1**) with *p*-methyl (**2**) *p*-chloro (**3**) and *p*-nitrobenzyl (**4**) chlorides were carried out under previous conditions used with benzyl chloride itself [3,4] (*i.e.* reaction time 3 hours at 250 ± 5°) using **1**

and **2**, **3** or **4** in a molar ratio of 1:2. In the case of reaction of **1** with **2** or **3**, formation of the corresponding 2-benzylamino-5-benzyl (**2a,3a**) and 2-amino-5-benzylpyridines (**2b,3b**) was found. The general reaction scheme can be shown as follows:

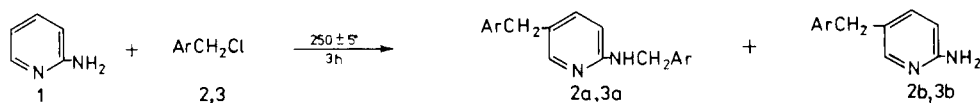
The attempted reaction of **1** with **4** failed, analogous to the situation of **4** with 2,6-diaminopyridine [2], in that only tar formed.

The present experimental results, show that **2**, **3** and benzyl chloride react with **1** in analogous fashion and support the electrophilic mechanism for the reaction [3,4].

Reaction of 2-Benzylaminopyridine with Benzyl Chlorides.

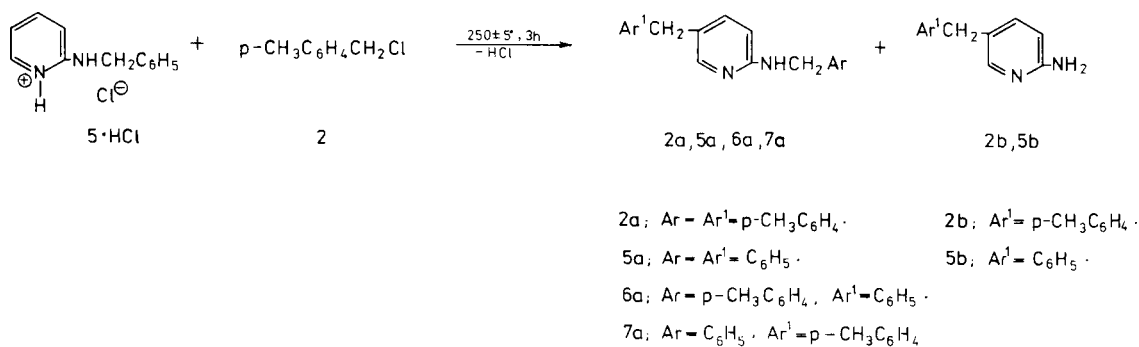
Previous experiments indicated that 2-benzylaminopyridines were formed after 0.5 hour at 250° as the first step of the reaction between 2-aminopyridines and benzyl chloride. The 5-benzyl derivatives then resulted from reaction with excess benzyl chloride [3,4]. In order to check on this proposed reaction sequence 2-benzylaminopyridine hydrochloride (**5**) was treated with *p*-methylbenzyl chloride (**2**) in a molar ratio of 1:1. The following compounds were identified in the reaction mixture: 2-(*p*-methylbenzylamino)-5-(*p*-methylbenzyl)pyridine (**2a**), 2-benzylamino-5-benzylpyridine (**5a**), 2-(*p*-methylbenzylamino)-5-benzylpyridine (**6a**), and/or 2-benzylamino-5-(*p*-methylbenzyl)pyridine (**7a**) as well as 2-amino-5-(*p*-methylbenzyl)pyridine (**2b**) and 2-amino-5-benzylpyridine (**5b**) (see Scheme 2).

Scheme 1



2,2q,2b; Ar = *p*-CH₃C₆H₄, 3,3a,3b; Ar = *p*-ClC₆H₄

Scheme 2



Fractional distillation of this mixture into two parts facilitated this identification on the basis of ¹H nmr and mass spectra and by comparison with reference substance obtained earlier [3,4].

The mixture of compounds **2b** and **5b**, collected in a fraction of bp 135-145°/1 mm, melted at 75-85° after crystallization. In the ¹H nmr spectra, from the integration of the signal corresponding to the CH₃- group (singlet at δ 2.31 ppm) in **2b** and that corresponding to -CH₂- groups (singlet at δ 3.76 ppm) in compounds **2b** and **5b**, a molar ratio of **2b** to **5b** in the amount of ca. 2:1, was detected. In the mass spectrum of the mixture, executed in a gc/ms apparatus, the molecular and fragmentation ions derived from **2b** and **5b** were observed.

