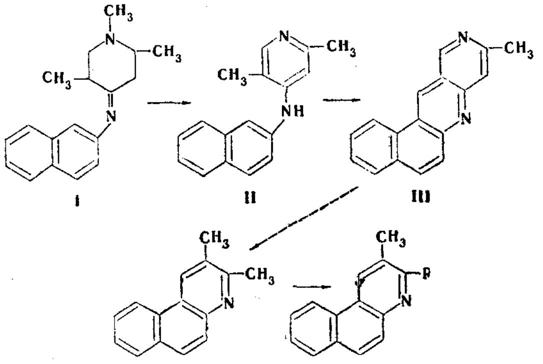
SCHIFF BASES IN SYNTHESES OF SUBSTITUTED NAPHTHYLAMINES, NAPHTHYRIDINES, AZAPHENANTHRENES, AND BENZOCARBAZOLE

N. S. Prostakov, V. G. Pleshakov,
T. Kholdarova, V. P. Zvolinskii,
and L. N. Plaksii

UDC 542.953.4 : 547.836.3 : 543.422.25.4.6

9-Methylnaphtho[2,1-b][1,6]naphthyridine and 2,3-dimethyl-1-azaphenanthrene were obtained on a K-16 dehydrogenating catalyst from N-(1,2,5-trimethyl-4-piperidylidene)-β-naphthylamine, while N-cyclohexylidene-α-naphthylamine yielded N-phenyl-α-naphthylamine and benzo[a]carbazole.

The conversions of Schiff bases obtained from γ-piperidones and aromatic amines to substituted naphthyridines and azaphenanthrenes on a commercially produced K-16 dehydrogenating catalyst apparently may represent an example of a general method for the synthesis of these inaccessible condensed nitrogen heterocycles. In a previous communication [1], we described one of these sorts of syntheses – the conversion of N-(1,2,5-trimethyl-4-piperidylidene)-α-naphthylamine to 10-methylnaphtho[1,2-b][1,6]naphthyridine and 2,3-dimethyl-4-azaphenanthrene. The isomeric naphthonaphthyridine (with respect to the fusion of the rings) and azaphenanthrene (with respect to the position of the nitrogen atom) should be formed from the analogous Schiff base obtained from the same 1,2,5-trimethyl-4-piperidone and β-naphthylamine [2]. On a K-16 catalyst at 380-400°C, N-(1,2,5-trimethyl-4-piperidylidene)-β-naphthylamine (I) undergoes dehydrogenation, N-demethylation, and hydrogenation of the C=N bond to give N-(2,5-dimethyl-4-pyridyl)-β-naphthylamine (II), the subsequent dehydrocyclization of which give 9-methylnaphtho[2,1-b][1,6]naphthyridine (III). 2,3-Dimethyl-1-azaphenanthrene (IV), the yield of which is considerably higher than the yield of II and III, is apparently formed from III as a result of its partial hydrogenation with subsequent thermal decomposition.



V $R=CH=CHC_6H_5$; VI $R=COOH$; VII $R=COOC_2H_5$; VIII $R=CONHNH_2$;
IX $R=CONHN=CHC_6H_5$; X $R=H$

P. Lumumba University, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1400-1403, October, 1972. Original article submitted October 4, 1971.

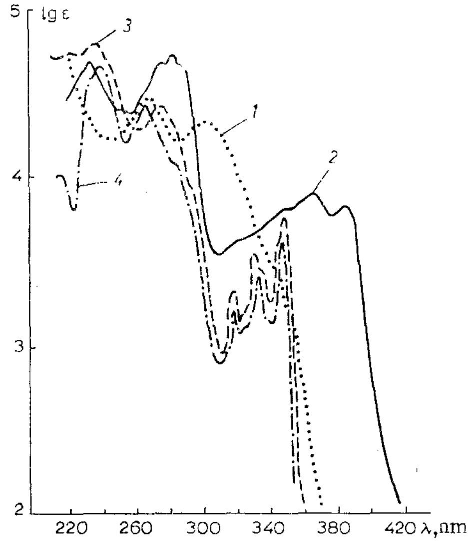


Fig. 1. UV spectra (in ethanol): 1) N-(2,5-dimethyl-4-pyridyl)-β-naphthylamine (II); 2) 9-methylnaphtho[2,1-b][1,6]naphthyridine (III); 3) 2,3-dimethyl-1-azaphenanthrene.

