THE SYNTHESIS OF DERIVATIVES OF BENZO[g]QUINOLINE

V. N-Acyl-1, 2, 34-tetrahydro-4-alkyl(aryl)iminobenzo[g]quinolines*

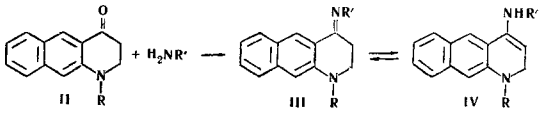
A. F. Bekhli, N. P. Kozyreva, and N. P. Kostyuchenko

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 1, pp. 71–73, 1970

UDC 547.832.5:07:543.422.4.6:541.67

A series of N-acyl-1, 2, 3, 4-tetrahydro-4-alkyl(aryl) iminobenzo[g]quinolines has been obtained by the condensation of N-acyl-1, 2, 3, 4-tetrahydro-4-oxobenzo[g]quinolines with primary amines.

In order to explain the mechanism of the condensation of 1, 2, 3, 4-tetrahydro-4-oxobenzo[g]quinoline (I) with amines, the similar reaction with amines of its N-acyl derivatives (II) has been examined. It is shown that II reacts with primary aliphatic and aromatic amines to form N-acyl-1, 2, 3, 4-tetrahydro-4-alkyl(aryl)iminobenzo[g]quinolines (III). The azomethine structure III is confirmed



by an examination of its UV, IR, and NMR spectra.

These compounds, in the UV spectra, do not show the maxima at 220–238 nm which are characteristic of enamines (see table).

In the IR spectra, no NH stretching bands occur, but bands are seen at 1670 and 1640 cm^{-1} which are apparently due to the azomethine ($\nu_{C=N}$) and amide ($\nu_{C=O}$) groups. This interpretation of the IR spectrum is supported by the literature data for acyl derivatives of tetrahydroquinoline [2]. The NMR spectra of a series of III (see table) show two triplets, each of intensity two proton units. The positions of these signals permit their assignment to the protons of the two methylene groups in positions 2 and 3. No signals are observed which are attributable to the protons of a double bond, which is further support for the exclusion of the tautomeric enamine form IV.

The bases obtained are readily hydrolyzed in acid media with the formation of I, II, or a mixture of I and II.

Comparison of the reactivity of 1, 2, 3, 4-tetrahydro-4-oxoquinolines, or their N-acyl derivatives [3, 4] with that of a series of benzo[g]quinolines in their reaction with amines, shows that the reactivity of the latter is the greater. This apparently is related to the reduced electron density at the 4-carbon atom of the benzo[g]-quinolines, which results in an increase in its electrophilicity and ease of attack by amines. The presence of a somewhat greater partial positive charge in this position in benzo[g]quinoline, in comparison with quinoline, is apparently due to the electron-acceptor influence of the additional benzene ring, as shown by comparison of their molecular diagrams [5].

EXPERIMENTAL

The UV spectra were taken on an SF-4 spectrophotometer in 96% ethanol. The IR spectra were recorded on a UR-10 spectrometer with KBr discs. The NMR spectra were obtained on a JNM-4H-100 instrument, using hexadeuterobenzene as solvent. Chemical shifts are given in ppm, relative to the signal of tetramethylsilane taken as zero.

N-Acyl-1, 2, 3, 4-tetrahydro-4-oxobenzo[g]quinolines (II). The methods of preparation of the N-acetyl- and N-benzoyl-derivatives have been described previously [6].

*For part IV, see [1].

N-Acyl-1, 2, 3, 4-tetrahydro-4-alkyl(aryl)iminobenzo[g]quinolines (III)

Compound	R	R′	Mp, ° C (solvent)	Molecular formula	Found, %		Calculated, %		UV Spectra		NMR Spectra δ, ppm		Yield, %
					N	Cl	N	Cl	λ_{max}, nm	lg ε	2-CH_2	3-CH_2	
IIIa	$COCH_3$	n-C_4H_9	116—117 (Heptane)	$C_{19}H_{22}N_2O$	9.30 9.23		9.52		255—260 345	4.66 2.93	3.67	2.11	66
IIIb	$COCH_3$	$C_6H_4OC_2H_5$-p	154—155 (Alcohol)	$C_{23}H_{22}N_2O_2$	7.56 7.40		7.81		264 355—360	4.71 3.76	3.59	2.34	75
IIIc	COC_6H_5	$C_6H_4OCH_3$-p	196—197 (Heptane)	$C_{27}H_{22}N_2O_2$	6.90 7.19		6.90		246 270—272 360—365	4.44 4.47 3.69	3.72	2.31	69
IIId	$COC_6H_3Cl_2$-2.4	$C_6H_4OCH_3$-p	195—196 (Alcohol)	$C_{27}H_{20}Cl_2N_2O_2$	6.37 6.35	14.60 14.43	5.89	14.92	246 266 360	4.58 4.67 3.74			93
IIIe	$COC_6H_3Cl_2$-2,4	$C_6H_4OC_2H_5$-p	148—149 (Alcohol)	$C_{28}H_{22}Cl_2N_2O_2$	5.75 5.58	14.25 14.15	5.72	14.49	265 355	4.71 3.81			61
IIIf	$SO_2C_6H_4CH_3$-p	$C_6H_4OCH_3$-p	199—200 (Acetone)	$C_{27}H_{24}N_2O_3S$*	6.26 6.50		6.14		260 360	4.78 3.94			57

*Found, %: S 6.78, 6.94. Calculated, %: S 7.02.

N-(2',4'-Dichlorobenzoyl)-1,2,3,4-tetrahydro-4-oxobenzo[g]quinoline was obtained in a similar way in 82% yield, mp 190–191° C (from alcohol), as a cream-colored crystalline powder, soluble in most organic solvents. Dilute alcoholic solutions show a violet fluorescence. Found, %: Cl 18.70, 18.82; N 3.85, 3.95. Calculated for $C_{20}H_{13}Cl_2NO_2$, %: Cl 19.15; N 3.78%.

N-Tosyl-1,2,3,4-tetrahydro-4-oxobenzol[g]quinoline was obtained by condensation of I with toluene-p-sulphonyl chloride in pyridine, in 52.8% yield, mp 133–134° C (from heptane), as a white powder which was readily soluble in most organic solvents. Found, %: N 4.19, 4.03; S 9.23. Calculated for $C_{20}H_{17}NO_3S$, %: N 4.00; S 9.12.

N-Acyl-1,2,3,4-tetrahydro-4-alkyl(aryl)iminobenzol[g]quinolines (III). A mixture of 0.01 mole of II, 0.02 mole of the amine and 15 ml of dry isopentanol was boiled with stirring for 3 hr, water being removed azeotropically. After removal of volatile reaction products, the residue crystallized. The compounds were obtained as cream-colored (IIIa–IIIc), yellow (IIIf) or lemon-yellow (IIId, IIIe) crystalline solids, readily soluble in most organic solvents, but insoluble in water.

Hydrolysis of III. A mixture of 0.5 g of III, 2.5 ml of conc H_2SO_4, 1 ml of acetic acid, and 0.5 ml of water was heated at 85–90° C for 1 hr. The mixture was worked up in the usual way to give I (~90% from IIIa and IIIb), or a mixture of I and II (42 and 54% from IIIc, respectively), or II (~90% from IIIe).

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11 January 1968

Martsionovskii Institute of Medicinal Parasitology and
Tropical Medicine, Moscow

Ordzhonikidze All-Union Scientific-Research Institute of
Pharmaceutical Chemistry, Moscow