# REACTIONS OF 2-ARYL(HETARYL)METHYLENE-3-OXOQUINUCLIDINES WITH BIFUNCTIONAL NUCLEOPHILIC REAGENTS

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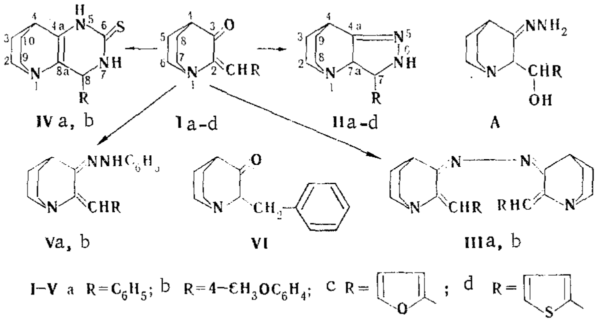
The reactions of 2-aryl(hetaryl)methylene-3-oxoquinuclidines with hydrazine hydrate, thiourea, and phenylhydrazine gave, respectively, 7-phenyl-7,7a,dihydropyrazolo[3,4-b]quinuclidine, 7-(4'-methoxyphenyl)-7,7a-dihydropyrazolo[3,4-b]quinuclidine, 7-(2'-thienyl)-7,7a-dihydropyrazolo-[3,4-b]quinuclidine, 3,3'-azinobis(2-benzylidenequinuclidine), 3,3'-azinobis[2-(4'-methoxybenzylidene)quinuclidine], 6-thio-8-phenyl-5,6,7,8-tetrahydropyrimido[5,4-b]quinuclidine, 2-benzylidene-3-oxoquinuclidine phenylhydrazone, and 2-(4'-methoxybenzylidene)-3-oxoquinuclidine phenylhydrazone. The structures of the compounds were confirmed by the IR and $^{1}$H and $^{13}$C NMR spectra.

We have previously studied the reaction of 2-methylene-3-oxoquinuclidine with hydrazine and thioureas. In the first case we obtained 7,7a-dihydropyrazolo[3,4-b]quinuclidine, while in the second case we obtained 4-α-hydroxy-6-thia-4a,5,6,7,8,8a-hexahydropyrimido[5,4-b]quinuclidines. The latter were unstable compounds: opening of the hexahydropyrimidine ring to give N-(3-oxo-2-quinuclidylmethyl)thioureas was observed in aqueous solutions at room temperature [1].

It seemed of interest to study the reactions of bifunctional nucleophilic reagents with 2-aryl- and 2-heteroarylmethylene-3-oxoquinuclidines (I), in which the olefinic bond, owing to conjugation with the aryl and heteroaryl groups, has a lower degree of electrophilicity than in 2-methylene-3-oxoquinuclidine.

For this, we carried out the reactions of I with hydrazine hydrate, thiourea, and phenylhydrazine.

The starting 2-benzylidene-, 2-(4-methoxybenzylidene)-, 2-furylmethylene-, and 2-thienylmethylene-3-oxoquinuclidines (Ia-d), which were obtained by condensation of 3-oxoquinuclidine with, respectively, benzaldehyde, p-methoxybenzaldehyde, furfural, and 2-formylthiophene [2], had trans configurations. As in the case of trans-2-benzylidene-3-oxoquinuclidine [2], trans isomers Ic and Id were converted to the cis isomers by the action of hydrogen chloride in solution in methylene chloride.



Unsaturated ketones I were subjected to reaction with an equimolar amount of hydrazine hydrate in alcohol by brief heating or with excess reagent at 20°C. Under these conditions the reaction took place at both functional groups to give 7-substituted 7,7a-dihydropyrazolo[3,4-b]quinuclidines (II) in higher than 80% yields, whereas the formation of a pyrazoline ring did not occur in the reaction of I with hydrazine hydrate in xylene in the presence of catalytic amounts of p-toluenesulfonic acid with removal of the water by azeotropic distillation, but 3,3'-azinobis(2-arylidenequinuclidines) (III), the structure of which is in agreement with the results of elementary analysis and mass spectroscopy, were formed.