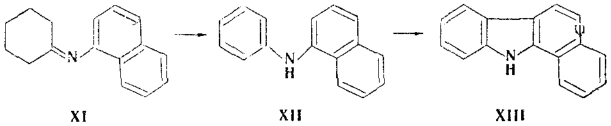
The condensation of IV with benzaldehyde yielded 3-methyl-2-styryl-1-azaphenanthrene (V), which was quantitatively oxidized with potassium permanganate to 3-methyl-1-azaphenanthrene-2-carboxylic acid (VI). The latter was characterized by the ethyl ester (VII), the hydrazide (VIII), and the benzylidenehydrazide (IX). 3-Methyl-1-azaphenanthrene (X) was obtained from VI after decarboxylation.

The IR spectrum of amine II (CCl_4 solution, band of medium intensity at 3440 cm^{-1}) corresponds to a secondary amino group that does not enter into the condensed aromatic system [3, 4]; the bands in the spectrum of a KBr pellet at 3100-3200 cm^{-1} correspond to associated NH groups. The UV spectrum of II (Fig. 1, curve 1) is similar to the spectrum of N-phenyl-β-naphthylamine [5]. In the PMR spectrum of II, the chemical shifts of the protons of the CH_3 groups attached to $C_{(5)}$ and $C_{(2)}$ of the pyridine ring are, on the δ scale, 2.33 and 2.39 ppm, respectively; the signal at 6.75 ppm is related to the NH group.

The IR and UV spectra of naphthyridine III (Fig. 1, curve 2) are similar to the spectra of 10-methylnaphtho[1,2-b][1,6]naphthyridine [1]. The electronic absorption spectra of these compounds are similar to the UV spectra of anthracene [6], acridine [7], and benzonaphthyridine [4]. The signal at 3.11 ppm in the PMR spectrum of III pertains to the CH_3 group.

The UV spectrum of IV is similar to the spectrum of 2,3-dimethyl-4-azaphenanthrene [1] (Fig. 1, curves 3 and 4). The signals at 2.56 and 2.36 ppm in the PMR spectrum of IV are related to the protons of the α-and β-methyl groups (relative to the nitrogen atom), respectively.

N-Phenyl-α-naphthylamine (XII) and benzo[a]carbazole (XIII) are formed from N-cyclohexylidene-α-naphthylamine (XI) on the same catalyst at 400-410°. As in the case of the dehydrocyclization of diphenylamine [8], XIII is formed only in low yield.



XI XII XIII

The catalytic transformations of I and XI are accompanied by a considerable amount of hydrogenolysis; as a result, ~ 50% of XI is converted to α-naphthylamine. This sort of cleavage of secondary and tertiary amines on a K-16 catalyst proceeds readily, as has been shown in many of our studies.

In the IR spectrum of XII, the band of the stretching vibrations of the NH group is found at 3411 cm^{-1}, while it is raised to 3439 cm^{-1} in the spectrum of XIII with an attendant increase in intensity by a factor of 1.5-2. This transition corresponds to the formation of a carbazole system from XII [3].

An increase in the dehydrocyclization temperature to 500° raises the yield of XII to 34% and that of XIII to 9%, based on the starting XI.

EXPERIMENTAL

N-(1,2,5-Trimethyl-4-piperidylidene)-β-naphthylamine (I). This compound was obtained via the method in [2] and had bp 181-185° (0.5 mm) and R_f 0.1 (benzene).* Found: N 10.3%. $C_{18}H_{22}N_2$. Calculated: N 10.5%. IR spectrum (liquid film), cm^{-1}: 2784 s (NCH_3), 1670 vs (>C=N). UV spectrum, λ_{max}, nm (log ε): 234 (4.71), 270 (3.87), 280 (3.88), 334 (3.34).

