SYNTHESIS OF AMINALS FROM 8-AMINOQUINOLINE

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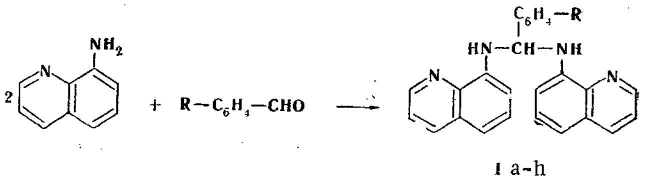
The reaction of 8-aminoquinoline with substituted aromatic aldehydes leads to aminals, which are the only reaction products. The reaction with 1-formyl-2-hydroxynaphthalene proceeds with the formation of a Schiff base. The UV and mass spectra of the aminals are discussed.

The reaction of secondary amines with aromatic aldehydes is a well-known method for the preparation of aminals. The hemiacetals that are formed in the first step in these cases cannot be stabilized with splitting out of water and the formation of a Schiff base but add a second amino component. In the case of primary aromatic amines the prevailing tendency is the formation of Schiff bases. Aminals of primary amines are obtained by an indirect method starting from the amides of acids and salts [1, 2].

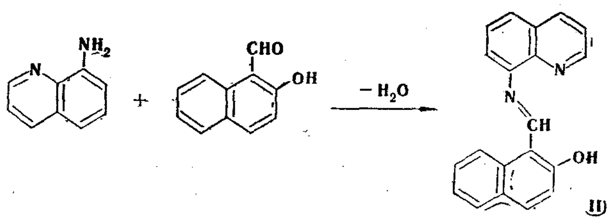
In contrast to these data, we were unable to obtain Schiff bases from 8-aminoquinoline. In its reaction with aromatic aldehydes, instead of the expected azomethines, we obtained primarily aminals. This can be explained by the existence of a rather strong hydrogen bond between the amino groups in the resulting aminals and the heteroring nitrogen atom. In the reaction with aldehydes one therefore observes the addition of a second molecule of the amine instead of splitting out of water and the formation of an azomethine. A similar reaction was previously noted for 2-aminopyridines [3].



I a-h

I a R=H, b R=*p*-Cl, c R=*p*-Br, d R=*p*-F, e R=*p*-OCH$_3$, f R=*p*-NO$_2$, g R=*m*-NO$_2$, h R=*p*-(CH$_3$)$_2$N

We were able to obtain a Schiff base only in the reaction of 8-aminoquinoline with 1-formyl-2-hydroxynaphthalene. The same reaction pathway was observed in the reaction of 8-aminoquinoline with salicylaldehyde and 2-formylpyridine [4, 5]. The presence of a hydroxy group in the α position relative to the formyl group evidently directs the reaction to favor of the formation of azomethine II.



II

A narrow distinct band at 3400 cm^{-1}, which often shows up in the form of a doublet and corresponds to stretching vibrations of an N—H group, is observed in the IR spectra of Ia-h. The UV spectra of the aminals are similar to the spectra of aromatic amines [6]; as compared with the spectrum of 8-aminoquinoline, a significant increase in the intensities of the α and p bands and a bathochromic shift of the α band [7] are observed in this case. The mass spectra of aminals Ia-h do not contain molecular-ion peaks, but intense [M − 144]$^+$ peaks due to the loss of an 8-aminoquinoline molecule and corresponding to the arylidene derivatives

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TABLE 1. Characteristics of Aminals Ia-h

Compound	R	mp, °C	Reaction time, min	UV spectrum, λ_{max}, nm (log ε)	Mass spectrum, $[M-144]^+$	Found, %			Empirical formula	Calc., %			Yield, %
						C	H	N		C	H	N	
Ia	H	89*	15—20	204 (4,27), 228 (4,32), 297 (4,22)	232	79,7	5,2	14,2	$C_{25}H_{20}N_4$	79,7	5,4	14,9	56
Ib	*p*-Cl	118*	30	239 (4,56), 252 (4,53), 343 (4,07)	266	73,3	5,1	13,5	$C_{25}H_{19}ClN_4$	73,1	4,7	13,6	89
Ic	*p*-Br	135*	30	239 (4,56), 251 (4,54), 342 (4,00)	310	65,5	4,4	12,0	$C_{25}H_{19}BrN_4$	65,9	4,2	12,3	82
Id	*p*-F	112†	5	245 (4,54), 253 (4,52), 348 (4,00)	250	—	—	14,3	$C_{25}H_{19}FN_4$	—	—	14,2	50
Ie	*p*-OCH_3	82‡	2—3	247 (4,56), 288 (4,13), 343 (4,07)	262	76,8	5,6	13,6	$C_{26}H_{22}N_4O$	76,8	5,5	13,8	48
If	*p*-NO_2	143**	2—3	254 (4,72), 358 (3,97) (dioxane)	277	71,3	4,6	16,2	$C_{25}H_{19}N_5O_2$	71,2	4,5	16,6	79
Ig	*m*-NO_2	95†	without heating	240 (4,21), 251 (4,17)	—	71,6	4,6	16,5	$C_{25}H_{19}N_5O_2$	71,2	4,5	16,6	31
Ih	*p*-$(CH_3)_2N$	88^b	5	250 (4,76), 347 (4,41)	275	77,4	6,1	16,8	$C_{27}H_{25}N_5$	77,3	6,0	16,7	52

