PYRIMIDINES.

LXV.* 3-ARYLBENZO[f]QUINAZOLINES

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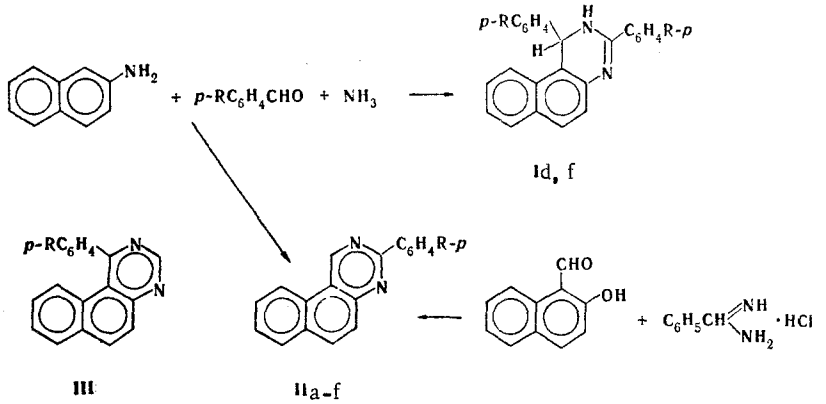
3-Arylbenzo[f]quinazolines were obtained by reaction in acetic or propionic acid of β-naphthylamine, ammonia, and aromatic aldehydes containing an NR_2 or OH group. A mechanism is proposed for the formation of monoarylbenzo[f]quinazolines from the corresponding intermediate 1,3-diaryldihydrobenzo[f]quinazolines by acid cleavage of the C—aryl bond in the 1 position. This mechanism was confirmed experimentally by establishment of the fact of cleavage of 1,3-bis(p-methoxyphenyl)-1,2-dihydrobenzo[f]quinazoline when the acidity of the medium is increased; 3-(p-methoxyphenyl)benzo[f]quinazoline and anisole were obtained in the reaction products. Condensation in the presence of formic acid gave α-arylidene-N-formyl-β-naphthylamines rather than arylbenzo[f]quinazolines.

We have previously shown that 1,3-diaryl-1,2-dihydrobenzo[f]quinazolines (I) are formed when a mixture of β-naphthylamine, an aromatic aldehyde, and ammonia in acetic acid is heated [1, 2]. When aromatic aldehydes that contain an NR_2 group are used in this reaction, compounds that were identified from their compositions and IR spectral data (particularly the presence of the characteristic absorption band of an aryl-substituted aromatic pyrimidine ring [3] at ∿ 1400 cm^{-1}) as monoarylbenzo[f]quinazolines II or III rather than dihydrobenzoquinazolines I were isolated from the reaction mixtures. The choice between structures II and III was made on the basis of a comparison of the PMR spectra of the compounds and the available literature data. As seen from Table 1, the signal of the proton in the 2 position of the pyrimidine ring is observed at weak field at 9.3-9.4 ppm. The signals in the spectra of the monoarylbenzoquinazolines that we obtained are shifted even more markedly to weak field (10-10.5 ppm).



II a R=$N(CH_3)_2$; b R=$N(C_2H_5)_2$; c R=$OCOCH_3$; I-II d R=OCH_3; f R=OH; I e R=H

These signals can be ascribed to the 1-H protons of benzoquinazolines II on the basis of data on the shift of the 4- and 5-H signals in the PMR spectra of phenanthrenes [7] and related systems [8-11]. Considering that the assignments of the signals in [6] are in complete agreement with the literature data and that the 1-H signal in the PMR spectrum of an authentic sample of benzoquinazoline isomer IIe obtained in analogy with [6] is also shifted

*See [1] for communication LXIV.