N-(2,3-Dimethyl-4-pyridyl)-β-naphthylamine (II), 9-Methylnaphtho[2,1-b][1,6]naphthyridine (III), and 2,3-Dimethyl-1-azaphenanthrene (IV). A solution of 59 g (0.22 mole) of I in 180 ml of benzene was

---

* In all experiments the thin-layer chromatography (TLC) was carried out on activity II Al_2O_3.

passed in the course of 7 h at a constant rate through a contact tube (100 ml of K-16 catalyst) at 380-400°. A total of 11 liters of gas was collected (19°, 755 mm; 77% H_2, 23% CH_4); the benzene and β-naphthylamine (1.5 g) were removed by distillation. Three experiments yielded 120 g of catalyzate, which was distilled: the first fraction was 15 g of β-naphthylamine with bp 155-165° (0.5 mm) and R_f 0.3 (benzene); the second fraction was 70.8 g of a substance with bp 165-185° (0.5 mm); the third fraction was 16.3 g of a substance with bp 185-200° (0.5 mm). Repeated crystallization of the second fraction from ether gave 25.4 g (18%, based on I) of yellowish needles of IV with mp 119-120° (from ether) and R_f 0.33 (benzene). Found: C 86.6; H 6.5; N 6.8%; Mol. wt. 207. $C_{15}H_{13}N$. Calculated: C 87.0; H 6.3; N 6.8%; Mol. wt. 207. IR spectrum (in KBr), cm^{-1}: 1609 m, 1486 m, 1456 m, 845 vs, 756 vs, 550 m. The picrate of IV had mp 240-241° (from alcohol). Found: N 12.5%. $C_{15}H_{13}N \cdot C_6H_3N_3O_7$. Calculated: N 12.8%. The perchlorate of IV had mp 262-263° (from alcohol). Found: N 4.2%. $C_{15}H_{13}N \cdot HClO_4$. Calculated: N 4.5%. Repeated crystallization of the third fraction from benzene gave 3.5 g (2%, based on I) of II with mp 166-166.5°. Found: C 82.3; H 6.7; N 11.5%. $C_{17}H_{16}N_2$. Calculated: C 82.3; H 6.5; N 11.3%. UV spectrum of II, λ_{max}, nm (log ε): 270 (4.44), 304 (4.32), 350 (shoulder). The mother liquor yielded 1 g (0.7%, based on I) of yellow crystals of III with mp 186-188° (from benzene) and R_f 0.06 (benzene). Found: C 83.7; H 4.9; N 11.4%; Mol. wt. 244. $C_{17}H_{12}N_2$. Calculated: C 83.6; H 4.9; N 11.5%; Mol. wt. 244. IR spectrum, cm^{-1}: 1615 vs, 1495 s, 1445 w, 1378 w, 830 vs, 755 vs, 680 m. The picrate of III had mp 238° (from alcohol). Found: N 14.6%. $C_{17}H_{12}N_2 \cdot C_6H_3N_3O_7$. Calculated: N 14.8%.

3-Methyl-2-styryl-1-azaphenanthrene (V). A mixture of 10.35 g (0.05 mole) of IV, 5.3 g (0.05 mole) of benzaldehyde, 3 g (0.05 mole) of glacial acetic acid, and 5.1 g (0.05 mole) of acetic anhydride was refluxed for 21 h. The acetic acid and anhydride were removed by vacuum distillation, and 100 ml of 18% hydrochloric acid was added to the residue. The neutral substances were separated with ether (two 100-ml portions), and the aqueous solution was neutralized with potassium hydroxide. The resulting organic bases were extracted with ten 100-ml portions of ether, and the ether extract was dried with magnesium sulfate and evaporated to 100 ml to give 11 g (75%) of V with mp 171-172° (from ether). Found: N 4.7%. $C_{22}H_{17}N$. Calculated: N 4.7%. The hydrochloride of V had mp 243-244° (from alcohol). Found: C 79.0; H 5.5; N 4.0; Cl 10.5%. $C_{22}H_{17}N \cdot HCl$. Calculated: C 79.6; H 5.4; N 4.2; Cl 10.7%. IR spectrum, cm^{-1}: 1636 vs (C=C), 1581 m, 1456 m, 1381 s, 836 m, 759 vs, 696 m. PMR spectrum of the hydrochloride of V: δ_{CH_3} 2.79 ppm. The picrate of V had mp 216.5-217.3° (from alcohol). Found: N 10.4%. $C_{22}H_{17}N \cdot C_6H_3N_3O_7$. Calculated: N 10.7%.