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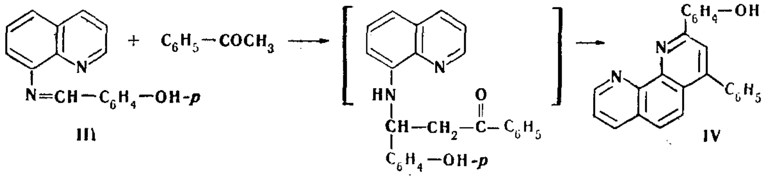
*From ethanol. †From benzene—hexane. ‡From hexane.
**From toluene.

of 8-aminoquinoline formed as a result of fragmentation are present.

Attempts to synthesize phenanthrolines by the reaction of aminals with acetophenone were unsuccessful. Under the conditions of the synthesis the aminals underwent cleavage to give α,β-unsaturated ketones due to the reaction of acetophenone with the aldehyde part of the aminal. Phenantholine derivative IV was obtained by the reaction of azomethine III with acetophenone, as in the synthesis of benzo-f-quinolines [8]:



Spectral studies confirm the proposed structure of IV. Bands at 3070 and 3050 cm^{-1} (=C—H) and at 1620 cm^{-1} (C=N), as well as a number of bands at 1500-1600 cm^{-1} (aromatic ring C=C bonds), are observed in the IR spectrum. Bands corresponding to N—H stretching vibrations are absent. The mass spectrum contains an intense molecular-ion peak and peaks corresponding to $[M - C_6H_5]^+$ and $[C_6H_5]^+$ ion fragments. The UV spectrum is similar to the spectrum of the isoelectronic phenanthrne [9]. The results of elementary analysis correspond to the structure of IV.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra were recorded with a Specord UV-vis spectrophotometer. The mass spectra were obtained with an MAT-311 mass spectrometer at an ionization energy of 70 eV and 50-150°C.

Phenylbis(8-quinolylamino)methane (Ia). A mixture of 1.06 g (0.01 mole) of benzaldehyde and 1.5 g (0.01 mole) of an alcohol solution of 8-aminoquinoline was heated on a water bath at 80°C for 15-20 min, after which it was cooled and allowed to stand for 24 h. The precipitated resinified product was treated with hexane and crystallized from ethanol. IR spectrum: 3400 (N—H) and 1335 cm^{-1} (C—N).

Aminals Ib-h (Table 1) were similarly obtained. Characteristic narrow intense bands at 3400-3410 (N—H) and 1335-1340 cm^{-1} (C—N) were observed in the IR spectra of all the aminals.

N-(2-Hydroxynaphthylidene)-8-aminoquinoline (II). Butanol solutions of 1.44 g (0.01 mole) of 8-aminoquinoline and 1.72 g (0.01 mole) of 1-formyl-2-hydroxynaphthalene were mixed, and the mixture was refluxed for 3 min. It was then cooled, and the resulting dark-red precipitate was crystallized from dimethylformamide (DMF) to give 2.6 g (90%) of a product with mp 221°C. IR spectrum: 1628 cm^{-1} (C=N). UV spectrum (in alcohol), λ_{max} (log ε): 204 (4.63), 229 (4.70), 354 (4.41), 454 (4.43), and 482 nm (4.49). Found: C 80.3; H 4.7; N 9.3%; M^+ 298 (by mass spectrometry). $C_{20}H_{14}N_2O$. Calculated: C 80.5; H 4.7; N 9.4%; M 298.

N-(2-Hydroxybenzylidene)-8-aminoquinoline (III). A 1.5-ml (0.01 mole) sample of salicylaldehyde was added to a warm alcohol solution of 1.44 g (0.01 mole) of 8-aminoquinoline, during which the solution darkened immediately and resinified. The mixture was cooled, and the resulting resin was crystallized from ethanol to give 1.9 g (78%) of orange crystals with mp 73°C. IR spectrum: 1620 cm^{-1} (C=N). UV spectrum (in ethanol), λ_{max} (log ε): 253 (4.59) and 332 nm (3.84). Found: C 77.3; H 4.9; N 11.0%; M^+ 248 (by mass spectrometry). $C_{16}H_{12}N_2O$. Calculated: C 77.4; H 4.9; N 11.3%; M 248.

2-Hydroxyphenyl-4-phenyl-1,10-phenanthroline (IV). A mixture of 2.48 g (0.01 mole) of Schiff base II and 2 ml of acetophenone was stirred at 100°C for 2 h in the presence of 10 drops of concentrated HCl and 1 ml of nitrobenzene. It was then cooled, and the resinified precipitate was treated with ammonia, washed with hexane, and crystallized from nitromethane to give 1.2 g (35%) of a product with mp 232-233°C. UV spectrum (in alcohol), λ_{max} (log ε): 232 (4.54), 250 (4.56), 291 (4.53), 333 (3.53), and 363 nm (3.39). Found: C 82.2; H 5.0; N 8.0%; M^+ 348 (by mass spectrometry). $C_{24}H_{16}N_2O$. Calculated: C 82.7; H 4.6; N 8.0%; M 348.

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