A fraction of bp 212-230°/1 mm contained compounds **2a** and **5a** plus **6a** and/or **7a**, melted at 111-115° after crystallization. In the ¹H nmr spectra ring attached -CH₂- groups are shown by a singlet at δ = 3.76 ppm and

-CH₂NH- methylene groups by a doublet at δ 4.41 ppm. Absence of the signal corresponding to a proton at the 5 position in the 2-aminopyridine ring proves that all compounds of this fraction are substituted at C-5. However, the differences in the chemical shifts of protons of these compounds are too small to allow for quantitative analysis of the mixture, from the integral of the signals corresponding to CH₃- and -CH₂- groups I can estimate the ratio of *p*-methylbenzyl and benzyl substituents in the mixture, in amount ca. 1:1.25. In the mass spectra of the mixture (gc/ms system), molecular and fragmentation ions coming from **2a** and **5a** were detected. The presence of **6a** and/or **7a** in the mixture was identified by a molecular ion at M = 288 and by intensive peaks at m/z 120 and 106; *p*-CH₃-C₆H₄-CH=NH₂⁺ and C₆H₅-CH=NH₂⁺ after rearrangement [6], that indicated the presence of the *p*-methylbenzyl-amino and benzylamino grouping in molecules **6a** and **7a** respectively [3,5,6].

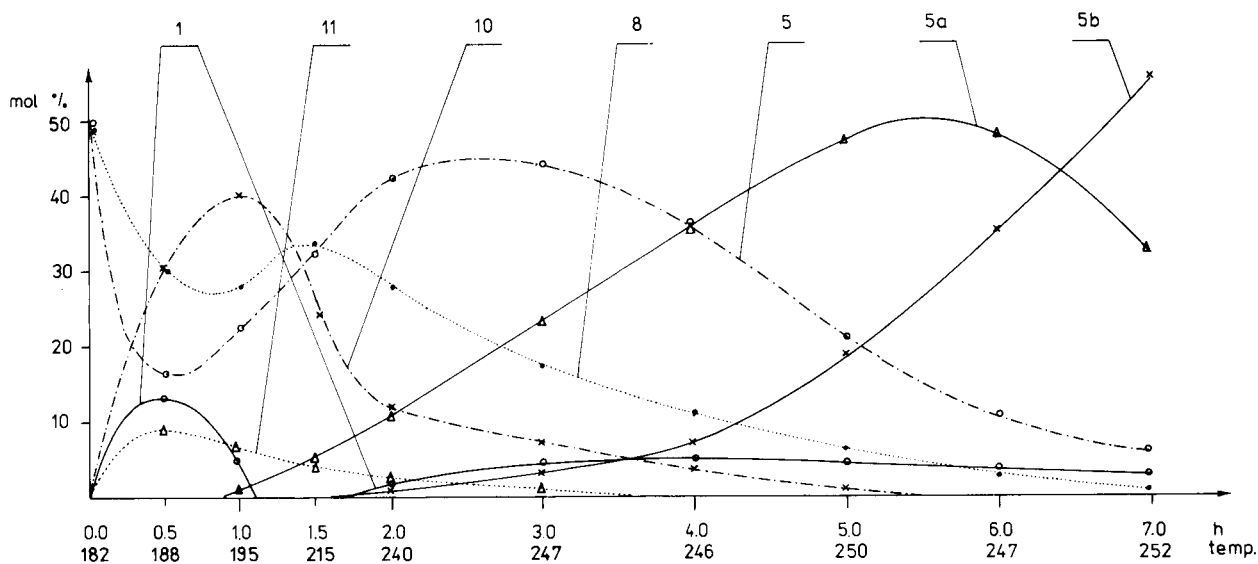


Figure 1. Transformations of compounds (in mol %) which occur in the reaction of 2-benzylaminopyridine hydrochloride (**5**) with benzyl chloride (**8**) in relation to reaction time and reaction temperature (°C).

Experimental results of the reaction of **5** hydrochloride with *p*-methylbenzyl chloride (**2**) proved, that *C*-benzylation of the 2-aminopyridine ring in 2-benzylaminopyridine (**5**) did not occur as the direct benzylation process with the use of *p*-methylbenzyl chloride (**2**). Generation of the compounds with the scrambled substituents reveals another route for the process.

