was dissolved in 100 ml of 50% ethanol, and 100 ml of acetone was added. The mixture was stored for a long time in the cold, after which it was worked up to give 8.1 g (29%) of the bright-yellow crystalline potassium salt IIIb.

PMR spectrum, δ: 4.35 (1H, s, 9-H), 2.38 (4H, s, 4-H, 5-H), 2.27 (4H, s, 2-H, 7-H), 2.22 (3H, s, 0.5 mole of CH_3COCH_3), and 1.05 ppm (12H, s, 3- and 6-CH_3). IR spectrum (in Nujol): 1720 (acetone C=O) and 1615-1650 cm^{-1} (COO^-, C=C, and C=O).* UV spectrum, λ_{max} (log ε): in ethanol, 253 (4.28) and 388 nm (3.84); in an ethanol solution of sodium hydroxide ($4 \cdot 10^{-4}$ mole/liter NaOH), 253 (4.22) and 392 nm (3.81); in an ethanol solution of sodium hydroxide ($4 \cdot 10^{-2}$ mole/liter NaOH), 257 (4.22), 268 sh (4.18), 402 (3.67), and 475 nm (3.79). Found: C 56.9; H 6.9; N 3.4%. $2C_{18}H_{22}NO_4K \cdot 3H_2O \cdot (CH_3)_2CO$. Calculated: C 56.9; H 6.9; N 3.4%. The crystallization solvents can be removed by heating salt IIIb at 110°C. A sample dried at 20°C was used for x-ray diffraction analysis.

LITERATURE CITED

1. G. Ya. Dubur and G. Ya. Vanag, Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 1, 119 (1962).
2. L. S. Geita, Yu. Yu. Popel, and G. Ya. Vanag, Khim. Geterotsikl. Soedin., No. 1, 26 (1967).
3. G. Ya. Dubur and Ya. R. Uldrikis, Khim. Geterotsikl. Soedin., No. 6, 1015 (1969).
4. R. J. Highet and J. F. Biellmann, J. Org. Chem. 37, 3731 (1972).
5. J. Krajewski, Z. Urbanczyk-Lipkowska, and P. Gluzinski, Acta Cryst., B33, 2967 (1967).
6. Y. F. Freimanis and É. I. Stankevich, Zh. Prikl. Spectrosk., 11, 124 (1969).
7. D. C. Philips, W. H. Ahmed, and W. H. Barnes, Acta Cryst., 13, 365 (1960).
8. A. Achari and S. Neidle, Acta Cryst., B33, 3269 (1977).
9. A. Gordon and R. Ford, Chemist's Companion: A Handbook of Practical Data, Techniques, and References, Wiley (1973).
10. A. F. Mishnev, A. E. Shvets, Ya. Ya. Bleidelis, G. Ya. Dubur, A. É. Sausin', and V. K. Lusis, Khim. Geterotsikl. Soedin., No. 9, 1229 (1977).
11. G. D. Smith, W. L. Duax, and S. Fortier, J. Am. Chem. Soc., 100, 6725 (1978).
12. G. Germain, P. Main, and M. M. Woolfson, Acta Cryst., A27, 368 (1971).
13. É. I. Stankevich and G. Ya. Vanag, Zh. Org. Khim., 1, 809 (1965).

*The difficulties involved in the interpretation of the IR spectra of 1,4-dihydropyridines are demonstrated in [13].

SUBSTITUTED 2- AND 4-BENZYLPYRIDINES IN THE SYNTHESIS OF BENZO[g]QUINOLINES AND BENZO[g]ISOQUINOLINES

N. S. Prostakov, V. I. Kuznetsov and G. Datta Rai

UDC 547.836

Nitrogen-containing heterocyclic analogs of anthracene, viz., benzo[g]isoquinolines and benzo[g]quinolines, were obtained by dehydrocyclization on a K-16 catalyst of mixtures of methyl-substituted 2- and 4-benzylpyridines with methyl groups in various positions of the pyridine and benzyl rings, which are formed by benzylation of β-picoline, as well as pyridine, by the Ladenburg method. The spectral characteristics of the synthesized compounds are presented.

In numerous investigations involving the study of the electrophysical properties of anthracene the latter has been regarded as a standard with which to compare the electrophysical properties of other organic compounds. In this respect, extremely little study has been devoted to nitrogen-containing heterocyclic analogs of anthracene because of the limited number of methods for their preparation.

