INVESTIGATION OF THE RECYCLIZATION OF QUATERNARY SALTS OF PAPAVERINE AND ITS STRUCTURAL ANALOGS*

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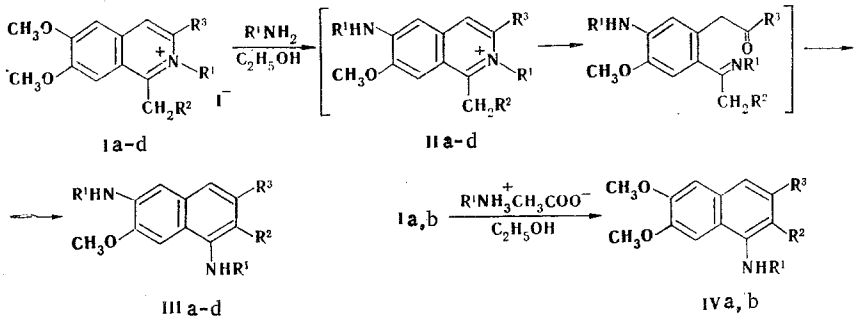
The rearrangement of salts of the alkaloid papaverine and its structural analogs under the influence of nucleophilic agents was studied. It is shown that when an alcohol solution of an alkylamine is used as the reagent, replacement of the methoxy group in the 6 position of the isoquinoline ring by an alkylamino group takes place simultaneously with the rearrangement. Rearrangement with retention of the methoxy group can be carried out under the influence of an alkylammonium acetate.

The pyridine ring of 1,2-dialkylisoquinolinium and 2,3-dialkylisoquinolinium salts under the influence of alcohol and aqueous solutions of alkylamines is readily cleaved at the nitrogen–carbon bond and recloses at the carbon–carbon bond to give N-substituted α- and β-naphthylamines [2, 3].

We found that quaternary salts of the alkaloid papaverine also undergo similar recyclization. When papaverine methiodide (Ia) is heated for a long time with an excess amount of an alcohol solution of methylamine at 110°C, the isoquinoline ring undergoes rearrangement to a naphthalene ring with simultaneous replacement of one of the methoxy groups by a methylamino group.



Ia-d IIa-d IIIa-d IVa,b

a $R^1=CH_3$, $R^2=3,4\text{-}(CH_3O)_2C_6H_3$, $R^3=H$; b $R^1=C_2H_5$, $R^2=3,4\text{-}(CH_3O)_2C_6H_3$, $R^3=H$; c $R^1=R^3=CH_3$, $R^2=C_6H_5$; d $R^1=C_2H_5$, $R^2=C_6H_5$, $R^3=CH_3$

It is known from the literature that a methoxy group in the 6 or 8 position of isoquinolinium salts is capable of being replaced by an alkylamino group when these salts are refluxed with aqueous or alcohol solutions of alkylamines [4-7].

In order to establish the position of the methylamino group in naphthylamine derivative IIIa formed in the recyclization of salt Ia was studied the ^{13}C NMR spectra of IIIa, 1-methylamino-2-(3,4-dimethoxyphenyl)-6,7-dimethoxynaphthalene (IVa) (the method for the preparation of which is described below), and a number of model compounds. For the assignment of the signals in the carbon spectra we used an additive scheme based on a comparison of the

*See [1] for our preliminary communication.
†Deceased.

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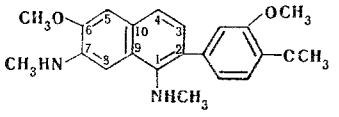
TABLE 1. Experimental and Calculated Values of the ^{13}C Chemical Shifts of the Naphthalene Ring for IIa and IIIa*

Compound	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$
A (calc.)	142,2	127,2	123,7	120,4	107,2	149,6	139,6	101,5	125,0	128,5
B (calc.)	142,6	125,8	125,1	120,0	105,8	140,0	149,2	102,9	121,5	131,8
IIIa (exptl.)	142,7	126,8	126,3	119,8	103,6	140,0	148,0	101,3	120,9	131,4
IVa (calc.)	143,4	127,6	125,5	120,5	107,8	150,5	150,1	103,5	124,2	131,0
IVa (exptl.)	143,0	128,8	126,8	120,7	107,2	149,7	149,4	103,7	123,4	130,5