In order to fully explain the transformations arising in the reactions of 2-aminopyridines with benzyl chlorides, detailed product analysis of the reaction of 2-benzylaminopyridine hydrochloride (**5**) with benzyl chloride (**8**) was carried out by means of high resolution chromatography. The compounds which were formed or possibly could be formed in the reaction of **5** hydrochloride with **8** were used as the reference standards. They were (in order of increasing retention time): 2-aminopyridine (**1**) 185-189 s; benzyl chloride (**8**) 230-233 s; bibenzyl (**9**) 548-551 s; 2-benzylaminopyridine (**5**) 635-637 s; 2-amino-5-benzylpyridine (**5b**) 667-669 s; 2-(*N,N*-dibenzylamino)pyridine (**10**) 898-902 s; 1-benzyl-2-benzylimino-1,2-dihydropyridine (**11**) 989-994 s; 2-benzylamino-5-benzylpyridine (**5a**) 1140-1146 s.

The qualitative and quantitative compositions of the reaction mixture in relation to reaction time and reaction temperature are displayed in Figure 1. Total quantity of the analyzed reaction products were over 96% in the first three hours and over 94% in the remaining time.

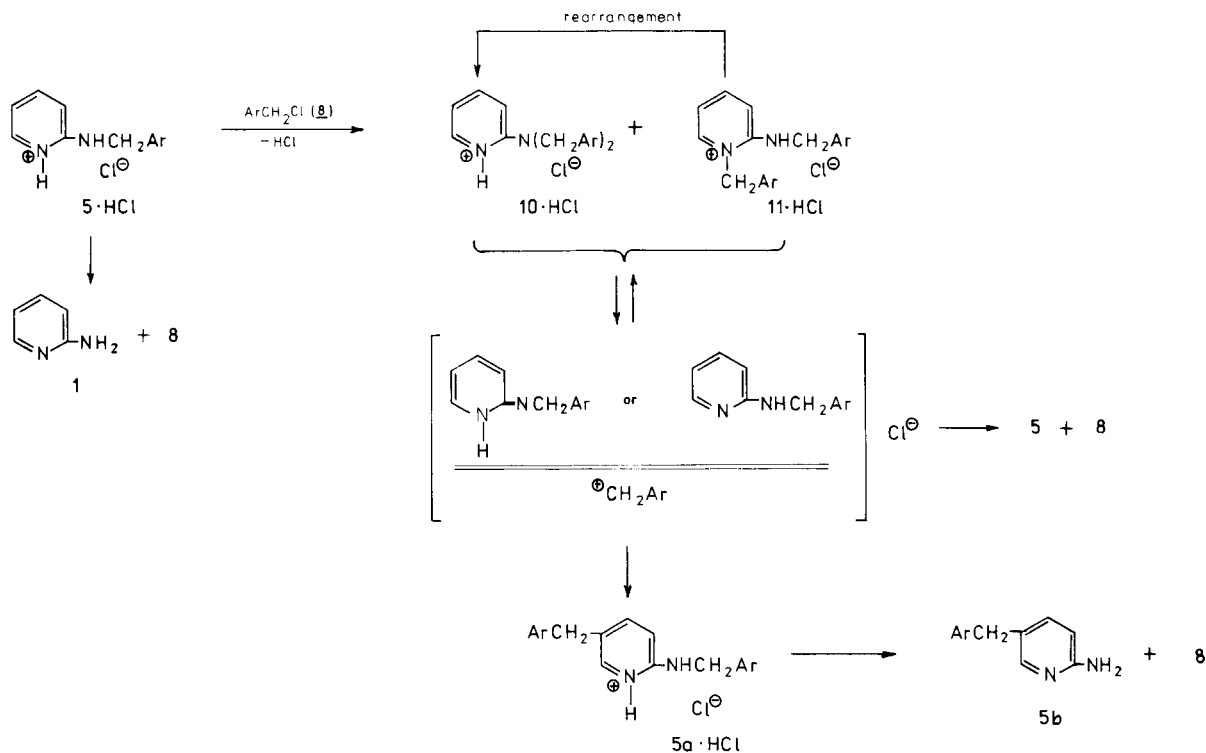
Presented in the Figure 1 experimental results indicated that: a) at the beginning mainly the formation of **10** occurred and **11** was formed in smaller amount, b) formation of **5a** followed the certain concentration of **10**, c) increase in the amount of **5a** ended together with the disappearance of **10**, d) **5b** formation occurs after **5a** creation, e) **9** was not produced, f) **1** was present in the reaction mixture almost all of the time.