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TABLE 1. Parameters of the $^1$H NMR Spectra of I, II, IV, and V

| Compound | Chemical shifts, δ, ppm | | | |
|---|---|---|---|---|
| | α | β | γ[a] | R and R[b] |
| trans-Ic[c] | 2,8—3,4 | 1,9—2,2 | 2,61 qn | 6,97 s (9-H); 7,26 m (3'-H); 6,47 q (4'-H); 7,52 m (5'-H) |
| cis-Ic[c] | 2,8—3,3 | 1,9—2,1 | 2,67 qn | 6,73 s (9-H); 7,53 m (3'-H); 6,52 q (4'-H); 8,03 m (5'-H) |
| trans-Id[c] | 2,7—3,3 | 1,9—2,1 | 2,61 qn | 7,28 s (9-H); 7,34 m (3'-H); 7,02 q (4'-H); 7,25 m (5'-H) |
| cis-Id[c] | 2,8—3,3 | 1,8—2,1 | 2,70 qn | 7,02 s (9-H); 7,08 m (3'-H); 7,48—7,58 m (4'-H, 5'-H) |
| IIa[d] | 3,3—3,9 | 2,0—2,3 | 3,24 qn | 4,83 d (7a-H), $J_{7aH7H}=13$ Hz; 5,27 d (7-H); 7,3—7,6 m (Ph) |
| IIb[d] | 3,3—3,9 | 2,0—2,3 | 3,23 qn | 4,77 d (7a-H), $J_{7aH7H}\approx 13$ Hz; 5,22 d (7-H); 6,87 m (2'-H, 6'-H); 7,42 m (3'-H, 5'-H); 3,79 s ($OCH_3$) |
| IIc[d] | 3,3—3,9 | 2,0—2,3 | 3,24 qn | 5,0 d (7a-H), $J_{7aH7H}\approx 13$ Hz; 5,39 d (7-H); 6,3—6,5 m (3'-H, 4'-H); 7,45 ks (5'-H) |
| IId[d] | 3,3—3,9 | 2,0—2,3 | 3,22 qn | 4,69 d (7a-H), $J_{7aH7H}\approx 13$ Hz; 5,61 d (7-H); 6,9—7,4 m (3'-H, 4'-H, 5'-H) |
| IVa[c] | 2,6—3,2 | 1,3—2,2 | 2,67 qn | 5,06 d (8-H), $J_{7H8H}\approx 2$ Hz; 6,87 ks and 8,36 br s (5,7-NH); 7,34 s (Ph) |
| IVb[c] | 2,5—3,2 | 1,4—2,1 | 2,55 qn | 5,01 d (8-H), $J_{7H8H}\approx 2$ Hz; 6,55 ks and 7,42 br s (5,7-NH); 7,28 m (2'-H, 6'-H); 6,87 m (3'-H, 5'H); 3,80 s ($OCH_3$) |
| Va[c] | 2,9—3,1 | 1,7—2,0 | 2,9—3,1 | 6,94 s (=CH—Ph); 7,94 m (2'-H, 6'-H); 7,0—7,4 m (3'-H, 4'-H, 5'-H, 2"-H—6"-H) |
| Vb[c] | 2,9—3,3 | 1,7—2,0 | 2,9—3,3 | 6,9 s (=CH—Ph); 7,92 m (2'-H, 6'H); 6,8—7,4 (3'-H, 5'-H, 2"-H—6"-H); 3,81 s ($OCH_3$) |

[a] The abbreviation "qn" denotes a quintet. [b] The hydrogen atoms of R are indicated by one apostrophe, while the hydrogen atoms of R' (furyl, thiophenyl, and phenyl) are indicated by two apostrophes. [c] In $CDCl_3$. [d] In $CD_3COOD$.

The results of the reaction of I with hydrazine hydrate in xylene compelled us to investigate the structure of II in greater detail.