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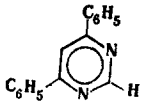
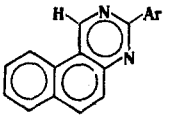
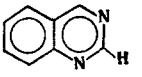
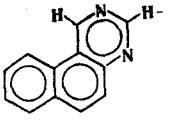
TABLE 1. Chemical Shifts of the Protons of the Pyrimidine Ring

Compound	δ, ppm (solvent)	Compound	δ, ppm (solvent)
	9,32* (DMSO)		
	9,4 (DMSO)[4]; $CDCl_3$[5])	IIa IIb	10,0 ($CDCl_3$) 10,1 ($CDCl_3$)
		IIc	10,6 (d_6-DMSO)
	1-H, 9,9, 3-H, 9,35 ($CDCl_3$[6])	IIe	10,4 (d_6-DMSO)

*Data supplied by O. P. Shkurko.

markedly to weak field (see Table 1), one may assume that the p-(dialkylaminophenyl)benzoquinazolines obtained have structures IIa and IIb.

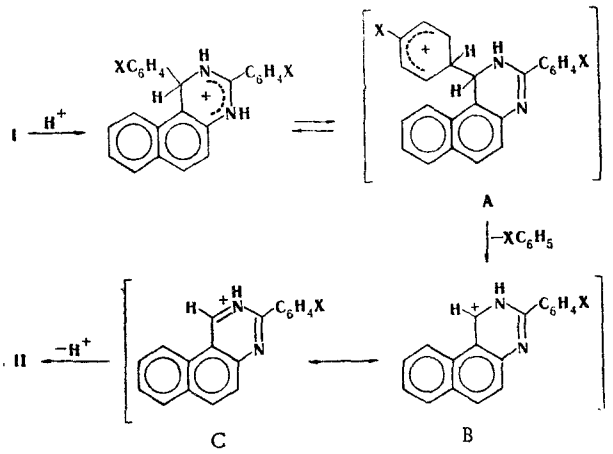
The question of methods for the formation of benzo[f]quinazolines of the II type is of particular interest. An aromatic aldehyde or acetic acid can be considered as the source of the $C_{(1)}$ atom in the formation of benzoquinazolines II. However, the same benzoquinazolines I or II are obtained when acetic acid is replaced by propionic acid; this excludes participation of the acid in the reaction. We assumed that monoarylbenzo[f]quinazolines are formed from the corresponding intermediate 1,3-diaryldihydrobenzo[f]quinazolines by splitting out of an aryl group from the 1 position with simultaneous aromatization of the benzoquinazoline molecule.* The heterolytic cleavage of the C—aryl bond that occurs under the influence of acidic agents is well known in the diaryl- and triarylmethane series [12-14], as well as in the phenylindane [15] and phenyldihydroanthracene series [16]. According to modern concepts, this cleavage (the aryl group is split out in the form of ArH) takes place with the intermediate formation of arenonium ions [16].

Our results are in good agreement with the known principles of this process. Thus it has been shown [13, 14] that the aromatic ring that has the highest basicity is most easily detached from the diarylmethane molecule. In fact, other things being equal, splitting out of an aryl residue from the NR_2 group occurred most readily in the investigated reaction to form benzoquinazolines: only compounds of the II type were obtained in this case. Benzoquinazolines of both the I and II types are formed when p-hydroxybenzaldehyde is used in the reaction (the OH group is a weaker donor), whereas only quinazoline I is formed in the case of anisaldehyde [2].

In comparison with the data in [12-16], the heterolytic cleavage of the C—aryl bond in dihydrobenzoquinazolines is distinguished by the fact that it occurs in media with relatively low acidities (CH_3COOH) as compared with the media that are usually employed in reactions of this sort. Reactions that take place in weakly acidic media (CD_3COOH [17] and $HCOOH \cdot N(C_2H_5)_3$ [18]),in which the degree of protonation of the starting compounds should be slight have been described; the results of these reactions are difficult to explain if one does not resort to the assumption that arenonium ions or structures similar to them are formed.

A possible mechanism for the detachment of the aryl group in dihydrobenzoquinazolines I can be represented by the following scheme. The initially formed (at least to a small extent) arenonium ion A is converted as a result of detachment of XC_6H_5 to an azacarbonium ion, stabilized by carbonium—immonium resonance B ↔ C, the subsequent ejection of a proton from which leads irreversibly to the formation of aromatic compounds II. (See scheme on following page).