It leads to the conclusion that 2-benzylaminopyridine hydrochloride (**5**) in the reaction with benzyl chloride (**8**) formed 2-(*N,N*-dibenzylamino)pyridine hydrochloride (**10**) [2-(*N,N*-dibenzylamino)pyridinium chloride] and 1-benzyl-2-benzylimino-1,2-dihydropyridine hydrochloride (**11**) [1-benzyl-2-benzylaminopyridinium chloride] first with the evolution of the hydrogen chloride (see Scheme 3).

The evolution of the hydrogen chloride was already observed from the reaction mixture of 2-aminopyridines with benzyl chloride [3,4], as well as in the reaction of 2-aminopyridine (**1**) with substituted benzyl chlorides **2-4** and **5** hydrochloride with **2**. The quantity of the aqueous ammonium hydroxide used for alkalizing the hydrogen chloride produced during the reactions were *ca.* 40% of the theoretical amount after 3 hours reaction at $250 \pm 5^\circ$.

Rationalization of the transformations of the **10** and **11** hydrochlorides were executed based on the literature and the performed MNDO calculation data. Katritzky and co-

Scheme 3



workers [7-10] who extensively investigated *N*-substituted pyridinium cations in the nucleophilic substitution reaction of its *N*-substituent found, that for example the reaction of *N*-benzylpyridinium cations [11] takes place *via* ion-molecule pair formation to produce mainly products of benzylation of the pyridine ring (as a leaving group after benzyl cation dissociation), when the reaction was carried out without solvent. In the case of the solvent use, additional benzylation occurs.

The fact, that transformations of **10** mainly and **11** to a smaller degree are connected with the 5-benzyl derivative formation (**5a**) according to electrophilic mechanism, indicate rearrangement of these compounds *via* an intermediate state, where the benzyl cation exists in free form. Calculation of charges by the MNDO-method [12] on nitrogen atoms and sp^3 benzylic carbon atoms and bond orders (see Figure 2) in the cationic part of **11** hydrochloride *i.e.* 1-benzyl-2-benzylaminopyridinium cation, indicated that the heterolytic $N_{annular}-C_{benzyl}$ bond breaking (bond order 0.823) should occur easier than $N_{exocyclic}-C_{benzyl}$ one (bond order 0.895) (Figure 2b). The same calculation performed

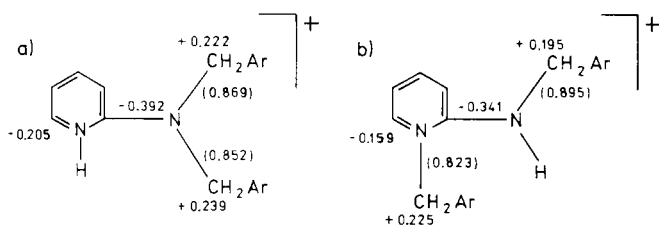


Figure 2. Charges, in a.u., on nitrogen atoms and sp^3 benzylic carbon atoms and bond orders (values in brackets), calculated by MNDO-method, in cationic part of **10** and **11** hydrochlorides; a) 2-(*N,N*-dibenzylamino)pyridinium cation, b) 1-benzyl-2-benzylaminopyridinium cation.

for the cationic part of **10** hydrochloride *i.e.* 2-(*N,N*-dibenzylamino)pyridinium cation (Figure 2a), indicated that the one of the $N_{exocyclic}-C_{benzyl}$ bond breaking (bond order 0.852) in **10** hydrochloride should take place under conditions close to $N_{annular}-C_{benzyl}$ bond breaking in **11** hydrochloride. This suggests that dissociation of the cationic part of **10** and **11** hydrochlorides should lead to benzylic cation formation and 2-benzylaminopyridine, in imino and amino forms respectively. These conclusions and the investigations of Katritzky substantiate the thesis that the structure of the cationic part of **10** and **11** hydrochlorides in the intermediate state should be heaving Winstein's solvent separated ion-molecule form (see Scheme 3) [13-15]. The solvent in this case are the ingredients of the melt reaction mixture, which influence the yield of formation of the *C*-benzyl derivatives [3].