According to the results of elementary analysis, II contain a molecule of crystallization water. Since structure A may also correspond to the indicated elementary composition, to establish the structure of IIa-d we studied their $^1$H and $^{13}$C NMR spectra. Two doublets of coupling protons ($J \approx 13$ Hz) with chemical shifts of 3.7-3.9 and 4.6-4.8 ppm are observed in the $^1$H NMR spectra (Table 1), in addition to signals of the protons of methylene groups, the 4-H proton, and the protons of substituent R. These doublets can be assigned both to the signals of the 7-H and 7a-H protons in structure II and to the 1-H and 9-H protons in structure A. Thus the data from the $^1$H NMR spectra do not make it possible to choose between structures II and A. The signal at 60-77 ppm in the $^{13}$C NMR spectra of II should be assigned to the $C_7$ atom. To solve the problem as to whether this signal may correspond to the carbon atom in alternative structure A, the chemical shift of the carbon atom in IIc ($R = C_6H_5$) at 60.0 ppm was compared with $\delta_{C_9} = 33.0$ in the spectrum of the investigated model compound VI. The difference $\Delta\delta = d_{C_9(VI)} - \delta_{C_7(IIc)} = 27$ ppm can be regarded as the effect of replacement of the hydrogen atom attached to $C_9$ in VI by a heteroatom. It is known that replacement of the hydrogen atom attached to the sp$^3$-hybridized carbon atom by a hydroxy group gives rise to a 41-48 ppm weak-field shift of this atom in the $^{13}$C NMR spectrum, while the analogous effect of the NHR group is 31-37 ppm [3]. It follows from the data presented above that the difference in the shifts $\Delta\delta = 27$ ppm that we found is in much better agreement with the increment of the NHR group than of the OH group. This serves as weighty evidence in favor of the proposed three-ring structure II for the compounds.

In the case of 2-methylene-3-oxoquinuclidine the reaction with hydrazine hydrate at 20°C proceeds ambiguously, and three-ring compound II (R = H) can be isolated in only 14% yield [1].

The reaction of unsaturated ketones I with thiourea by heating in alcohol in the presence of equimolar amounts of sodium ethoxide led to 6-thio-8-aryl-5,6,7,8-tetrahydropyrimido[5,4-b]quinuclidines (IV) in higher than 90% yields. The formation of 6-hydroxy derivatives of hexahydropyrimido[5,4-b]quinuclidines, which was observed in the reaction of thiourea with 2-methylene-3-oxoquinuclidine, was not observed in this case.

TABLE 2. Parameters of the $^{13}$C NMR Spectra of II, IV, V, and VI

| Compound | Chemical shifts, δ, ppm | | | | | |
|---|---|---|---|---|---|---|
| | α | α' | β | β' | γ | R and R'[a] |
| IIa[b] | 42,0t<br>48,2t | 74,4 d | 22,3 t<br>31,3 t | 163,8 s | 26,8d | 66,3 d ($C_7$); 140,9 s ($C_{1'}$); 126,8 d; 127,8 d ($C_{2'}$, $C_{6'}$ and $C_{3'}$, $C_{5'}$); 126,7 d ($C_{4'}$) |
| IIc[b] | 42,0t<br>48,0t | 71,5 d | 22,3 t<br>31,4 t | 153,0 s | 26,8d | 60,0 ($C_7$); 163,8 s ($C_{2'}$); 107,1 d ($C_{3'}$); 110,1 d ($C_{4'}$); 141,85 d ($C_{5'}$) |
| IVa[b] | 49,8t<br>49,5t | 121,4 s[c] | 28,6 t | 136,0 s[c] | 27,0d | 57,6 d ($C_8$); 172,7 s ($C_6$); 143,07 s* ($C_{1'}$); 130,0 d ($C_{2'}$, $C_{6'}$); 126,6 d ($C_{3'}$, $C_{5'}$); 127,9 d ($C_{4'}$) |
| IVb[b] | 49,5t<br>49,8t | 121,5 s[c] | 28,6 t | 135,28 s[c] | 26,9d | 57,0 d ($C_8$); 172,4 s ($C_6$); 135,8 s* ($C_{1'}$); 127,8 d ($C_{2'}$; $C_{6'}$); 113,3 d ($C_{3'}$, $C_{5'}$); 158,3 ($C_{4'}$); 54,9 q ($OCH_3$) |
| Vb[d] | 47,4 t | 148,3 t[c] | 25,9 t | 145,2 s[c] | 24,9d | 115,8 d (=CH); 129,0 s ($C_{1'}$); 129,0 d ($C_{2'}$, $C_{6'}$); 113,4 d ($C_{3'}$, $C_{5'}$); 158,5 s ($C_{4'}$); 55,1 q ($OCH_3$); 143,2 s ($C_{1''}$); 112,7 d ($C_{2''}$, $C_{6''}$); 131,4 d ($C_{3''}$, $C_{5''}$); 119,7 d ($C_{4''}$) |
| VId | 41,0t<br>48,8t | 71,4d | 26,7 t<br>25,1 t | 221,9 s | 40,0d | 33,6 m ($C_9$); 138,9 s ($C_{1'}$); 128,5 d and 128,2 d ($C_{2'}$, $C_{6'}$ and $C_{3'}$, $C_{5'}$); 126,1 d ($C_{4'}$) |