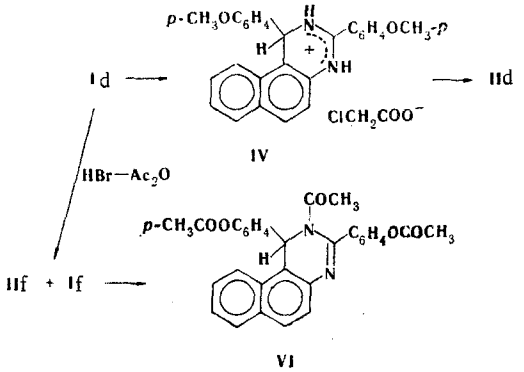
*We thank V. A. Bushmelev for his participation in the discussion of the results.



In our opinion, the described [19] decomposition in acidic media (HCl) of the benzofuryldihydrotriazine derivative to benzofuran and triazine derivatives is yet another example of the facile acidic cleavage of the C—aryl bond in dihydro derivatives of the heterocyclic series. The transformations observed in this research and in [19] are essentially reversible reactions with respect to the recently described heteroarylation by pyrimidine derivatives of aromatic hydrocarbons under unexpectedly mild conditions [20].

We were able to experimentally verify our assumption regarding the scheme of the formation of benzoquinazolines II in the following manner. Since it is known that the cleavage of the C—aryl bond depends on the acidity of the medium and the donor—acceptor properties of the substituent in the aryl group (i.e., a more acidic medium is needed for a weaker donor) [14], we investigated the possibility of the cleavage of a diaryldihydrobenzoquinazoline that is stable in acetic acid in a medium with greater acidity. We used 1,3-bis(p-methoxyphenyl)-1,2-dihydrobenzo[f]quinazoline (Id) as the compound to be cleaved and chloroacetic acid and a mixture of hydrobromic acid and acetic anhydride, which was previously used for the solvolysis of the methoxy group [2], as the media.

A compound with an IR spectrum that is extremely characteristic for amidinium salts [1], at 1580-1690 cm^{-1}, which attests to the formation of salt IV, was obtained when benzoquinazoline Id was heated with chloroacetic acid under mild conditions (see Table 2). Cleavage of diarylquinazoline Id to give monoaryl derivative IId occurs when the cleavage reaction is carried out under more severe conditions and when salt IV or reaction mixture V (Id + IId, mp 97-115°; see Table 2) is heated further. The leaving aryl group (anisole in this case) was also detected by gas—liquid chromatography (GLC) during an investigation of the benzene extract from the mixture in the reaction of Id with $ClCH_2COOH$.



Heating benzoquinazoline Id in $HBr-(CH_3CO)_2O$ showed that the corresponding monoarylbenzoquinazoline IIf is actually formed in this case also (solvolysis of the methoxy group also occurs simultaneously as the mixture is heated). However, considerable protonation of the benzoquinazoline Id or If molecule at the hydroxy (methoxy) group probably still occurs in this case, since, in addition to IIf, simply the product of demethylation of quinazoline Id — benzoquinazoline If — is formed in significant amounts. 1,3-Bis(o-methoxyphenyl)benzo[f]-quinazoline [2] did not undergo cleavage under the investigated conditions.

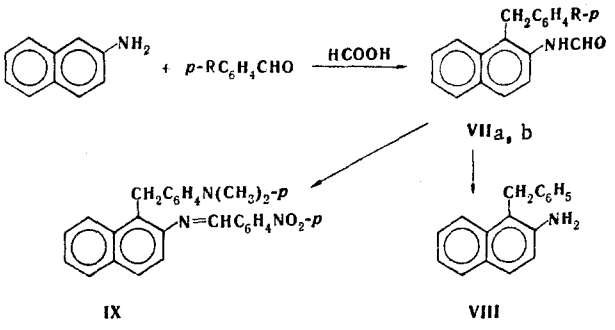
TABLE 2. Cleavage of Benzo[f]quinazoline Id in Chloroacetic Acid

