INTERACTION OF ARYLIDENE-2-NAPHTHYLAMINES WITH α- AND β-TETRALONE TO FORM DERIVATIVES OF DIBENZAZAPHENANTHRENE

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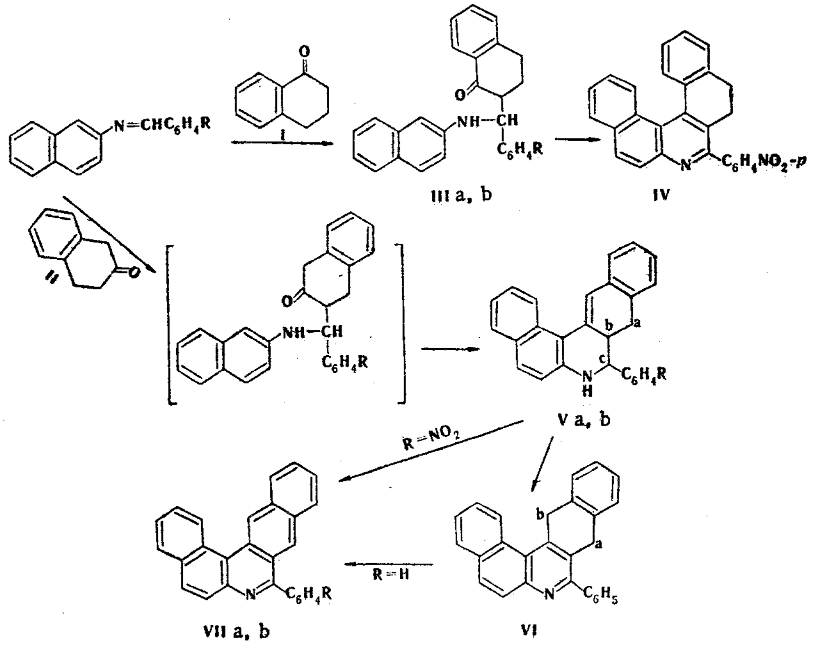
The reaction of arylidene-2-naphthylamines with cyclanones results in the formation of β-arylamino ketones, which are then cyclized to form derivatives of benzo[f]quinoline [1]. As a continuation of these investigations, in the present work we examined the interaction of arylidene-2-naphthylamines with α- (I) and β-tetralone (II).

It may be postulated that the presence of a benzene ring in the tetralone molecule lowers the mobility of the α-hydrogen atoms in the reaction under study in comparison to that of the cyclanones [2]. In addition, the two nucleophilic centers in β-tetralone (at C_1 and C_3) determine the two possible directions for addition across the double bond of an azomethine.



a R=H; b R=p-NO$_2$

Compounds I and II require more severe conditions for the realization of reactions with azomethines than do cyclanones, and it was not possible to effect reactions with azomethines containing electron-donor substituents. Tetralone I is less active than II. This is clearly attributable to the conjugation of the carbonyl with the benzene ring in I, which causes significant lowering of the C=O frequency (1690 and 1723 cm^{-1} for I and II, respectively) and lowering of the activity of the hydrogen atom at C_2 [3]. Benzylidene-2-naphthylamine reacts with I only upon heating to form amino ketone IIIa. At the same time, significant amounts of β-naphthylamine, whose formation probably occurs either as a result of the hydrolysis of the azomethine or as a result of the "hydramino" splitting of the amino ketone, are also detected. The IR spectra of amino ketones IIIa and IIIb contain absorption bands of the stretching vibrations of NH (3385, 3380 cm^{-1}) and C=O (1670, 1660 cm^{-1}) bonds. The electronic spectra, which are similar in character to the spectra of amino ketones of the cyclohexane series

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[1], contain two principle maxima (248 and 252 nm). The data from the PMR spectra are also in agreement with the proposed structure. The mass spectra of these compounds are characterized by low-intensity peaks of the molecular ions (377 and 422) and intense peaks of the [M− tetralone]$^+$ ions (232 and 277, respectively).

We were able to obtain the cyclization product of amino ketone IIIb by heating in the presence of a catalyst and an oxidizing agent. The same product can be obtained in one step from the original azomethine and α-tetralone. In the IR spectrum of product IV there are no bands which correspond to vibrations of NH or C=O, and the PMR spectrum shows a broadened singlet of the equivalent methylene protons at 2.64 ppm (4 H). The UV spectrum has a form characteristic of the benzo[f]quinoline structure [4]. The mass spectrum shows an intense peak of the molecular ion, and the system is stable. These findings allow us to assert that the cyclization of IIIb to dibenzazaphenanthrene derivative IV took place. Ketone IIIa could not undergo cyclization, apparently because of the complete "hydramino" splitting of the amino ketone.