The reaction of the benzyl cation with one of the nucleophilic centers in 2-benzylaminopyridine, carbon 5, leads *via* the 5-benzyl-2-benzylaminopyridine cation to 5-benzyl-2-benzylaminopyridine hydrochloride (**5b**), but its reaction

with the chloride anion produced the benzyl chloride (**8**) with the evolution of 2-benzylaminopyridine (**5**). The reaction with the remaining nucleophilic centers in 2-benzylaminopyridine, annular and exocyclic nitrogen atoms, led in the reversible reaction to **10** and **11** hydrochlorides where the scrambling of the benzyl substituent is possible which is supported by the yield of the reaction of **5** hydrochloride with **2**. The transformation, however, of the **11** hydrochloride to the more stable **10** hydrochloride structure, may also turn up in an independent rearrangement process.

The formation of 2-amino-5-benzylpyridine (**5b**) did not occur during the rearrangement of 2-benzylaminopyridine (**5**) [1,3,4] but was the result of the aminomethylene bond thermolysis in 2-benzylamino-5-benzylpyridine (**5a**) hydrochloride (see the relation between **5b** and **5a** formation in Figure 1). The same process is responsible for the formation of 2-aminopyridine (**1**) and benzyl chloride (**8**) from **5** hydrochloride (see Figure 1 where the essential changes in concentration of **5** are accompanied by the changes in the concentration of **1**). Bases and benzyl chloride (**8**) obtained in this way may again undergo reaction with the ingredients of the reaction mixture and the yield of the reaction of **5** hydrochloride with **2** verifies this possibility.

EXPERIMENTAL

Elemental analyses were performed on a Perkin-Elmer 240 analyzer, mass spectra were carried out with a LKB GC/MS 9000S spectrometer at 70 eV. The 1H nmr spectra were recorded in deuteriochloroform with a Tesla 487C (80 MHz) spectrometer and tetramethylsilane (TMS) as an internal standard; the chemical shifts are reported in ppm (δ); coupling constants were taken from the expanded spectrum. Melting points, measured in a Boetius apparatus, are uncorrected. Chromatographic analyses were performed on a Carlo Erba Vega 6330-50 capillary gas chromatograph with a flame ionization detector (FID-40). Hydrogen was used as a carrier and nitrogen as a make up gas. Temperature was programmed: 80°/3 minutes, 20°/minute to 160°, then to 250° at 5°/minute and then held at 250° until all the compounds were eluted. As the internal standard, *n*-dodecane was used. Quantum chemical calculations were performed on an IBM-PC computer using standard MNDO-method with full geometry optimization (gradient norm < 0.1); structures with minimum energy were used into considerations.

General Procedure for the Reaction of 2-Aminopyridine (**1**) with Substituted Benzyl Chlorides **2-4**.

A mixture of 4.7 g (0.05 mole) of 2-aminopyridine **1** and 0.10 mole of freshly distilled or crystallized substituted benzyl chloride (14.1 g of **2**, 16.1 g of **3**, or 17.2 g of **4**) was treated as described previously for the reaction of 2-aminopyridines with benzyl chloride, except that the original temperature obtained was *ca.* 200° instead of 180° [3]. Processing proceeded as previously described.

2-(*p*-Methylbenzylamino)-5-(*p*-methylbenzyl)pyridine (**2a**).

This compound was collected at 230-245°/1 mm (36%). After crystallization from toluene:cyclohexane 1:1, colorless prisms were obtained, mp 126-128°; ¹H nmr: δ 2.31 (s, 6H, 2 CH₃), 3.75 (s, 2H, PyCH₂Ar), 4.40 (d, 2H, CH₂NH, J_{NH,CH} = 5.8 Hz), 5.00 (br t, 1H, NH), 6.19 (d, 1H, 3-H, J_{3,4} = 8.1 Hz), 7.00-7.25 (m, 9H, 8 phenyl protons and 4-H), 7.90 ppm (d, 1H, 6-H, J_{4,6} = 1.4 Hz); ms: m/z (1%) M, 302 (96), M-H, 301 (37), 120 (100), 105 (66), 91 (22), 77 (15).

Anal. Calcd. for C₂₁H₂₂N₂ (302.41): C, 83.40; H, 7.33; N, 9.27. Found: C, 83.51; H, 7.30; N, 9.42.