Starting mixture	Temp., °C	Time, h	Solvent	mp of the reaction product, °C	Reaction products (yields in grams per gram of starting Id or mixture V)
Id + $ClCH_2COOH$ (1 : 1)	60	1	$CHCl_3$	130—134	IV
Id + $ClCH_2COOH$ (excess)	70—80	10		132—134	IV (1.2)
	120	6	$ClCH_2COOH$	110—120	Id + IId* (0,6)
	120—130	22		97—115	Id + IId* (V); (0,7)
V	130—140	2		145—158	IId (0,85 †)
	150	2	Fusion	158—164	IId (0,28)
	200	1		160—167	IId (0,4)

*According to the TLC and mass-spectrometric data.
†This is the yield of the crude reaction product.

Since benzoquinazolines I are cleaved in acidic media, whereas dihydrobenzoquinazolines readily form stable salts under these conditions [1], we also checked the possibility of the utilization of the previously obtained benzoquinazolinium chlorides for the cleavage reaction. Heating at 250-270°C showed that cleavage occurs in the case of salt Ia·HCl, for which the presence of a donor substituent in the benzene ring facilitates the formation of intermediate carbonium ion A, whereas 1,3-diphenyl-1,2-dihydrobenzo[f]quinazolinium chloride did not give even traces of monophenyl derivative IIe: only a small amount of dehydrogenation occurred (according to the mass-spectrometric data).

Thus the results confirm the proposed scheme for the formation of monoarylbenzoquinazolines.



VII a R = $N(CH_3)_2$; b R = H

We verified the possibility of the preparation of monoarylbenzoquinazolines II by condensation of β-naphthylamine, aldehydes, and ammonia [2] while increasing the acidity of the medium by the addition of formic acid (in the form of ammonium or triethylammonium formate [18]). However, β-naphthylamine derivative VIIa was obtained rather than benzoquinazoline IIa in this case even when p-dimethylaminobenzaldehyde was used in the reaction. The reaction with benzaldehyde proceeded similarly; however, the corresponding quinazoline was also formed in this case.

EXPERIMENTAL

The IR spectra of the compounds were recorded with a UR-20 spectrometer. The UV spectra of solutions of the compounds in ethanol were recorded with a Specord UV-vis spectrophotometer. The PMR spectra were recorded with a Varian A56/60A spectrometer with hexamethyldisiloxane as the internal standard. The molecular weights were determined with an MS-902 high-resolution mass spectrometer with a system for direct introduction of the samples at 120-140°C.

3-(p-Dimethylaminophenyl)benzo[f]quinazoline (IIa). A) A mixture of 10 g (0.07 mole) of β-naphthylamine, 20.8 g (0.14 mole) of p-dimethylaminobenzaldehyde, 15.2 g (0.2 mole) of ammonium acetate, and 40 ml of CH_3COOH was refluxed at 140°C for 5 h, after which it was cooled and poured into 300 ml of water. The aqueous mixture was neutralized with dry sodium bicarbonate and extracted with chloroform (three 80-ml portions). The chloroform extract was washed with water, dried with magnesium sulfate, and evaporated in vacuo. The residue

was triturated with alcohol, and the precipitated quinazoline IIa (5 g) was removed by filtration. The filtrate was allowed to stand for 1 week, and an additional 2.6 g of IIa precipitated from it. The overall yield of benzoquinazoline IIa, with mp 214-216°C (from alcohol), was 36%. UV spectrum, λ_{max} (log ε): 206 (4.73), 220 (4.63), 235 (4.67), 257 (4.60), 300 (4.41), 325 (4.50), 358 nm (4.76). PMR spectrum (in $CDCl_3$): 2.85 (6H, s, NCH_3), 6.74-8.66 (10H, m, H_{arom}), and 10.0 ppm (1H, s, 1-H). Found: C 79.7; H 5.9; N 14.1%; M 299. $C_{20}H_{17}N_3$. Calculated: C 80.2; H 5.7; N 14.0%; M 299.

B) Benzoquinazoline IIa was obtained in 46% yield when the condensation was carried out in propionic acid.