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[a] The carbon atoms in R are indicated by one apostrophe, while the carbon atoms in R' are indicated by two apostrophes. [b] In DMSO. [c] The reverse assignment of the signals is possible. [d] In $CDCl_3$.

The structure of IVa, b was confirmed by data from the $^1$H and $^{13}$C NMR spectra. The numbers of quaternary carbon atoms and CH, $CH_2$, and $CH_3$ groups determined from the $^{13}$C NMR spectra with incomplete decoupling of the protons correspond to the indicated cyclic structure. The signal at 172 ppm ($C_6$) indicates that IVa, b exist in the amino thione form, while the signal at 57 ppm corresponds to the $C_8$ atom.

In the $^1$H NMR spectra recorded in $CDCl_3$ the signal of the 8-H proton (≈5 ppm) is a doublet with spin–spin coupling constant (SSCC) J ≈2 Hz due to coupling of the 8-H proton with the labile $N_7$–H proton; this is an additional confirmation of the existence of IVa, b in the amino thione form.

In contrast to the reactions of I with hydrazine hydrate and thiourea, heating I with phenylhydrazine in both alcohol and acetic acid leads to the formation of 2-arylidene-3-oxoquinuclidine phenylhydrazones (V) due to the fact that the process takes place only at the oxo group of the unsaturated ketones.

The data from the $^{13}$C NMR spectra of V are in agreement with the proposed structures.

## EXPERIMENTAL

The $^1$H and $^{13}$C NMR spectra were recorded with a Varian XL-100 A-12 spectrometer with operating frequencies of 100 MHz for the protons and 25.2 MHz for the $^{13}$C atoms; the internal standard was tetramethylsilane. The IR spectra of mineral oil suspensions of the compounds were recorded with a Perkin-Elmer 599 spectrometer. The mass spectra were obtained with a Varian MAT-112 spectrometer with direct introduction of the samples into the source; the ionizing-electron energy was 70 eV, and the temperature of the ionization chamber was 180°C.

Substances Ia, b were obtained by the method in [2].

trans-2-Furfurylidene-3-oxoquinuclidine (Ic). A 10-g (80 mmole) of 3-oxoquinuclidine and 7.6 g (80 mmole) of furfural were added to a solution of 0.15 g of sodium hydroxide in 20 ml of ethanol, and the mixture was refluxed for 40 min. It was then decolorized with charcoal and cooled, and the precipitate was removed by filtration and washed with ethanol to give 8 g (49.3%) of a product with mp 89-91°C (from ethanol). IR spectrum: 1612 (C=C) and 1700 cm$^{-1}$ (C=O). Found: C 70.8; H 6.5; N 6.8%; M$^+$ 203. $C_{12}H_{13}NO_2$. Calculated: C 70.9; H 6.5; N 6.9%.