2-Amino-5-(*p*-methylbenzyl)pyridine (2b).

This compound was collected at 150-160°/1 mm (32%). After crystallization from toluene:cyclohexane 1:2, colorless plates were obtained, mp 110-112°; ¹H nmr: δ 2.30 (s, 3H, CH₃), 3.78 (s, 2H, CH₂), 4.30 (br s, 2H, NH₂), 6.39 (d, 1H, 3-H, J_{3,4} = 8.0 Hz), 7.05 (s, 4H, phenyl protons), 7.19 (dd, 1H, 4-H, J_{4,6} = 1.3 Hz), 7.94 (d, 1H, 6-H); ms: m/z (1%) M, 198 (100), M-H, 197 (59), M-CH₃, 183 (51), 107 (30), 105 (11), 91 (9), 77 (8).

Anal. Calcd. for C₁₃H₁₄N₂ (198.26): C, 78.75; H, 7.12; N, 14.13. Found: C, 78.72; H, 7.31; N, 14.03.

2-(*p*-Chlorobenzylamino)-5-(*p*-chlorobenzyl)pyridine (3a).

This compound was collected at 240-255°/1.5 mm (34%). After crystallization from isopropyl alcohol colorless needles were obtained, mp 150-152°; ¹H nmr: δ 3.76 (s, 2H, PyCH₂Ar), 4.44 (d, 2H, CH₂NH, J_{NH,CH} = 6.2 Hz), 4.96 (br t, 1H, NH), 6.28 (d, 1H, 3-H, J_{3,4} = 8.0 Hz), 6.98-7.32 (m, 9H, 8 phenyl protons and 4-H), 7.91 ppm (d, 1H, 6-H, J_{4,6} = 1.3 Hz); ms: m/z (1%) M, 346 (5), 345 (7), 344 (36), 343 (21), M, 342 (51), M-H, 341 (20), 204 (5), 202 (13), 142 (27), 140 (83), 127 (31), 125 (100).

Anal. Calcd. for C₁₉H₁₆N₂Cl (343.25): C, 66.48; H, 4.70; N, 8.16. Found: C, 66.31; H, 4.52; N, 8.30.

2-Amino-5-(*p*-chlorobenzyl)pyridine (3b).

This compound was collected at 155-165°/1.5 mm (22%). After crystallization from *n*-hexane colorless plates were obtained, mp 96-98°; ¹H nmr: δ 3.76 (s, 2H, CH₂), 4.49 (br s, 2H, NH₂), 6.38 (d, 1H, 3-H, J_{3,4} = 8.1 Hz), 6.98-7.28 (m, 5H, 4 phenyl protons and 4-H), 7.90 ppm (d, 1H, 6-H, J_{4,6} = 1.0 Hz); ms: m/z (1%) 220 (32), 219 (29), M, 218 (100), M-H, 217 (44), 183 (63), 107 (53).

Anal. Calcd. for C₁₂H₁₁N₂Cl (218.68): C, 65.91; H, 5.07; N, 12.81. Found: C, 65.80; H, 5.18; N, 12.98.

When a mixture of **1** and **4** was heated to ca. 160°, the temperature then rose violently to ca. 270° and tar formed.

Reaction of 2-Benzylaminopyridine Hydrochloride (5) with *p*-Methylbenzyl Chloride (2).

A sample of 9.2 g (0.05 mole) of 2-benzylaminopyridine (**5**) was placed in a distilling flask and an ethanol solution of anhydrous hydrogen chloride was added until pH 3 was reached. After evaporation of ethanol 7.0 g (0.05 mole) of *p*-methylbenzyl chloride (**2**) was added and the temperature of the reaction mixture was raised to 200° during 3-4 minutes. Next, during 3 hours the temperature gradually increased to 250 ± 5° and the reaction mixture was kept at that temperature during additional 3 hours. After cooling, it was worked up in the manner described in general procedure for the reaction of **1** with **2-4**. Distillation of the product mixture yielded two fraction.

The first fraction, collected at 135-145°/1 mm, contained the mixture of the compounds **2b** and **5b**. After crystallization from benzene:*n*-hexane 1:1, 2.9 g of a mixture of **2b** and **5b** was ob-

tained, mp 75-85°.