3-(p-Diethylaminophenyl)benzo[f]quinazoline (IIb). The reaction of 3 g (0.021 mole) of β-naphthylamine, 7.43 g (0.042 mole) of p-diethylaminobenzaldehyde, and 15.4 g (0.2 mole) of ammonium acetate was carried out as in the preceding experiment, and the mixture was worked up in the same manner to give IIb in a mixture with a compound with a molecular weight of 326,1772 ($C_{23}H_{22}N_2$) and mp 194-196°C (from xylene). We were able to purify IIb by repeated recrystallization from xylene. The product was obtained in 27% yield from acetic acid and 51% yield from propionic acid and had mp 170-172°C (from xylene). UV spectrum, λ_{max} (log ε): 208 (4.52), 235 (4.45), 255 (4.42), 299 (4.18), 368 nm (4.60). PMR spectrum (in $CDCl_3$): 1.27 (t, CH_3), 3.50 (q, CH_2), 6.93-8.68 (m, H_{arom}), and 10.1 ppm (s, 1-H). Found: C 80.3; H 6.6; N 12.0%; M 327. $C_{22}H_{21}N_3$. Calculated: C 80.7; H 6.4; N 12.8%; M 327.

1,2-Bis(p-hydroxyphenyl)-1,2-dihydrobenzo[f]quinazoline (If) and 3-(p-Hydroxyphenyl)benzo[f]quinazoline (IIf). A mixture of 8 g (0.055 mole) of β-naphthylamine, 13.4 g (0.11 mole) of p-hydroxybenzaldehyde, 15.4 g (0.2 mole) of ammonium acetate, and 35 ml of CH_3COOH was refluxed at 140°C for 5 h, after which it was cooled and poured into 320 ml of water. The aqueous mixture was neutralized with solid sodium bicarbonate, and the precipitate was removed by filtration and washed thoroughly with ether to give 14.7 g of a light-yellow crystalline substance with mp 198-202°C. The product was recrystallized successively from dioxane and xylene to give quinazoline If with mp 192-194°C. Found: M 366, 1368. The empirical formula $C_{24}H_{18}N_2O_2$ was calculated from this molecular weight. The ether filtrate was evaporated, and the resulting oil was refluxed with 25 ml of acetic anhydride for 2.5 h. The mixture was then cooled and allowed to stand in a refrigerator overnight. The precipitate was removed by filtration and washed with 10% $NaHCO_3$ solution and water to give 0.3 g of acetyl derivative IIc in the form of small needles with mp 200-205°C (from xylene). IR spectrum (in KBr): 1220 (C—O—C), 1410, and 1770 cm^{-1} (O—C=O). UV spectrum, λ_{max} (log ε): 219 (4.48), 246 (4.23), 286 (4.74), 343 (3.86), 357 nm (3.83). Found: C 76.5; H 4.5; N 9.1%; M 314. $C_{20}H_{14}N_2O_2$. Calculated: C 76.5; H 4.5; N 8.9%; M 314.

3-(p-Methoxyphenyl)benzo[f]quinazoline (IId). A) A mixture of 0.5 g of quinazoline Id and 4 g of chloroacetic acid was heated at 70-80°C for 10 h, after which it was poured into water, and the aqueous mixture was neutralized with $NaHCO_3$ to give 0.6 g of salt IV with mp 132-134°C. IR spectrum (in $CHCl_3$): 1595, 1620 vs, and 1650 cm^{-1}. A 0.6 g sample of salt IV was heated with 2 g of chloroacetic acid at 130°C, after which the mixture was washed thoroughly with benzene and worked up to give 0.5 g of a mixture with mp 110-120°C. Recrystallization from alcohol gave 0.1 g of benzoquinazoline IId with mp 160-165°C. UV spectrum, λ_{max} (log ε): 204 i (inflection) (4.20), 227 (4.41), 263 i (4.05), and 296 nm (4.57). Found: M 286, 1106. The empirical formula $C_{19}H_{14}N_2O$ was calculated from this molecular weight. Anisole was detected in the benzene extract by GLC.*