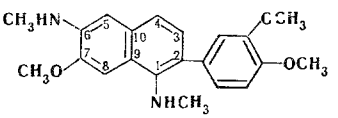
*The ^{13}C chemical shifts are presented in parts per million relative to tetramethylsilane and were measured for 10-15% solutions in $CDCl_3$ at 35°C with a Varian FT-80A spectrometer.

increments of the substituents in the α and β positions of naphthalene. The increments were obtained from an analysis of the ^{13}C chemical shifts of the following model subjects: α- and β-methylaminonaphthalenes, β-methoxynaphthalene, and 1-methylamino-2-phenylnaphthalene. In the assignment of the signals in the spectra of the model compounds we used data on the ^{13}C chemical shifts for a number of mono- and disubstituted naphthalenes presented in [8, 9] by Ernst.

In the ^{13}C NMR spectra of IIa and IVa it is necessary to assign 10 signals of the carbon atoms of the naphthalene ring, of which six are assigned to tertiary carbon atoms and four are assigned to C–H carbon atoms. In addition, one must isolate six signals belonging to the phenyl group in the 2 position. The latter problem was solved by means of the additive scheme for monosubstituted benzenes. The utilization of the method of incomplete suppression of spin–spin coupling made it possible to separate the signals from the C–H and tertiary carbon atoms. Compound IIIa may have two alternative structures A and B:



A



B

We used the additive scheme to calculate the ^{13}C chemical shifts for both structures A and B, as well as for IVa, which can have only one structure. These data, as well as the experimental values of the chemical shifts of IIIa and IVa, are presented in Table 1.

It follows from the data in Table 1 that the selection of one of the structures (A or B) can be made by comparison of the calculated and experimental values of the chemical shifts of the $C_{(5)}$ and $C_{(8)}$ atoms, as well as the $C_{(9)}$ and $C_{(10)}$ atoms, since the shifts of the other carbon atoms change only slightly when the substituents in the 6 or 7 position of the ring are "exchanged." Thus a comparison of the experimental and calculated values of the chemical shifts of these carbon atoms makes it possible to conclude unambiguously that the structure of IIIa corresponds to structure B. A comparison of the data for IVa confirms the correctness of the assignment of the signals in the ^{13}C NMR spectra.

The recyclization of papaverine ethiodide (Ib) under the influence of an alcohol solution of ethylamine is also accompanied by replacement of the methoxy group in the 6 position of the isoquinoline ring by an ethylamino group to give naphthylamine IIIb.

The recyclization of 1-benzyl-2,3-dimethyl-6,7-dimethoxyisoquinolinium (Ic) and 1-benzyl-2-ethyl-3-methyl-6,7-dimethoxyisoquinolinium (Id) iodides under similar conditions proceeds only at the methyl group, the CH acidity of which is higher than the CH acidity of the methyl group in the 3 position of the isoquinoline ring. Replacement of the methoxy group in the 6 position takes place simultaneously with the rearrangement of these salts to give, respectively, naphthylamines IIIc, d.

Recyclization products cannot be isolated when 1,2-dimethyl-6,7-dimethoxyisoquinolinium and 1,2,3-trimethyl-6,7-dimethoxyisoquinolinium iodides are heated with an alcohol solution of methylamine.

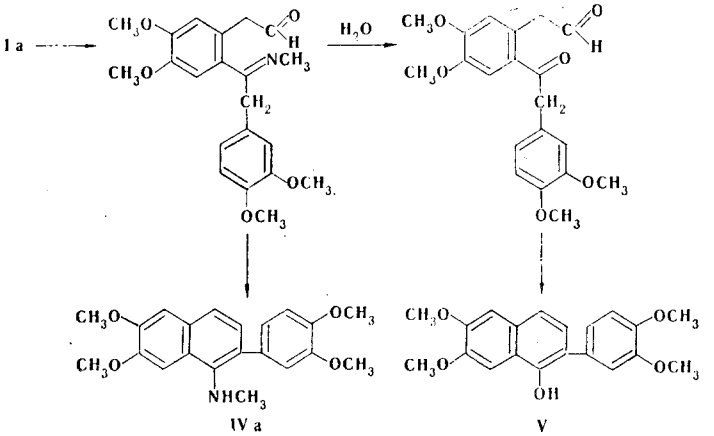
Replacement of the methoxy group evidently takes place initially when salts Ia-d are heated with alcohol solutions of alkylamines, after which the resulting salts undergo rearrangement to naphthylamines IIIa-d. It should be noted that recyclization does not occur at temperatures below 100°C and that at temperatures above 120°C the reaction is accompanied by pronounced resinification, and the yields of napthylamines IIIa-d decrease markedly. Under optimum conditions the yields of naphthylamines IIIa-d range from 7 to 24%, while the rearrangement of 1,2-dialkylisoquinolinium salts gives the products in 70-90% yields [2]. The introduction of donor substituents in the benzene ring decreases the electrophilicity of the pyridine ring of the isoquinolinium salt and hinders nucleophilic attack and opening of the pyridine ring.