The latter fraction, collected at 212-230°/1 mm, contained a mixture of the compounds **2a**, **5a**, **6a** and/or **7a**. After crystallization from benzene:*n*-hexane 1:1, 5.0 g of a mixture of **2a**, **5a**, **6a** and/or **7a** was obtained, mp 111-115°.

Analysis of the compounds contained in both fractions has already been performed in the main text.

Chromatographic Analysis of the Reaction Products of 2-Benzylaminopyridine Hydrochloride (5) with Benzyl Chloride (8).

Reaction of 2-benzylaminopyridine hydrochloride (**5**) with benzyl chloride (**8**) was prepared and carried out in the manner described for the reaction of 2-benzylaminopyridine (**5**) with *p*-methylbenzyl chloride (**2**), 9.2 g (0.05 mole) of **5** and 6.3 g (0.05 mole) of **8** was used. The samples for chromatographic analysis were taken during the reaction run at 0.5 hour intervals during the first 2 hours and then at the 1.0 hour intervals. The first sample was taken at 182°, when the reaction mixture started boiling. Each sample before analysis was dissolved in benzene and next alkalinized with an ethanolic solution of sodium hydroxide until pH 9-10 was reached. Samples for analysis in concentration of 10-50 µg/ml were prepared. The analytical results obtained are presented in Figure 1.

Reference standards 2-aminopyridine (**1**), benzyl chloride (**8**) and bibenzyl (**9**) are the commercial products. 2-Benzylaminopyridine (**5**), 2-benzylamino-5-benzylpyridine (**5a**) and 2-amino-5-benzylpyridine (**5b**) were prepared according to literature data [3,4,16].

2-(*N,N*-Dibenzylamino)pyridine (**10**) was obtained by the reaction of 2-benzylaminopyridine with benzyl chloride carried on in toluene in the presence of sodium amide in 83% yield, bp 184-186°/1 mm; ¹H nmr: δ 4.79 (s, 4H, 2 CH₂), 6.42-6.69 (m, 2H, 3-H and 4-H), 7.16-7.54 (m, 11H, 10 phenyl protons and 4-H), 8.21 ppm (dd, 1H, J_{4,6} = 1.4 Hz, J_{5,6} = 5.4 Hz); ms: m/z (1%) M, 274 (6), 183 (74), 91 (100).

Anal. Calcd. for C₁₉H₁₈N₂ (274.35): C, 83.18; H, 6.61; N, 10.21. Found: C, 83.02; H, 6.72; N, 10.14.

1-Benzyl-2-benzylaminopyridinium chloride (**11**) was obtained from the reaction of 2-benzylaminopyridine with benzyl chloride carried out in nitromethane with a 52% yield, mp 195-197° (isopropyl alcohol); ¹H nmr: δ 4.71 (d, 2H, CH₂NH, J_{NH,CH} = 6.1 Hz), 6.12 (s, 2H, N_{annular}CH₂), 6.67-6.88 (m, 2H, 3-H and 5-H), 7.18-7.75 (m, 11H, 10 phenyl protons and 4-H), 8.04 (dd, 1H, J_{4,6} = 1.0 Hz, J_{5,6} = 6.3 Hz), 10.76 ppm (br t, 1H, NH); ms: m/z (1%) M-HCl, 274 (12), 183 (100), 91 (68).

Anal. Calcd. for C₁₉H₁₉N₂Cl (310.81): C, 73.42; H, 6.16; N, 9.01. Found: C, 73.58; H, 6.20; N, 8.85.

1-Benzyl-2-benzylimino-1,2-dihydropyridine (**11**) was obtained from **11** hydrochloride after alkanization of its chloroform solution with anhydrous potassium carbonate. After distillation of the solvent a yellow oil was obtained in almost quantitative yield; ¹H nmr: δ 4.44 (s, 2H, N_{exocyclic}CH₂), 5.25 (s, 2H, N_{annular}CH₂), 5.70 (m, 1H, 5-H), 6.44 (d, 1H, 3-H, J_{3,4} = 8.2 Hz), 6.86-7.49 ppm (m, 12H, 10 phenyl protons, 4-H and 6-H); ms: m/z (1%) M, 274 (7), 183 (100), 91 (83).

Anal. Calcd. for C₁₉H₁₈N₂ (274.35): C, 83.18; H, 6.61; N, 10.21. Found: C, 83.30; H, 6.53; N, 10.34.

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