trans-2-(2'-Thienylmethylene)-3-oxoquinuclidine (Id). A mixture of 5 g (40 mmole) of 3-oxoquinuclidine, 4.48 g (40 mmole) of 2-formylthiophene, and 0.1 g of sodium hydroxide in 25 ml of ethanol was maintained at 20°C for 30 h. The resulting precipitate was removed by filtration and washed with ethanol to give 6.84 g (78%) of a product with mp 123-124°C (from isopropyl alcohol). IR spectrum: 1612 (C=C) and 1696 cm$^{-1}$ (C=O). Found: C 65.6; H 6.0; N 6.6; S 14.5%; M$^+$ 219. $C_{12}H_{13}NOS$. Calculated: C 65.7; H 6.0; N 6.4; S 14.6%.

7-Phenyl-7,7a-dihydropyrazolo[3,4-b]quinuclidine (IIa). A 0.96-g (19 mmole) sample of hydrazine hydrate was added to a solution of 4 g (19 mmole) of 2-benzylidne-3-oxoquinuclidine [2] in 40 ml of ethanol, and the mixture was heated until a homogeneous solution was obtained. The solution was cooled and allowed to stand at 20°C for 1 h, and the resulting precipitate was removed by filtration and washed with ethanol to give 3.5 g (82%) of a product with mp 125-126°C (from ethanol). IR spectrum: 1605 (C = N); 3290, 3300 $cm^{-1}$ (NH, OH). Found: C 68.4; H 7.9; N 17.4; $H_2O$ 7.3%; $M^+$ 227. $C_{14}H_{17}N_3 \cdot H_2O$. Calculated: C 68.6; H 7.8; N 17.1; $H_2O$ 7.3%.

7-(4'-Methoxyphenyl)-7,7a-dihydropyrazolo[3,4-b]quinuclidine (IIb). A suspension of 2.5 g (10 mmole) of 2-(4'-methoxybenzylidene)-3-oxoquinuclidine in 20 ml of hydrazine hydrate was maintained at 20°C for 8 days with periodic shaking, during which the yellow crystals of the starting ketone vanished, and white crystals of IIb formed. The precipitate was removed by filtration and washed thoroughly with ethanol to give 2.6 g (98.4%) of a product with mp 124-126°C (from isopropyl alcohol). IR spectrum: 1610, 1645 (C = N); 3100, 3290, 3300 $cm^{-1}$ (NH, OH). Found: C 65.0; H 7.5; N 15.2%; $M^+$ 275. $C_{15}H_{19}N_3O \cdot H_2O$. Calculated: C 65.4; H 7.7; N 15.3%.

7-(2'-Furyl)-7,7a-dihydropyrazolo[3,4-b]quinuclidine (IIc). This compound, with mp 129-130°C (from ethanol), was similarly obtained in 87% yield. IR spectrum: 1595 (C = N); 3292, 3300 $cm^{-1}$ (NH, OH). Found: C 61.3; H 7.0; N 18.2%; $M^+$ 217. $C_{12}H_{15}N_3O \cdot H_2O$. Calculated: C 61.3; H 7.2; N 17.9%.

7-(2'-Thienyl)-7,7a-dihydropyrazolo[3,4-b]quinuclidine (IId). This compound, with mp 131-132°C (from isopropyl alcohol), was similarly obtained in 87.3% yield (the reaction time was 18h). IR spectrum: 1630-1660 (C = N) and 3320 $cm^{-1}$ (NH, OH). Found: C 57.6; H 6.8; N 16.6%; $M^+$ 233. $C_{12}H_{15}N_3S \cdot H_2O$. Calculated: C 57.3; H 6.8; N 16.7%.