3-Methyl-1-azaphenanthrene-2-carboxylic Acid (VI). A 15.8-g (0.1 mole) sample of potassium permanganate was added in portions in the course of 2 h at −1 to −5° to a solution of 5.9 g (0.02 mole) of V in 600 ml of acetone, after which the mixture was stirred at the same temperature for 4 h. The manganese dioxide was removed by filtration and washed successively with acetone and hot water. The aqueous solution was evaporated to 200 ml and acidified with 50% sulfuric acid until it was slightly acidic. The resulting crystals were removed by filtration and washed with warm water (200 ml). Evaporation of the aqueous solution to 5 ml yielded 1 g of benzoic acid (mp 120-121°). The benzoic acid was removed by water, and the crystalline residue yielded 4.45 g (94%) of VI with mp 184-185° (from heptane). Found: C 75.8; H 4.5; N 5.8%. $C_{15}H_{11}NO_2$. Calculated: C 75.9; H 4.6; N 5.9%. IR spectrum of VI, cm^{-1}: 3066 m (associated OH), 1758 vs (C=O), 1450 m, 1370 s, 837 s, 759 s.

Ethyl Ester of VI (VII). This compound was obtained in 72% yield by refluxing 1.5 g (6.3 mmole) of VI with 75 ml of ethanol and 0.3 ml of concentrated sulfuric acid for 27 h. The product had mp 88-89° (from heptane). Found: C 76.6; H 5.9; N 5.1%. $C_{17}H_{15}NO_2$. Calculated: C 77.0; H 5.7; N 5.3%.

Hydrazide of VI (VIII). This compound was obtained in 82% yield by heating 0.45 g (1.7 mmole) of VII with 9 ml of hydrazine hydrate for 1.5 h. The product had mp 187.5-189° (from alcohol). Found: N 16.7%. $C_{17}H_{13}N_3O$. Calculated: N 16.7%.

Benzylidenehydrazide of VI (IX). This compound was obtained in 89% yield by refluxing 0.1 g (4 mmole) of VIII with 0.4 g (0.004 mole) of benzaldehyde and 30 ml of ethanol for 11 h. It had mp 212-213.5° (from alcohol). Found: N 12.3%. $C_{22}H_{17}N_3O$. Calculated: N 12.4%.

3-Methyl-1-azaphenanthrene (X). A mixture of 0.71 g (0.003 mole) of acid VI and 50 ml of water was heated in an autoclave at 200° for 3 h. The reaction products were extracted with ether, and the extract was washed with 10% sodium carbonate solution. The ether solution yielded 0.5 g (88%) of X with mp 81.5-82° (from heptane). Found: C 86.9; H 5.6; N 7.0%. $C_{14}H_{11}N$. Calculated: C 87.0; H 5.7; N 7.2%. The picrate of X had mp 255-257° (from alcohol). Found: N 13.2%. $C_{14}H_{11}N \cdot C_6H_3N_3O_7$. Calculated: N 13.3%. PMR spectrum: δ_{CH_3} 2.55 ppm. UV spectrum, λ_{max}, nm (log ε): 235 (4.58), 270 (4.32), 318 (3.36), 332 (3.59), 348 (3.64).

N-Cyclohexylidene-α-naphthylamine (XI). This compound was obtained in 95% yield from 1.5 mole of cyclohexanone and 1 mole of α-naphthylamine in the presence of acetic acid (refluxing for 12 h). It had bp 200-204° (7 mm), mp 56-58° (from ligroin), and R_f 0.36 (benzene). Found: N 6.2%. $C_{16}H_{17}N$. Calculated: N 6.3%. IR spectrum, cm^{-1}: 1666 vs (C=N–), 1578 m, 809 s, 787 vs, 720 m.