A comparison of the reactivities of isoquinolinium salts Ia-d and 1,2-dialkylpyridinium salts, the rearrangement of which does not proceed under the influence of alcohol and aqueous solutions of alkylamines [10], indicates that annelation of the pyridine ring with the benzene ring, even one containing donor substituents, promotes recyclization.

If an alkylammonium acetate in alcohol is used as the reagent for cyclization, the rearrangement of papaverine salts Ia, b proceeds with retention of the methoxy group in the 6 position, and naphthylamines IVa, b are formed.

In addition to naphthylamine IVa, 1-(3,4-dimethoxybenzyl)-2-methyl-6-methylamino-7-methoxyisoquinolinium iodide (IIa) was isolated in the reaction of papaverine methiodide (Ia) with methylammonium acetate. In the case of methylammonium acetate replacement of the methoxy group apparently proceeds more slowly than with methylamine, and papaverine salt Ia has time to undergo partial rearrangement to naphthylamine IVa. Naphthylamine IIIa is formed when isoquinolinium salt IIa is heated with an alcohol solution of methylamine.

It has been previously demonstrated that 2-(3,4-dimethoxyphenyl)-6,7-dimethoxy-1-naphthol (V) is formed when papaverine methiodide (Ia) is heated with an alcohol solution of alkali [11]. The reaction scheme proposed by Decker [11] assumes cleavage of the C_1—N bond. It is apparent that this scheme excludes the possibility of the formation of naphthylamine IVa. At the same time, the described transformation does fit into our previously proposed scheme with



cleavage of the C_3—N bond [2]. Thus the conversion of isoquinolinium salt Ia to naphthylamine IVa is isomerizational recyclization of the isoquinoline ring to a napthalene ring, whereas the reaction described by Decker is essentially a competitive process involving hydrolysis of the opened intermediate.

A study by means of thin-layer chromatography (TLC) and PMR spectroscopy of the reaction mixture formed when salt Ia was refluxed with an alcohol solution of alkali showed that it contains, in addition to naphthol V, naphthol VI, in which the methoxy group in the 6 position is replaced by an ethoxy group. If an alcohol solution of sodium ethoxide is used as the reagent, only naphthol VI is formed as a result of the reaction.