P. Lumumba International-Friendship University, Moscow 117923.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 673-676, May, 1980. Original article submitted October 2, 1979.

0009-3122/80/1605-0525$07.50

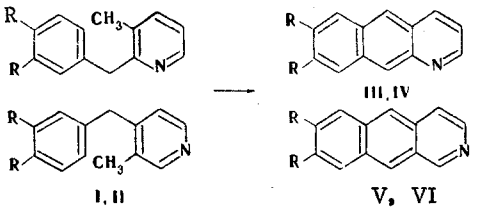
TABLE 1. Characteristics of Mixtures of Substituted α- and γ-Benzylpyridines

Mixtures of pyridine bases	bp, °C (mm)	n_D^{20}	Found		Empirical formula	Calc.		Yield, %
			N, %	M+		N, %	M	
I	155—175 (4)	1,5789	7,3	183	$C_{13}H_{13}N$	7,6	183	49
II	150—170 (2)	1,5741	6,8	211	$C_{15}H_{17}N$	6,6	211	46
IX	142—175 (4)	1,5851	5,8	211	$C_{15}H_{17}N$	6,6	211	52
XIV	135—147 (4)	1,5832	—	197	$C_{14}H_{15}N$	7,2	197	35

One of the methods for the synthesis of compounds of this type is dehydrocyclization in the presence of copper filings at 580-590°C of o-methyl-substituted α- and γ-benzylpyridines, which are produced via the Ladenburg reaction in the form of a mixture of both isomers [1, 2]. The preparation of benzo[g]quinoline, benzo[g]isoquinoline, 3-methylbenzo[g]isoquinoline, and, evidently, 8-methylbenzo[g]isoquinoline by this method was described in [3]. These compounds were characterized only by their melting points and the results of analysis.

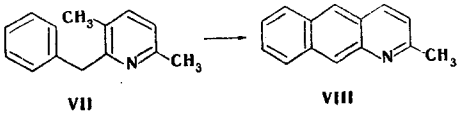
In the present communication we present the results of our research on the synthesis of analogous heterocyclic compounds by dehydrocyclization of mixtures of substituted α- and γ-benzylpyridines on a K-16 industrial dehydrogenating catalyst [4]. We used those substituted pyridines whose dehydrocyclization occurs via splitting out of a hydrogen atom from the β-methyl group of the pyridine ring and the ortho position of the benzyl group or from the o-methyl group of the benzyl group and of a hydrogen atom from the β position of the pyridine ring.

Benzo[g]quinoline (III) [3] and 7,8-dimethylbenzo[g]quinoline (IV), as well as benzo[g]isoquinoline (V) [3] and 7,8-dimethylbenzo[g]isoquinoline (VI) in greater than 30% yield, were isolated in very low yield (∿3%) in the dehydrocyclization of a mixture (I) of 3-methyl-2-benzylpyridine and 3-methyl-4-benzylpyridine (obtained from β-picoline and benzyl chloride), as well as a mixture (II) of 3-methyl-2-(m,p-dimethylbenzyl)pyridine and 3-methyl-4-(m,p-dimethylbenzyl)pyridine (obtained from β-picoline and m,p-dimethylbenzyl chloride).



I, III, V R=H; II, IV, VI R=CH_3

The isolation of isomeric azaanthracenes from the mixtures formed as a result of the reaction of the mixtures (III and V, and IV and VI) was realized by crystallization from petroleum ether (because of the limited solubility of benzo[g]isoquinolines) and by chromatography. 2,5-Dimethyl-4-benzylpyridine was separated from the mixture with 2,5-dimethyl-6-benzylpyridine (VII), which is formed by benzylation of α,β'-lutidine by the Ladenburg method, relatively easily by crystallization from hexane. Catalytic dehydrocyclization of the residual mixture, which, according to gas—liquid chromatography (GLC), contained 80% pyridine base VII, gave 2-methylbenzo[g]quinoline (VIII) (in 26% yield), which is described in [5].



VII VIII

Various azaanthracenes are formed in the dehydrocyclization of a mixture (IX) of 3-methyl-2-(o,p-dimethylbenzyl)pyridine and 3-methyl-4-(o,p-dimethylbenzyl)pyridine (obtained from β-picoline and o,p-dimethylbenzyl chloride).