N-Phenyl-α-naphthylamine (XII) and Benzo[a]carbazole (XIII). A solution of 77 g (0.345 mole) of XI in 340 ml of benzene was passed in the course of 12 h through a contact tube (100 ml of K-16 catalyst) at 400-410°. A total of 14.5 liters of gas was collected (22°, 770 mm; 100% H_2). The benzene was removed by distillation, and the residue (61 g) was distilled. The first fraction was 24.3 g (49%, based on XI) of α-naphthylamine with bp 105-145° (0.5 mm) and R_f 0.17 (benzene); the second fraction was 21 g of a substance with bp 145-180° (0.5 mm) and R_f 0.8 (benzene); the third fraction was 8.75 g of a substance with bp 180-230° (0.5 mm) and R_f 0.17, 0.8, and 0.55 (benzene). The second fraction yielded 17 g (23%, based on XI) of XII with mp 57-58° (from ligroin) and R_f 0.8 (benzene). The N-benzoyl derivative of XII had mp 152-153° (from ether). The physical characteristics of XII and its benzoyl derivative [9] and the UV spectral data for XII [5] corresponded to the literature data. Chromatography of the third fraction with a column filled with Al_2O_3 and elution with ligroin yielded 2 g (3%, based on XI) of XIII with mp 227-228° (from ligroin) and R_f 0.43 (benzene). Found: C 88.2; H 5.2; N 6.2%. $C_{16}H_{11}N$. Calculated: C 88.5; H 5.1; N 6.4%. IR spectrum, cm^{-1}: 1597 w, 820 s, 741 vs. UV spectrum, λ_{max}, nm (log ε): 224 (4.66), 244 (4.69), 252 (4.74), 278 (4.76), 304 (4.52), 322 (3.82), 336 (3.82), 354 (3.87). This same fraction yielded 0.9 g of dark-green crystals with mp 133-142°, the nature of which has not yet been established.

The IR spectra from 400 to 3800 cm^{-1} were recorded with a UR-20 spectrometer with LiF, NaCl, and KBr prisms. The UV spectra of alcohol solutions were measured with SF-4a and Hitachi spectrometers. The PMR spectra (δ scale) were recorded with a Varian NA-100D spectrometer at 100 MHz. The positions of the signals in the PMR spectra for II, III, V, and X were measured relative to tetramethylsilane, while the positions for IV were measured relative to hexamethyldisiloxane. Trifluoroacetic acid was used as the solvent for II and III, CCl_4 was used for X, and a mixture of CCl_4 and CF_3COOH was used for the hydrochloride of V. The molecular weights were determined with an MKh-1303 mass spectrometer.

LITERATURE CITED

1. N. S. Prostakov, V. G. Pleshakov, T. Kholdarova, V. P. Zvolinskii, and L. N. Plaksii, Khim. Geterotsikl. Soedin., 378 (1972).
2. I. N. Nazarov, N. S. Prostakov, N. N. Mikheeva, and V. N. Dobrynin, Izv. Vuzov, Ser. Khim., 2, 726 (1959).
3. R. A. Russel and H. W. Thompson, J. Chem. Soc., 483 (1955).
4. N. S. Prostakov, L. M. Kirillova, Dkharvar Pkhal'gumani, L. A. Shakhparonova, and V. P. Zvolinskii, Khim. Geterotsikl. Soedin., 1068 (1967).
5. V. S. Fikhtengol'ts, R. V. Zolotareva, and Yu. A. L'vov, Atlas of UV Absorption Spectra of Substances Used in the Manufacture of Synthetic Rubbers [in Russian], Moscow–Leningrad (1965), p. 42.
6. A. J. Scott, Interpretation of the Ultraviolet Spectra of Natural Products, Pergamon Press (1964), p. 127.
7. C. N. R. Rao, Electronic Spectra in Organic Chemistry [Russian translation], Goskhimizdat, Leningrad (1959), p. 423.
8. B. N. Dolgov, Catalysis in Organic Chemistry [in Russian], Goskhimizdat, Leningrad (1959), p. 423.
9. E. Knoevenagel, J. Prakt. Chem., 89, 17 (1914).