The reaction of arylidene-2-naphthylamines with II proceeds more actively than with I to form cyclic products Va-Vb and VI. In the IR spectra of compounds Va and Vb, besides the bands characteristic of the benzene and pyridine rings, there are characteristic bands of the stretching vibrations of NH and C=C groups. There is no absorption attributable to vibrations of a carbonyl group. The shape of the absorption curve in the UV spectrum is similar to the curve of tetrahydronaphthoquinoline [5]. Its significant bathochromic shift is evidence of the presence of conjugation between the naphthyl and phenyl nuclei, i.e., of the formation of a double bond in the tetralone fragment of the molecule.

The PMR spectrum of Va shows signals of methylene protons at 2.28 ppm (2 H, split doublet) and methine protons at 3.15 (1 H, doublet) and 4.1 ppm (1 H, doublet). The assignment of the signals was confirmed by the double resonance method. When the H_c spin system was perturbed at a frequency of 410 Hz, the H_a doublet (with $J \approx 9$ Hz) remained unchanged, the the H_b multiplet took on the character of a triplet (with $J \approx 9$ Hz). When the spin system of the H_a protons was perturbed at a frequency of 228 Hz, the H_c doublet (with $J \approx 11$ Hz) remained unchanged, and the H_b multiplet took on the form of a broadened doublet (with $J \approx 11$ Hz). When the H_b spin system was perturbed at a frequency of 315 Hz, the H_a and H_c signals took on the form of broadened singlets.

The formation of VI in a mixture with Va apparently occurs as a result of the disproportionation of Va, which is attributable to the sensitivity of the dihydro derivatives of nitrogenous heterocycles to acids [6]. The IR spectrum of VI does not contain absorption bands of NH or C=C. In the UV spectrum the long-wave band at 325-368 nm has a clear vibrational structure. The shape and arrangement of the bands are characteristic of benzo[f]quinoline, indicating that there is no conjugation between the aromatic tetralone ring and the benzoquinoline ring system. The PMR spectrum has two slightly split (homoallyl interaction) singlets of identical character at 2.6 and 3.5 ppm. When double resonance with frequencies equal to 260 and 350 Hz was used, the signals alternately took on the form of clear singlets.

Prolonged heating of tetrahydro derivatives of azaphenanthrene Va and Vb in an acid medium in the presence of an oxidizing agent results in the further aromatization of the azaphenanthrene system. The bands associated with vibrations of the alicyclic CH and CH_2 groups vanish in the IR spectra of VIIa and VIIb. A characteristic feature of the PMR spectrum is the absence of resonance signals in the 0-6-ppm range. The UV spectrum of VIIa is similar to the spectrum but has undergone a significant bathochromic shift, which is evidence of the elongation of the conjugation chain. The mass spectra of compounds IV-VII contain intense (maximal) peaks of the molecular ions, providing evidence of a stable cyclic structure.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer in tablets with KBr, and the UV spectra were recorded on a Specord UV-vis instrument. The mass spectra were obtained on an MAT-311 mass spectrophotometer at an ionization energy of 70 eV in the 100-180°C temperature range. The PMR spectra were recorded on a Jeol JNM-PS-100 instrument (Japan) in the form of 10% solutions in trifluoroacetic acid. The internal reference was TMS. The melting points were determined on a Kofler device.

2-[(Phenyl) (2'-naphthylamino)methyl]-α-tetralone (IIIa). A reaction mass consisting of 2.31 g (0.01 mole) of benzylidene-2-naphthylamine, 1 ml of compound I, 5 ml of ethanol, and 10 drops of BF_3 etherate was heated in a sealed ampul for 1 h at 100°C. After cooling and treatment with NH_4OH, a white precipitate was crystallized from ethanol.