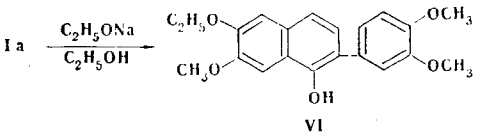


TABLE 2. Spectral Characteristics of the Naphthylamines

Compound	PMR spectrum, δ, ppm	UV spectrum λ_{max}, nm (log ε)	IR spectrum, cm^{-1} (NH)
IIIa	2,74 (3H, s, CH_3N); 2,90 (3H, s, CH_3N); 3,76 (3H, s, CH_3O); 3,78 (3H, s, CH_3O); 3,92 (3H, s, CH_3O); 6,56—7,26 (7H, m, aromatic protons)	230 (4,53), 356 (4,59), 344 (3,47)	3455, 3365
IIIb	1,03 (3H, t, CH_3CH_2); 1,28 (3H, t, CH_3CH_2); 2,98—3,32 (4H, m, CH_2CH_3); 3,80 (3H, s, CH_3O); 3,84 (3H, s, CH_3O); 3,91 (3H, s, CH_3O); 6,71—7,41 (7H, m, aromatic protons)	232 (4,37), 257 (4,49), 344 sh (3,44)	3435, 3350
IIIc	2,05 (3H, s, CH_3); 2,65 (6H, s, CH_3N); 3,9 (3H, s, CH_3O); 6,5 (1H, s, 5-H); 7,0 (1H, s, 4-H); 7,1—7,4 (6H, m, aromatic protons)	212 (4,30), 233 (4,51), 261 (4,59), 328 (3,53), 342 (3,53)	3440, 3355
IIId	1,0 (3H, t., CH_3CH_2); 1,35 (3H, t., CH_3CH_2); 2,05 (3H, s., CH_3); 2,85—3,45 (4H, m, CH_2CH_3); 3,9 (3H, s, CH_3O); 6,5 (1H, s, 5-H); 7,0 (1H, s, 4-H); 7,1—7,4 (6H, m, aromatic protons)	211 (4,38), 234 (4,60), 262 (4,68), 328 (3,64), 343 (3,64)	3440, 3340
IVa	2,74 (3H, s, CH_3N); 3,76 (3H, s., CH_3O); 3,78 (3H, s, CH_3O); 3,84 (3H, s., CH_3O); 3,86 (3H, s, CH_3O); 6,80—7,33 (7H, m, aromatic protons)	231 (4,64), 261 (4,62)	3365
IVb	1,03 (3H, t, CH_3CH_2); 3,08 (2H, q, CH_2CH_3); 3,76 (3H, s, CH_3O); 3,78 (3H, s., CH_3O); 3,84 (3H, s, CH_3O); 3,86 (3H, s, CH_3O); 6,78—7,77 (7H, m, aromatic protons)	231 (4,69), 261 (4,65)	3350

Consequently, the rate of replacement of the methoxy group increases on passing from an alcohol solution of alkali to an alcohol solution of sodium ethoxide, in which the ethoxide ion concentration is considerably higher.

Thus, on the one hand, the introduction of donor substituents into the benzene ring of the isoquinolinium salt decreases the electrophilicity of the pyridine ring and hinders recyclization of the isoquinoline ring to a naphthalene ring. On the other hand, in the case of quaternization the electron density of the isoquinoline ring is decreased to such an extent that the methoxy substituent in the benzene ring becomes capable of being replaced under the influence of a nucleophile.

EXPERIMENTAL

The IR spectra of solutions of IIIa, b and IVa, b in chloroform and suspensions of IIIc, d, II, V, and VI in mineral oil were recorded with a UR-20 spectrometer. The UV spectra of solutions in methanol were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of IIIa, b and IVa, b were recorded with a Varian XL-100 spectrometer, while the PMR spectra of IIIc, d, II, and VI were recorded with a Varian T-60 spectrometer with CCl_4 ($CDCl_3$ in the case of IIIb and VI and CF_3COOH in the case of II) as the solvent and hexamethyldisiloxane as the standard. The mass spectra of IIIa, b, IVb, and VI were recorded with a Varian MAT-CH-8 spectrometer, while the mass spectra of IIIc, d were recorded with a Varian MAT-112 spectrometer. The course of the reaction was monitored by means of TLC on Silufol UV-254 in a benzene–ethyl acetate (1:1) or chloroform system.

1,6-Dimethylamino-2-(3,4-dimethoxyphenyl)-7-methoxynaphthalene (IIIa). A mixture of 0.48 g (1 mmole) of papaverine methiodide (Ia) and 10 ml of a 35% solution of methylamine in alcohol was heated in a sealed ampul at 110°C for 50 h, after which the ethanol was removed from the reaction mixture by distillation, and the residue was separated with a column filled with silica gel by elution with chloroform to give 0.08 g (23%) of a product with mp 177–178°C (from benzene). Mass spectrum*: 352 (100), 338 (5), 337 (10), 322 (5), 321 (4), 307 (7), 306 (17), 305 (9), 278 (5), 277 (4). Found, %: C 71.5; H 6.9; N 7.9. $C_{21}H_{24}N_2O_3$. Calculated, %: C 71.6; H 6.9; N 7.9.

*Here and subsequently, the molecular-ion peak and the nine most intense peaks are presented (the relative intensities are given in parentheses).