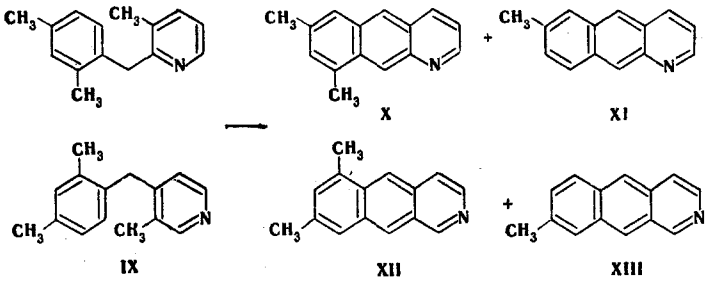
Workup of the catalyzate yielded two fractions of crystals, which were found to be difficult-to-separate mixtures: 7,9-dimethylbenzo[g]quinoline (X) and its demethylation

TABLE 2. Benzo[g]quinolines and Benzo[g]isoquinolines

Compound	mp, °C	UV spectrum, λ_{max}, nm (log ε)	PMR spectrum, δ, ppm	Found				Empirical formula	Calc.				Yield, %
				C, %	H, %	N, %	M+		C, %	H, %	N, %	M	
III	120—122	254 (4,96), 274 sh (4,24), 330 (3,60), 350 (3,68), 370 (3,78), 392 (3,71), 430 (2,25)	8,87 (q, 1H, 2-H), 7,91 (s, 1H, 5-H), 6,74 (q, 1H, 3-H), 8,94 (s 1H, 10-H)[a]	—	—	7,7	179	$C_{13}H_9N$	87,1	5,0	7,8	179	3
IV	182—183	263 (5,25), 348 (3,68), 356 sh (3,74), 366 (3,80), 380 sh (3,71), 398 (3,56)	8,95 (q, 1H, 2-H), 7,17 (q, 1H, 3-H), 8,51 (s, 1H, 10-H), 8,11 (s, 1H, 5-H), 2,44 (s, 6H, 7,8-CH_3)[b]	86,9	6,3	6,5	207	$C_{15}H_{13}N$	87,0	6,3	6,7	207	3
V	166—168	253 (4,86), 270 sh (4,09), 315 (3,34), 330 (3,58), 348 (3,68), 372 sh (3,54), 392 (3,46)	9,08 (s, 1H, 1-H), 8,45 (s, 1H, 10-H), 8,40 (d, 1H, 3-H), 8,25 (s, 1H, 5-H)[b]	86,9	5,5	7,6	179	$C_{13}H_9N$	87,1	5,0	7,8	179	38
VI	219—221	230 (4,65), 258 (5,34), 320 (3,34), 335 (3,54), 366 (3,64), 380 (3,72), 400 (3,62)	9,60 (s, 1H, 1-H), 8,92 (s, 1H, 10-H), 8,73 (s, 1H, 5-H), 7,95 (s, 2H, 6-H, 9-H), 2,54 (s, 6H, 7,8-CH_3)[c]	87,2	6,4	6,8	207	$C_{15}H_{13}N$	87,0	6,3	6,7	207	34
VIII	126—129		8,88 (s, 1H, 10-H), 7,97 (s, 1H, 5-H), 6,75 (d, 1H, 3-H), 2,55 (s, 3H, 2-CH_3)[a]	86,9	6,0	7,5	193	$C_{14}H_{11}N$	87,0	6,1	7,3	193	23
X and XI	142—144	260 (5,28), 306 sh (3,28), 320 (3,52), 338 (3,72), 347 sh (3,74), 356 (3,76), 366 sh (3,74), 384 (3,60)	6,72 (q, 1H, 3-H), 2,25 (s, 6H, 7,9-CH_3)[a]	86,7	6,6	6,7	193/100, 207/60	$C_{15}H_{13}N$	87,0	6,3	6,7	207	2
XII and XIII	190—191	256 (5,32), 316 (3,52), 330 (3,68), 346 (3,70), 358 (3,70), 380 (3,88), 398 (3,76)	9,71 (d, 1H, 1-H), 9,09 (s, 1H, 10′-H), 9,02 (s, 10-H), 8,73 (s, 1H, 5′-H), 8,64 (s, 5-H), 2,71 (s, 3H, 9-CH_3)[c]	86,8	6,4	6,7	193/100, 207/30	$C_{15}H_{13}N$	87,0	6,3	6,7	207	26
XV	127—129	262 (5,24), 346 sh (3,56), 354 sh (3,60), 362 (3,62), 370 (3,62), 393 (3,44)		86,9	6,1	7,3	193	$C_{14}H_{11}N$	87,0	5,7	7,3	193	4
XVI	194—196	256 (5,00), 274 sh (4,44), 314 (3,32), 329 (3,52), 345 (3,53), 355 (3,53), 375 (3,71), 394 (3,64)	9,60 (d, 1H, 1-H), 8,83 (s, 1H, 10-H), 8,56 (s, 1H, 5-H), 6,85 (d, 1H, 7-H), 2,55 (s, 3H, 8-CH_3)[c]	86,8	5,8	7,1	193	$C_{14}H_{11}N$	87,0	5,7	7,3	193	29