B) A mixture of 1.95 g of dihydroquinazoline Id and 7.5 g of chloroacetic acid was heated at 120-130°C for 22 h, after which it was poured into water. The aqueous mixture was neutralized with dry sodium bicarbonate, and the precipitate was removed by filtration and washed with water to give 1.4 g of mixture V with mp 97-115°C. A 0.3 g sample of mixture V was heated at 200°C for 1 h, after which it was cooled and triturated with alcohol to give 0.12 g of a light-gray precipitate of quinazoline IId with mp 160-167°C. The IR spectrum was identical to the IR spectrum of the product obtained in experiment A and had R_f 0.62. [Silufol UV-254, $CHCl_3$—alcohol (20:1)].

3-Phenylbenzo[f]quinazoline (IIe). A mixture of 1 g (5.8 mmole) of β-hydroxynaphthaldehyde, 0.91 g (5.8 mmole) of benzamidine hydrochloride, 0.23 g (5.8 mmole) of KOH, and 7 ml

*Gas—liquid chromatography was carried out with an LKhM-7A chromatograph with a 400 by 0.4 cm column filled with 18% SKTFV-803 on Chromosorb W; the carrier gas was helium, and the flow rate was 60 ml/min at 80-250°C.

of 2-octanol was refluxed with stirring in a nitrogen atmosphere for 3 h, after which it was cooled, and the precipitate was removed by filtration and washed with ether to give 0.7 g of a violet substance, from which 0.2 g (13%) of quinazoline IIe, with mp 182-185°C (from alcohol), was obtained by sublimation (at 7 mm and 210°C for 6 h). UV spectrum, λ_{max} (log ε): 217 (4.61), 244 (4.38), 261 (4.50), 283 (4.75), 341 (3.60), 356 nm (3.56). Found: C 84.5; H 4.6; N 11.1%; M 256. $C_{18}H_{12}N_2$. Calculated: C 84.5; H 4.7; N 10.7%; M 256.

Cleavage of Quinazoline Id by Heating with HBr and $(CH_3CO)_2O$. A mixture of 1.3 g of quinazoline Id, 4.2 ml of acetic anhydride, and 2 ml of concentrated hydrobromic acid was refluxed for 19 h; after 10 h, another 4.2 ml of acetic anhydride and 2 ml of HBr were added. The mixture was cooled and allowed to stand overnight in a refrigerator, and the bright-yellow precipitate was removed by filtration and washed with 10% $NaHCO_3$ solution, during which it turned dark crimson. To decompose the stable hydrobromide we heated it with 10% $NaHCO_3$ solution at 75°C for 16 h. The mixture was filtered, and the solid was washed with water to give 0.95 g of a product with mp 228-234°C. The mass-spectrometric determination of the molecular weight showed that the precipitate was a mixture of quinazolines If (M 366) and IIf (M 272). A portion of the precipitate was recrystallized from xylene, and triacetyl derivative VI was obtained by reaction with acetic anhydride. The product had mp 144-148°C (from xylene and petroleum ether). IR spectrum (in $CHCl_3$): 1680 and 1760 cm^{-1} (C=O). Found: C 72.9; H 4.3; N 6.1%; M 492. $C_{30}H_{24}N_2O_5$. Calculated: C 73.1; H 4.8; N 5.7%; M 492.

Cleavage of 1,3-Bis(p-methoxyphenyl)-1,2-dihydrobenzo[f]quinazolinium Chloride (Id·HCl). Dry methanol (40 ml) was saturated with HCl, 0.33 g of quinazoline Id was added, and the mixture was stirred at room temperature for 2 h. The precipitated Id·HCl (0.2 g), with mp 130-140°C, was removed by filtration. A 0.1 g sample of the salt was heated at 270°C for 1 h, after which the mixture was cooled and triturated with alcohol, and the mixture was filtered. The filtrate was evaporated, and the residue was triturated with ether to give 0.06 g of a light-yellow substance with mp 169-176°C. Lines of two molecular ions with m/e 286 (quinazoline IId) and 272 (quinazoline IIf) are present in the mass spectrum.