1,6-Diethylamino-2-(3,4-dimethoxyphenyl)-7-methoxynaphthalene (IIIb). A similar procedure was used to obtain 0.3 g (7%) of IIIb, with mp 146-147°C (from benzene), from 0.50 g (1 mmole) of papaverine ethiodide (Ib) and 10 ml of a 35% solution of ethylamine in alcohol. Mass spectrum: 380 (100), 366 (6), 365 (10), 350 (5), 334 (8), 333 (5), 32 (14), 320 (11), 319 (6), 307 (5). Found, %: C 72.3; H 7.4; N 7.2. $C_{23}H_{28}N_2O_3$. Calculated, %: C 72.6; H 7.4; N 7.4.

1-6-Dimethylamino-2-phenyl-3-methyl-7-methoxynaphthalene (IIIc). A similar procedure was used to obtain 0.07 g (24%) of IIIc, with mp 116-117°C (from hexane), from 0.43 g (1 mmole) of 1-benzyl-2,3-dimethyl-6,7-dimethoxyisoquinolinum iodide (Ic) and 10 ml of a 35% solution of methylamine in alcohol. Mass spectrum: 306 (100), 291 (74), 277 (48), 276 (83), 275 (61), 248 (57), 247 (48), 232 (35), 231 (43). Found, %: C 78.2; H 7.2. $C_{20}H_{22}NO$. Calculated, %: C 78.4; H 7.2.

1-6-Diethylamino-2-phenyl-3-methyl-7-methoxynaphthalene (IIId). A similar procedure was used to obtain 0.03 g (9%) of IIId, with mp 97-98°C (from hexane), from 0.45 g (1 mmole) of 1-benzyl-2-ethyl-3-methyl-6,7-dimethoxyisoquinolinium iodide (Id) and 10 ml of a 35% solution of ethylamine in alcohol. Mass spectrum: M 334 (100), 320 (35), 319 (83), 304 (61), 303 (30), 290 (26), 289 (39), 274 (33), 261 (26), 246 (28).

1-Methylamino-2-(3,4-dimethoxyphenyl)-6,7-dimethoxynaphthalene (IVa). A mixture of 0.48 g (1 mmole) of papaverine methiodide, 5 g of methylamine acetate, and 5 ml of ethanol was heated in a sealed ampul at 110°C for 50 h, after which the ethanol was removed from the reaction mixture by distillation, 20 ml of water was added, and the aqueous mixture was extracted successively with chloroform and chloroform–methanol (10:1). The chloroform extract was dried with magnesium sulfate, the solvent was removed by distillation, and the residue was separated with a column filled with silica gel by elution with chloroform to give, initially, 0.02 g (6%) of IVa with mp 178-179°C (from benzene). The acetyl derivative had mp 168-169°C (from benzene) [12]. Also obtained was 0.24 g (50%) of 1-(3,4-dimethoxybenzyl)-2-methyl-6,7-dimethoxyisoquinolinium iodide (IIa) with mp 222-224°C. IR spectrum: 3395 cm^{-1} (NH). UV spectrum, λ_{max}(log ε): 225 (4.56), 257 (4.59), 290 (4.19), and 3.75 nm (4.24). PMR spectrum: 3.3 (3H, s, CH_3N), 3.7 (6H, s, CH_3O), 4.0 (3H, s, CH_3O), 4.3 (3H, s, CH_3N^+), 4.9 (2H, s, CH_2), and 6.1-8.45 ppm (7H, m, aromatic protons). Found, %: C 52.8; H 5.7; N 5.5. $C_{21}H_{25}IN_2O_3$. Calculated, %: C 52.5; H 5.3; N 5.8.

1-Ethylamino-2-(3,4-dimethoxyphenyl)-6,7-dimethoxynaphthalene (IVb). A procedure similar to that in the preceding experiment was used to obtain 0.01 g (3%) of IVb, with mp 157-158°C (from benzene), from 0.50 g (1 mmole) of papervine ethiodide (Ib), 5 g of ethylamine acetate, and 5 ml of ethanol. Mass spectrum: 367 (100), 353 (7), 352 (3), 351 (2), 337 (3), 336 (4), 324 (2), 309 (3), 308 (2), 294 (2). Found, %: C 71.7; H 7.0; N 3.8. $C_{22}H_{25}NO_4$. Calculated, %: C 72.0; H 6.9; N 3.8.