2-[(p-Nitrophenyl) (2'-naphthylamino)methyl]-α-tetralone (IIIb). A mixture of 1.4 g (5 mmole) of p-nitrobenzylidene-2-naphthylamine, 0.5 ml of I, 10 drops of conc. HCl, and 10 ml of ethanol was heated for 20 min at

TABLE 1. Characteristics of Amino Ketones IIIa and IIIb and Azaphenanthrenes IV–VII

Compound	mp,* °C	UV spectrum, λ_{max}, nm (log ε)	Found, %			Empirical formula	Calc., %			M+	Yield, %
			C	H	N		C	H	N		
IIIa	149—150	209 (4,59); 248 (4,73); 283 (4,03); 293 (3,98)	85,4	6,4	3,9	$C_{27}H_{23}NO$	85,9	6,1	3,7	377	35
IIIb	179—180	248 (4,90); 272 (4,42); 282 (4,45); 291 (4,39); 345 (3,79)	76,4	5,2	6,6	$C_{27}H_{22}N_2O_3$	76,8	5,2	6,6	422	52
IV	274—275	239 (4,48); 298 (4,58); 340 sh. (4,15); 361 (4,04); 381 (3,97)	80,5	4,6	7,0	$C_{27}H_{18}N_2O_2$	80,6	4,5	7,0	402	55
Va	203—204	210 (4,57); 257 (4,48); 286 (4,40); 327 sh. (4,04); 409 (4,15)	90,1	5,8	3,8	$C_{27}H_{21}N$	90,2	5,8	3,9	359	60
Vb	268—269	257 (4,47); 284 (4,56); 320 sh. (4,08); 404 (4,10)	79,9	5,0	6,5	$C_{27}H_{20}N_2O_2$	80,0	5,0	7,0	404	60
VI	214—215	237 (4,41); 271 (4,62); 325 (4,24); 351 (3,86); 368 (3,89)	90,7	5,0	3,4	$C_{27}H_{19}N$	90,7	5,4	3,9	357	22
VIIa	183—184	229 (4,61); 262 (4,35); 308 (4,61); 345 (3,71); 361 (3,85); 380 (3,81)	90,8	4,8	3,8	$C_{27}H_{17}N$	91,2	4,8	3,9	355	90
VIIb	226—228	222 (3,97); 306 (4,67); 364 (3,92); 431 (3,88)	81,0	4,3	6,9	$C_{27}H_{16}N_2O$	81,0	4,0	7,0	400	80

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*The UV spectra of IIIa, Va, VIa, and VIIa were measured in ethanol, and the others were measured in dioxane.

60°C. After cooling, the resinous precipitate was treated with NH_4OH and crystallized from toluene. PMR spectrum (C_5D_5N): 1.8–2.5 (m, 2 H CH_2), 2.65 (d, 2 H, CH_2), 3.0 (s, 1 H, CH), 5.45 (s, 1 H, CH), 6.4–7.8 (m, 15 H, aromatic H and NH).

5,6-Dihydro-7-p-nitrophenyldibenz[c, d]-8-azaphenanthrene (IV). This compound was also synthesized and treated as IIIb with heating for 1 h (120°C) in an ampul in the presence of 10 drops of conc. HCl and 1 ml of $C_6H_5NO_2$. IR spectrum: 2950, 2860 (CH_2), 1520, 1346 cm^{-1} (NO_2). PMR spectrum: 2.64 (s, 4 H, $2CH_2$), 6.56–8.35 (m, 14 H, aromatic H).

6,6',7,8-Tetrahydro-7-phenyldibenz[b, d]-8-azaphenanthrene (Va). A hot ethanolic solution of 2.31 g (0.01 mole) of benzylidene-2-naphthylamine was given an addition of 2 drops of conc. HCl and 1 ml of ketone and heated for 3 min at 70°C. Upon cooling, bright greenish yellow crystals precipitated. They were treated with NH_4OH and recrystallized form CH_3NO_2 and toluene. IR spectrum: 3391 (NH), 2930–2840 (CH_2), 1620 cm^{-1} (C=C). PMR spectrum: 2.29 (d, 2 H, a-CH_2), 3.15 (q, 1 H, b-CH), 4.1 (d, 1 H, c-CH), 6.4–7.54, 8.1 (m, 17 H, aromatic H and NH).

6,6',7,8-Tetrahydro-7-p-nitrophenyldibenz[b, d]-8-azaphenanthrene (Vb). This compound was synthesized from 1.4 g of p-nitrobenzylidene-2-naphthylamine under the conditions for Va. It was crystallized from toluene in the form of dark and red crystals. IR spectrum 3365 (NH), 2930–2850 (CH_2), 1615 (C=C), 1510, 1340 cm^{-1} (NO_2).