3,3'-Azinobis(2-benzylidenequinuclidine (IIIa). A catalytic amount of p-toluenesulfonic acid was added to a solution of 2 g (9.4 mmole) of 2-benzylidene-3-oxoquinuclidine and 0.46 g (9.4 mmole) of hydrazine hydrate in 100 ml of xylene, and the mixture was heated for 6 h with removal of the water by azeotropic distillation. It was then allowed to stand at 20°C for 60 h, and the resulting precipitate was removed by filtration and washed with ethanol to give 1.45 g (72%) of a product with mp 290-292°C (from DMF). IR spectrum: 1584 and 1678 $cm^{-1}$ (C = C, C = N). Found: C 79.3; H 7.4; N 13.3%; $M^+$ 422. $C_{28}H_{30}N_4$. Calculated: C 79.6; H 7.2; N 13.2%.

3,3'-Azinobis[2-(4'-methoxybenzylidene)quinuclidine] (IIIb). A solution of 2 g (8 mmole) of 2-(4'-methoxybenzylidene)-3-oxoquinuclidine, 0.82 g (16 mmole) of hydrazine hydrate, and a few crystals of p-toluenesulfonic acid in 100 ml of xylene was heated for 17 h with removal of the water by azeotropic distillation. The solvent was removed by vacuum distillation, and the residue was triturated with ether to give 0.4 g (20%) of a product with mp 255-257°C (from DMF). Found: C 74.9; H 7.0; N 11.7%; $M^+$ 482. $C_{30}H_{34}N_4O_2$. Calculated: C 74.6; H 7.1; N 11.6%.

6-Thio-8-phenyl-5,6,7,8-tetrahydropyrimido[5,4-b]quinuclidine (IVa). A 3-g (14 mmole) sample of 2-benzylidene-3-oxoquinuclidine and 1.07 g (14 mmole) of thiourea were added to a solution of sodium ethoxide obtained from 0.33 g (14 mg-atom) of sodium and 30 ml of ethanol, and the mixture was refluxed for 3 h. The resulting precipitate was removed by filtration and washed with 50 ml of ethanol to give 3.5 g (91.8%) of a product with mp 235-237°C (from isopropyl alcohol). IR spectrum: 1700 (C = C); 3170, 3360 $cm^{-1}$ (NH, OH). Found: C 61.9; H 6.8; N 14.2%; $M^+$ 271. $C_{15}H_{17}N_3S \cdot H_2O$. Calculated: C 62.2; H 6.6; N 14.5%. The hydrochloride had mp 216-218°C. Found: C 55.1; H 6.2; Cl 11.2; N 12.6; S 9.8%. $C_{15}H_{17}N_3S \cdot HCl \cdot H_2O$. Calculated: C 55.3; H 6.1; Cl 10.9; N 12.9; S 9.8%.

6-Thio-8-(4'-methoxyphenyl)-5,6,7,8-tetrahydropyrimido[5,4-b]quinuclidine (IVb). A mixture of 3 g (12 mmole) of 2-(4'-methoxybenzylidene)-3-oxoquinuclidine, 0.93 g (12 mmole) of thiourea, and 30 ml of an ethanol solution of sodium ethoxide obtained from 0.28 g (12 mg-atom) of sodium was refluxed for 18 h, after which it was cooled, and the resulting precipitate was removed by filtration and washed with ethanol. IR spectrum: 1707 (C = C) and 3200-3260 $cm^{-1}$ (NH, OH). Found: C 62.0; H 6.0; N 13.5%; $M^+$ 301. $C_{16}H_{19}N_3OS \cdot 0.5H_2O$. Calculated: C 62.1; H 5.8; N 13.5%.

2-Benzylidene-3-oxoquinuclidine Phenylhydrazone (Va). A) A solution of 2 g (9.4 mmole) of 2-benzylidene-3-oxoquinuclidine and 1.02 g (9.4 mmole) of phenylhydrazine in 15 ml of ethanol was refluxed for 3 h, after which it was cooled, and the precipitate was removed by filtration to give 1.58 g (55.6%) of a product with mp 193-196°C (from ethanol). IR spectrum: 1600 (C = C – C = N) and 3350 $cm^{-1}$ (NH). Found: C 79.3; H 6.9; N 14.0%. $C_{20}H_{21}N_3$. Calculated: C 79.2; H 7.0; N 13.8%.