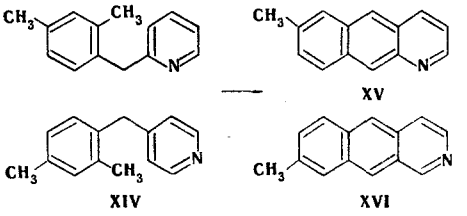
[a] In C_6D_6. [b] In $CDCl_3$. [c] In CF_3COOH.

product [7-methylbenzo[g]quinoline (XI) (the petroleum ether-soluble fraction)] and 6,8-dimethylbenzo[g]isoquinoline (XII) and its demethylation product [8-methylbenzo[g]isoquinoline (XIII) (the fraction that is almost insoluble in petroleum ether)]. The position of



the methyl groups in these compounds was established on the basis of data from their PMR spectra. In this case also the substituted benzo[g]quinolines are formed in considerably smaller amounts (∿2%) than in the case of substituted benzo[g]isoquinolines (∿26%).

The isomeric azaanthracenes were isolated in approximately the same ratios in the dehydrocyclization of a mixture (XIV) of 2-(o,p-dimethylbenzyl)pyridine and 4-(o,p-dimethylbenzyl)pyridine (obtained from pyridine and o,p-dimethylbenzyl chloride).



7-Methylbenzo[g]quinoline (XV) and 8-methylbenzo[g]isoquinoline (XVI) also differ with respect to their solubilities in petroleum ether.

EXPERIMENTAL

The electronic spectra of solutions of the compounds in chloroform were recorded with a Specord UV-vis spectrophotometer. The PMR spectra were obtained with Bruker WP-80 CW and Tesla BS-487C (80 MHz) spectrometers. The molecular weights were obtained with an MKh-1303 mass spectrometer at an ionizing voltage of 70 V.

Preparation of Mixtures of Substituted 2- and 4-Benzylpyridines. The reactions were carried out by the method described in [2]. A mixture of 1.1 mole of the pyridine base, 1 mole of the corresponding benzyl chloride, and 1 g of powdered copper was heated at 270°C for 7 h, after which it was cooled to 100°C and poured over ice. The aqueous mixture was acidified to pH 1 with 18% hydrochloric acid and extracted with ether. The aqueous solution was made alkaline to pH 12 with potassium hydroxide, the organic bases were extracted with ether, and the extract was dried with sodium sulfate and subjected to fractionation in vacuo. The characteristics of the mixtures (I, II, IX, and XIV) of pyridine bases obtained are presented in Table 1.

Dehydrocyclization of a Mixture (II) of 3-Methyl-2-(m,p-dimethylbenzyl)pyridine and 3-Methyl-4-(m,p-dimethylbenzyl)pyridine. A solution of 60.6 g (0.29 mole) of a mixture of these pyridine bases in 150 ml of benzene was passed at a constant rate in the course of 4 h over K-16 catalyst (100 cm^3). The temperature in the catalyst zone was 560°C. A total of 8.5 liters of gas was collected (at 20°C and 749 mm). The catalyzate was dried with fused potassium hydroxide, the benzene was removed by distillation, and the residue was treated with 100 ml of petroleum ether. Workup gave 8.14 g of VI in the form of yellow crystals. The petroleum ether was removed from the mother liquor, and the residue was distilled to give 37.9 g of a mixture of the starting pyridine bases. The still residue (7.2 g) was chromatographed [on activity II Al_2O_3 with elution with ether–hexane (1:1)] to give 0.8 g of IV, which was crystallized from hexane (greenish-yellow crystals). Benzo[g]quinolines III and IV, a mixture of X and XI, and XV, as well as benzo[g]isoquinolines V and VI, a mixture of XII and XIII, and XVI, the characteristics of which are presented in Table 2, were similarly obtained.