1-(p-Dimethylaminobenzyl)-N-formyl-2-naphthylamine (VIIa). A mixture of 4 g (0.028 mole) of β-naphthylamine, 8.35 g (0.056 mole) of p-dimethylaminobenzaldehyde, 17.7 g (0.28 mole) of ammonium formate, and 20 ml of glacial acetic acid was refluxed for 5 h, after which it was cooled and poured into 200 ml of water. The aqueous mixture was neutralized with solid sodium bicarbonate and extracted with $CHCl_3$ (three 50 ml portions). The chloroform extract was dried with magnesium sulfate, the chloroform was removed by distillation, and the residual oil was triturated with ether to give 2.5 g (33%) of amide VIIa with mp 160-162°C (from alcohol). IR spectrum (in CCl_4): 1700 (C=O) and 3390 cm^{-1} (N—H). UV spectrum, λ_{max} (log ε): 207 (4.38), 239 (4.61), and 292 nm (4.00). PMR spectrum (in $CDCl_3$): 2.87 (6H, s, N—CH_3), 4.37 (2H, s, CH_2), and 6.57-8.45 ppm (NH, m, H_{arom} and N—CHO). Found: C 79.1; H 6.5; N 9.4%; M 304. $C_{20}H_{20}N_2O$. Calculated: C 79.0; H 6.6; N 9.2%; M 304.

1-Benzyl-N-formyl-2-naphthylamine (VIIb). A mixture of 3 g (0.021 mole) of β-naphthylamine, 13.2 g (0.210 mole) of ammonium formate, and 15 ml of glacial acetic acid was refluxed for 5 h, after which it was cooled and poured into water. The aqueous mixture was neutralized with solid sodium bicarbonate and extracted with $CHCl_3$. The extract was dried with magnesium sulfate, and the chloroform was removed by chloroform to give a light-yellow oil, which began to crystallize when ether was added. The solid material was removed by filtration and washed with ether to give 2.7 g of a mixture of VIIb and 1,3-diphenyl-1,2-dihydrobenzo[f]quinazoline [2]. The mixture was separated by fractional crystallization from xylene and by chromatography on KSK silica gel by preparative thin-layer chromatography in a chloroform—benzene—alcohol system (20:20:1). The R_f value of amide VIIb was 0.56, and the R_f value of diphenyldihydroquinazoline was 0.10-0.15. A total of 1.35 g of diphenyldihydroquinazoline and 0.86 g of amide VIIb were obtained. The amide had mp 112-113°C (from xylene). IR spectrum (in mineral oil): 1680 (C=O) and 3350 cm^{-1} (N—H). UV spectrum, λ_{max} (log ε): 220 i (4.58), 240 (4.54), 267 (4.39), and 278 nm (4.39). PMR spectrum (in $CDCl_3$): 5.1 (2H, s, CH_2), 8.65 (1H, s, CHO), and 7.28-7.90 ppm (m, H_{arom}). Found: C 83.2; H 5.7; N 5.3%; M 261. $C_{18}H_{15}NO$. Calculated: C 82.9; H 5.7; N 5.4%; M 261.

1-Benzyl-2-naphthylamine (VIII) Hydrochloride. A mixture of 0.5 g (0.19 mmole) of formylamine VIIb and 4 ml of concentrated hydrochloric acid was refluxed for 2 h, after which it was cooled, and the precipitate was removed by filtration to give 0.35 g of the hydrochloride of amine VIII with mp 190-193°C (from alcohol). The product gave a bright-yellow

reaction with p-dimethylaminobenzaldehyde. UV spectrum, λ_{max} (ε): 210-214 (4.82), 244 (5.10), 274 i (3.39), 283 (4.52), 292 (4.47), and 345 nm (3.90). PMR spectrum (in d_6-DMSO): 4.52 (2H, s, CH_2), 6.00 (N—H_{br}), and 7.36-7.95 ppm (m, H_{arom}). Found: C 75.2; H 5.9; N 5.4; Cl 13.5%; M 233. $C_{17}H_{15}N \cdot HCl$. Calculated: C 75.8; H 5.9; N 5.2; Cl 13.2%; M 233 + 36.5.