B) A solution of 2 g (9.4 mmole) of 2-benzylidene-3-oxoquinuclidine and 1.02 g (9.4 mmole) of phenylhydrazine in 30 ml of acetic acid was refluxed for 4 h, after which it was cooled, neutralized with 50% potassium carbonate solution, and extracted with chloroform. The solvent was removed by distillation, and the residue was recrystallized from ethanol to give 1.01 g (35.5%) of a product with mp 193-196°C.

C) A mixture of 3 g (14 mmole) of 2-benzylidene-3-oxoquinuclidine, 1.52 g (14 mmole) of phenylhydrazine, and 30 ml of toluene was refluxed for 8 h with removal of the water by azeotropic distillation in the presence of a catalytic amount of p-toluenesulfonic acid. It was then cooled, and the precipitate was removed by filtration and washed with toluene to give 1.42 g (33%) of a product with mp 193-196°C (from ethanol). The substances obtained by the three methods were identical with respect to their IR spectra.

2-(4'-Methoxybenzylidene)-3-oxoquinuclidine Phenylhydrazone (Vb). This compound was synthesized in the same way as phenylhydrazone Va by method A; the reaction time was 8 h. Workup gave a product with mp 176-178°C (from isopropyl alcohol) in 36% yield. Found: C 75.8; H 7.3; N 12.5%. $C_{21}H_{23}N_3O$. Calculated: C 75.6; H 7.0; N 12.6%.

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# SYNTHESIS AND PROPERTIES OF SUBSTITUTED 10-PHENYL-10-HYDROXY-10H-PYRIDO[2,3-b]CHROMENES

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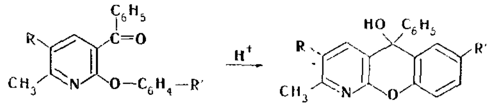
It is shown that 2-aryloxy-3-benzoyl-6-methylpyridines undergo cyclization to the corresponding derivatives of 10-phenyl-10-hydroxy-10H-pyrido[2,3-b]chromenes under the influence of concentrated sulfuric acid in glacial acetic acid. The $pK_{R^+}$ values of the products, which range from −6.28 to −9.27 and correlate with the $\sigma_p^0$ and $\sigma_R^0$ meta substituent constants, depending on the position of the substituent, were determined by spectrophotometry.

In previous papers [1, 2] we studied the acid−base transformations of 10-aryl-10-hydroxy-pyrido[2,3-b]-chromenes. In order to extend these studies to ascertain the transmission of electronic effects we used a previously described method [1] to synthesize 10-phenyl-10-hydroxy-10H-pyrido[2,3-b]chromenes with substituents in both the benzene and pyridine rings of this heterocyclic system and determined their ionization constants. We used 2-aryloxy-3-benzoyl-6-methylpyridines (Ia-g) as the starting substances [3].



Ia-g IIa-g

Under the influence of concentrated sulfuric acid in glacial acetic acid ketones Ia-g undergo cyclization to give substituted 10-phenyl-10-hydroxy-10H-pyrido[2,3-b]chromenes (IIa-g; Table 1). The rate of cyclization depends on the substituents in both the pyridine ring and in the phenoxy group Ia-g. Compounds IIa-g are colorless crystalline substances. Their structure was confirmed by their IR spectra, in which bands at 3590 $cm^{-1}$ ($\nu$OH) are observed, and, in contrast to the spectra of starting ketones Ia-g, a band of a carbonyl group is absent. The UV spectra of alcohol solutions of IIa-g contain maxima at 270 and 292 nm and an absorption band at 220 nm. As in the case of previously described analogous compounds, in sulfuric acid they undergo stepwise conversion with the formation of III ions and IV ions, which is accompanied initially by a bathochromic shift of the spectrum and then by the appearance of maxima at 374-392 and 480 nm.

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