LITERATURE CITED

1. A. Ladenburg, Ber., 16, 1410, 2059 (1883).
2. A. E. Chichibabin and P. F. Ryumshin, Zh. Russ. Fiz.-Khim. Ova., No. 4, 1297 (1915).
3. I. Braun and I. Nelles, Ber., 70, 1760 (1937).
4. N. S. Prostakov, Usp. Khim., 38, 1710 (1969).
5. I. Lindner and M. Stanfer, Monatsh., 46, 231 (1926).

2,5-DIMETHYL-4-(p-AMINOBENZYL)PYRIDINE IN THE SYNTHESIS OF SUBSTITUTED QUINOLINES, PYRIDOINDAZOLES, AND ISOQUINOLINOQUINOLINES

N. S. Prostakov, A. P. Krapivko,
A. T. Soldatenkov, and N. D. Sergeeva

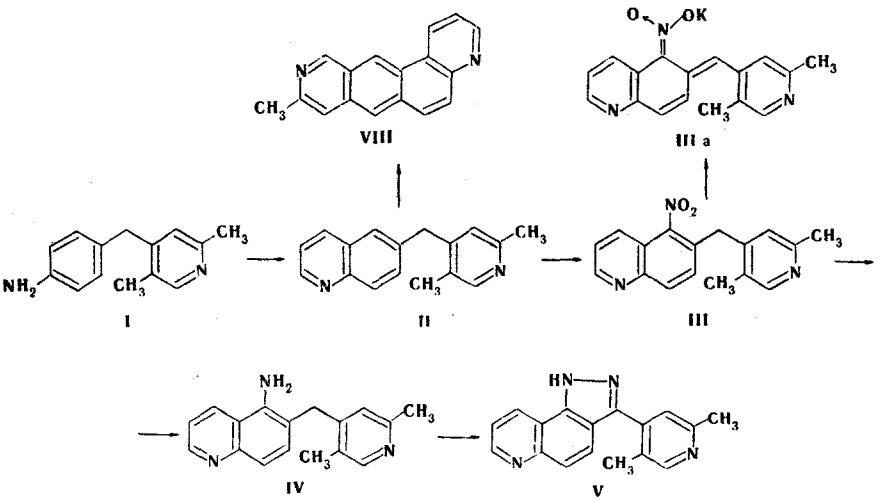
UDC 547.837

2,5-Dimethyl-4-pyridyl(6-quinolyl)methane was obtained from 2,5-dimethyl-4-(p-aminobenzyl)pyridine via the Skraup reaction. The product was nitrated to 2,5-dimethyl-4-pyridyl(5-nitro-6-quinolyl)methane, which was reduced to 2,5-dimethyl-4-pyridyl(5-amino-6-quinolyl)methane. It was established that the diazo compound formed from this amino derivative is converted to 1H,3-(2,5-dimethyl-4-pyridyl)-pyrido[2,3-g]indazole as a result of intramolecular cyclization. 9-Methylisoquinolino[7,6-f]quinoline was obtained by catalytic dehydrocyclization of 2,5-dimethyl-4-pyridyl(6-quinolyl)methane. 2,5-Dimethyl-4-pyridyl(5-nitro-6-quinolyl)methane has chemochromic properties.

A previously unknown substituted quinoline, viz., 2,5-dimethyl-4-pyridyl(6-quinolyl)-methane (II), was obtained from 2,5-dimethyl-4-(p-aminobenzyl)pyridine (I) [1] via the Skraup reaction. 2,5-Dimethyl-4-(p-nitrobenzyl)pyridine, from which amino derivative I was obtained, was used as the oxidizing agent in its synthesis.

We have accomplished the nitration of substituted quinoline II and subsequent transformations at the nitro and amino groups with allowance for the fact that some functionally substituted quinolines have specific physiological properties [2].

As a result of nitration under relatively severe conditions we isolated only one mononitro derivative, viz., 2,5-dimethyl-4-pyridyl(5-nitro-6-quinolyl)methane (III). Its PMR spectrum does not contain a signal of the 5-H proton, but the 7-H and 8-H protons of the



P. Lumumba International-Friendship University, Moscow 117923. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 677-680, May, 1980. Original article submitted October 1, 1979.

0009-3122/80/1605-0529$07.50