2-(3,4-Dimethoxyphenyl)-6-ethoxy-7-methoxy-1-naphthol (VI). A 0.48-g (1 mmole) sample of papaverine methiodide (Ia) was added to a solution of 1 g of sodium in absolute ethanol, and the mixture was refluxed for 20 h. It was then neutralized with hydrochloric acid, the alcohol was removed by distillation, and the residue was extracted with chloroform. The chloroform extract was dried with magnesium sulfate, the solvent was removed by distillation, and the residue was separated with a column filled with silica gel by elution with chloroform to give 0.07 g (20%) of a product with mp 178-180°C. Mass spectrum: 354 (100), 340 (19), 339 (5), 326 (8), 325 (8), 311 (8), 297 (4), 295 (3), 293 (3), 279 (4). IR spectrum: 3455 cm^{-1} (OH). UV spectrum, λ_{max}(log ε): 226 (4.68), 263 (4.66), and 290 nm (sh) (4.28). PMR spectrum: 1.5 (3H, t, CH_3CH_2), 3.8 (6H, s, CH_3O), 3.9 (3H, s, CH_3O), 4.15 (2H, q, CH_2CH_3), 5.9 (1H, s, OH), and 6.9-7.5 ppm (7H, m, aromatic protons). Found, %: C 71.4; H 6.4. $C_{21}H_{22}O_5$. Calculated, %: C 71.3; H 6.3.

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CATALYTIC CARBONYLATION OF NITROBENZYL- AND NITROARYLPYRIDINES

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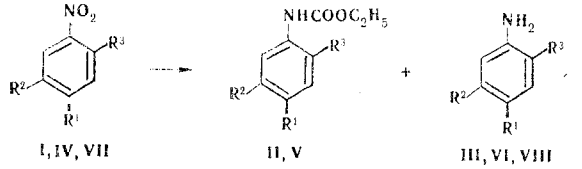
The corresponding carbamates were obtained by carbonylation in the presence of selenourea of benzyl- and aryl-substituted pyridines that contain a nitro group in the benzene ring and as a result of carbonylation of 7-nitro-1-azafluorene. The reaction is accompanied by simultaneous reduction of the nitro group to an amino group.

The catalytic carbonylation of nitro compounds is a convenient method for the synthesis of carbamic acid derivatives that are of interest as pesticides [1]. The search for new pesticides among carbamic acid derivatives with a pyridine ring is promising, since it is known that some active pesticides are pyridine derivatives [1]. Accessible nitrobenzyl- and nitrophenyl-substituted pyridines, the catalytic carbonylation of which has not been previously studied, can be the starting compounds for such studies.

We used 4-methyl-2-(4'-nitrobenzyl)-, 2,5-dimethyl-4-(4'-methyl-3'-nitrophenyl)-, and 2-methyl-3-(4'-nitrophenyl)pyridines (I, IV, and VII) as the starting pyridine bases for the preparation of carbamoylarylpyridines.

The carbonylation was carried out in ethanol at 170-180°C and a carbon monoxide pressure of 60-100 atm in the presence of selenourea. Since the initial step in the carbonylation of nitro compounds is evidently the formation of nitrenes [5], the corresponding amines may also be formed in addition to ethoxycarbamoyl derivatives as a result of the reaction. Complete conversion of the starting compounds occurs after 2 h under the indicated conditions. In the carbonylation of I and IV the principal reaction products are, respectively, 4-methyl-2-(4'-ethoxycarbamoylbenzyl)pyridine (II) and 2,5-dimethyl-4-(4'-methyl-3'-ethoxycarbamoylphenyl)-pyridine (V). 4-Methyl-2-(4'-aminobenzyl)- and 2,5-dimethyl-4-(4'-methyl-3'-aminophenyl)-pyridines (III, VI) were obtained in very low yields in these experiments:



I, IV, VII II, V III, VI, VIII

I–III, VII, VIII $R^2 = R^3 = H$; IV–VI $R^1 = H$, $R^3 = CH_3$; I–III R^1 = 4-methyl-2-picolyl; IV–VI R^2 = 2,5-dimethyl-4-pyridyl; VII, VIII R^1 = 2-methyl-3-pyridyl

A carbamic acid derivative was not detected in the carbonylation of nitrophenyl-substituted pyridine base VII, and only 2-methyl-3-(4'-aminophenyl)pyridine (VIII) was obtained.

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