1,6-Dihydro-7-phenylbenz[b, d]-8-azaphenanthrene (VI). This compound was synthesized under the conditions for the synthesis of Va with an addition of 5–6 drops of conc. HCl. It was separated from an admixture of Va by fractional crystallization on the basis of the greater solubility of Va in ethanol. It was crystallized from ethanol and toluene in the form of white plates. IR spectrum: 2920–2840 cm^{-1} (CH_2). PMR spectrum: 2.6 (s, 2 H, a-CH_2), 3.5 (s, 2 H, b-CH_2), 6.3–8.22 ppm (m, 15 H, aromatic H).

7-Aryldibenz[b, d]-8-azaphenanthrenes (VIIa and VIIb). A mixture of 1 g of Va or Vb, 0.5 ml of $C_6H_5NO_2$, five drops of conc. HCl, and 5 ml of ethanol was heated in an ampul at 120°C for 3 h, cooled, treated with NH_4OH, and crystallized from toluene. PMR spectrum of Va: 7.65–8.40 (m, 13.5 H), 8.99 (s, 1 H), 9.1 (d, 1 H), 9.57 ppm (s, 1 H), i.e., resonance signals of aromatic protons.

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HYDROACRIDINES AND RELATED COMPOUNDS.

17.* 10-SUBSTITUTED 9,9-PENTAMETHYLENEHYDROACRIDINES

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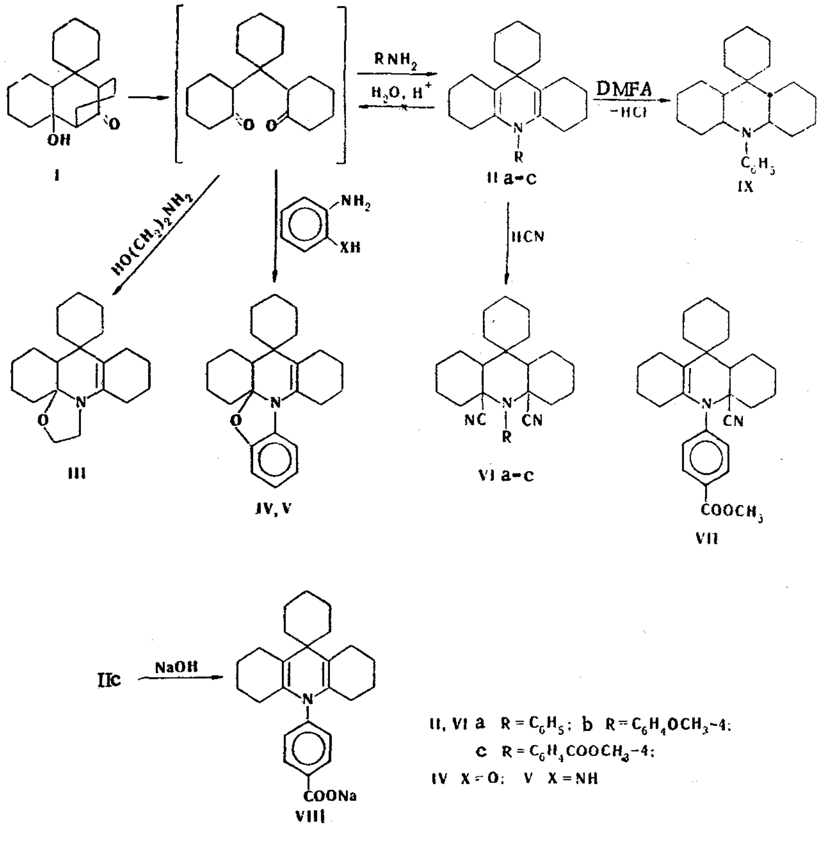
Rather few examples of the synthesis of 4,4-disubstituted 1,4-dihydropyridines [2, 3] and only a few cases of the synthesis of such derivatives which do not contain electron-acceptor groups [4] are known.



II, VI a R = C_6H_5; b R = $C_6H_4OCH_3$-4;
c R = $C_6H_4COOCH_3$-4;
IV X = O; V X = NH

For the purpose of obtaining and studying the properties of compounds of the latter type, we reacted the product of the trimolecular self-condensation of cyclohexanone, i.e., 8,8-pentamethylenetricyclo-[7, 3, 1, $0^{2,7}$]-tridecan-2-ol-13-one (I) [5, 6], with primary amines. In the present reaction, ketol I behaved similarly to the previously studied self-condensation products of 1,5-diketones [7]. With aniline and its para-substituted derivatives we obtained the corresponding 10-substituted 9,9-pentamethylenedecahydroacridines (IIa-IIc), and with ethanolamine, o-aminophenol, and o-phenylenediamine we obtained products of double cyclization [8] (III-V).

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*For report 16, see [1].

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