1-(p-Dimethylaminobenzyl)-N-(p-nitrobenzylidene)-2-naphthylamine (IX). A suspension of 1 g (3.3 mmole) of formylamine VIIa in 10 ml of concentrated hydrochloric acid was refluxed for 2 h, after which it was cooled and poured over ice. The aqueous mixture was neutralized with concentrated NaOH solution and extracted with $CHCl_3$. The extract was dried with magnesium sulfate, and the chloroform was removed by distillation. The residual oil was dissolved in 20 ml of alcohol, 0.3 g (2.0 mmole) of p-nitrobenzaldehyde was added, and the mixture was refluxed for 1 h. It was then allowed to stand in a refrigerator for 3 days, during which a bright-red precipitate formed. The precipitate was removed by filtration to give 0.45 g (34%) of amine IX with mp 147-149°C (from xylene). IR spectrum (in KBr): 1620 cm^{-1} (C=N). UV spectrum, λ_{max} (log ε): 207 (4.60), 231 (4.58), 257 (4.47), 288 (4.41), and 388 nm (3.98). Found: C 76.1; H 5.6; N 10.3%. $C_{26}H_{23}N_3O_2$. Calculated: C 76.4; H 5.6; N 10.3%.

LITERATURE CITED

1. M. A. Mikhaleva, G. N. Chernikova, and V. P. Mamaev, Khim. Geterotsikl. Soedin., No. 9, 1259 (1978).
2. M. A. Mikhaleva, G. N. Chernikova, and V. P. Mamaev, Khim. Geterotsikl. Soedin., No. 1, 100 (1978).
3. V. A. Koptyug (editor), Atlas of the Spectra of Aromatic and Heterocyclic Compounds. Vol. 4. Infrared and Ultraviolet Absorption Spectra of Compounds of the Pyrimidine Series [in Russian], Nauka, Novosibirsk (1974), p. 8.
4. A. R. Katritzky, R. E. Reavill, and F. J. Swinbourne, J. Chem. Soc., B, No. 4, 351 (1966).
5. The Sadtler Standard Spectra, Sadtler Research Laboratory, Philadelphia, NMR Spectrum No. 6142.
6. A. Rosowsky and E. Modest, J. Org. Chem., 31, 2607 (1966).
7. A. Zhunke, Nuclear Magnetic Resonance in Organic Chemistry [Russian translation], Mir, Moscow (1974), p. 41.
8. C. Reid, J. Mol. Spectrosc., 1, 18 (1957).
9. R. H. Martin and J. C. Nouls, Tetrahedron Lett., No. 23, 2727 (1968).
10. T. Keumi, Y. Oshima, and N. Tokura, Bull. Chem. Soc. Jpn., 48, 1065 (1975).
11. B. P. Roques, S. Combrisson, R. Oberlin, and J. Barbet, Tetrahedron Lett., No. 17, 1641 (1974).
12. V. F. Lavrushin and Z. N. Tarakhno, Zh. Org. Khim., 1, 1642 (1965).
13. H. Pines and J. T. Arrigo, J. Am. Chem. Soc., 80, 4369 (1958).
14. O. Tsuge and M. Tashiko, Bull. Chem. Soc. Jpn., 38, 184 (1965).
15. V. A. Bushmelev and V. A. Koptyug, Zh. Org. Khim., 6, 1853 (1970).
16. V. A. Koptyug, V. A. Bushmelev, and T. N. Gerasimova, Zh. Obshch. Khim., 37, 140 (1967).
17. V. G. Shubin, A. A. Tabatskaya, B. G. Derendyaev, D. V. Korchagina, and V. A. Koptyug, Zh. Org. Khim., 6, 2072 (1970).
18. M. Sekiya and K. Suzuki, Chem. Pharm. Bull. (Tokyo), 22, 1788 (1974).
19. K. Takagi and M. Hubert-Habart, Chim. Ther., 5, 264 (1970).
20. W. Girke, Tetrahedron Lett., No. 39, 3537 (1976).