*Chemistry of Heterocyclic Compounds, Vol. 42, No. 1, 2006*

# CONDENSED ISOQUINOLINES. 19*. SYNTHESIS OF 1'-R-SPIRO[6a,11b-DIAZABENZ[*e*]ACEANTHRYLENE-6(7H),4'(1'H)-PYRIDINE]-5,7(12H)-DIONES

**V. M. Kysil, L. M. Potikha, R. M. Gutsul, V. A. Kovtunenko, and A. V. Turov**

*During acylation of 7-isonicotinoyl-6,12-dihydro-5H-isoquino[2,3-a]quinazolin-5-one or its alkylation followed by treatment with organic bases, spirocyclization occurs with formation of derivatives of a novel heterocyclic system: 1'-acyl- and 1'-alkylspiro[7H,12H-6a,11b-diazabenz[e]aceanthrylene-6(5H),4'(1'H)-pyridine]-5,7-diones. We have studied the spectral properties of the synthesized spirans. We have shown that 7-nicotinoyl-6,12-dihydro-5H-isoquino[2,3-a]quinazolin-5-one does not undergo an analogous reaction of repeated acylation, while treatment of its quaternary salt with bases leads to a complex mixture of unidentified products.*

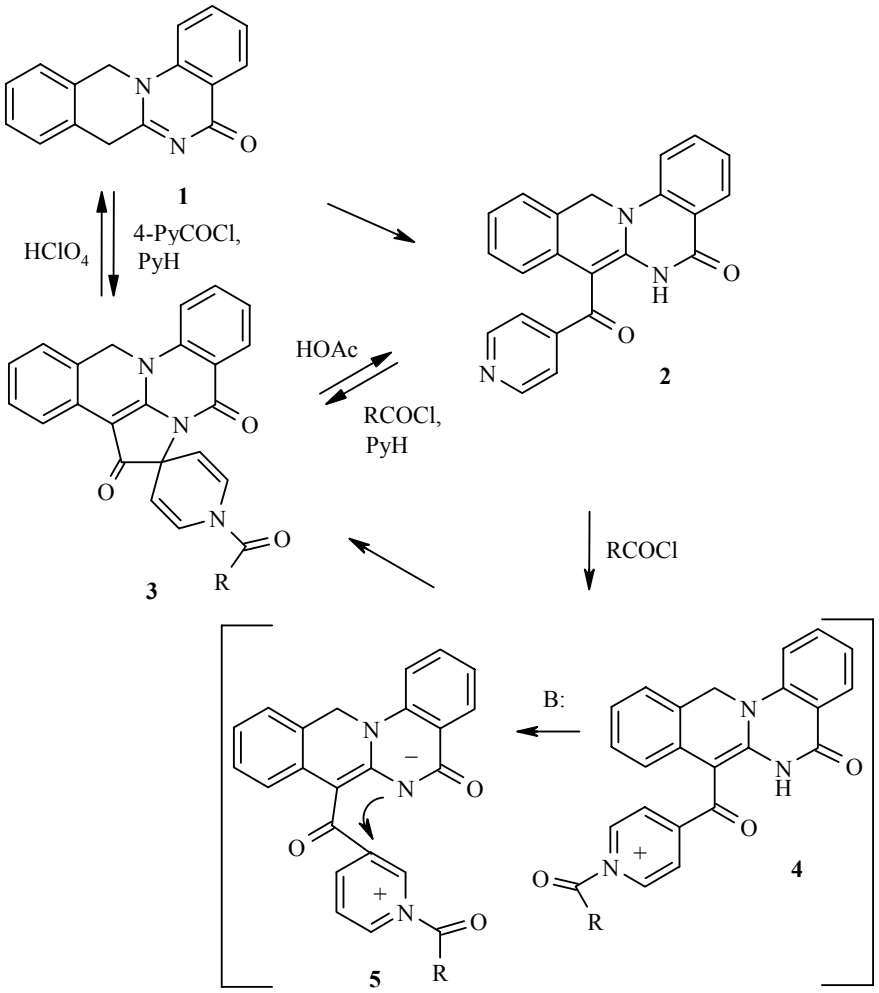
**Keywords:** isoquinoline, condensed isoquinolines, spiropyridines, spiro compounds, isonicotinoylation, spirocyclization.

Earlier [1, 2] we studied acylation of 7,12-dihydro-5H-isoquino[2,3-*a*]quinazolin-5-one (**1**) by carboxylic acid anhydrides and carboxylic acid halides, leading to 7-acyl-6,12-dihydro-5H-isoquino[2,3-*a*]-quinazolin-5-ones, including (when starting from isonicotinoyl chloride) 7-isonicotinoyl-6,12-dihydro-5H-isoquino[2,3-*a*]quinazolin-5-one (**2**). This paper (also see our brief communication [3]) is devoted to an unexpected property of this compound which is manifested in its ability to undergo further acylation in the presence of excess isonicotinoyl chloride. Since in a number of other acyl derivatives we see this property only in the isonicotinoylation product **2**, it was logical to hypothesize that it is due to the presence of an additional nucleophilic center: the nitrogen atom of the isonicotinoyl group in the structure of **2**. Based on the spectral characteristics (see below) for the product of repeated acylation of compound **2**, also obtained by acylation of isoquinoquinazolone **1** by a two-fold excess of isonicotinoyl chloride and also literature data [4-6] on the behavior of various enamines under conditions for acylation by excess isonicotinoyl chloride, we assign this compound the structure of 1'-isonicotinoylspiro[7H,12H-6a,11b-diazabenz[*e*]aceanthrylene-6(5H),4'(1'H)-pyridine]-5,7-dione (**3a**). Its formation can be represented as the result of successive deprotonation of the initially formed acylpyridinium salt **4** when treated with base, and further intramolecular attack by the anionic center at the electron-poor γ-position of the pyridinium ring in the intermediate zwitterion **5**.

* For Communication 18, see [1].

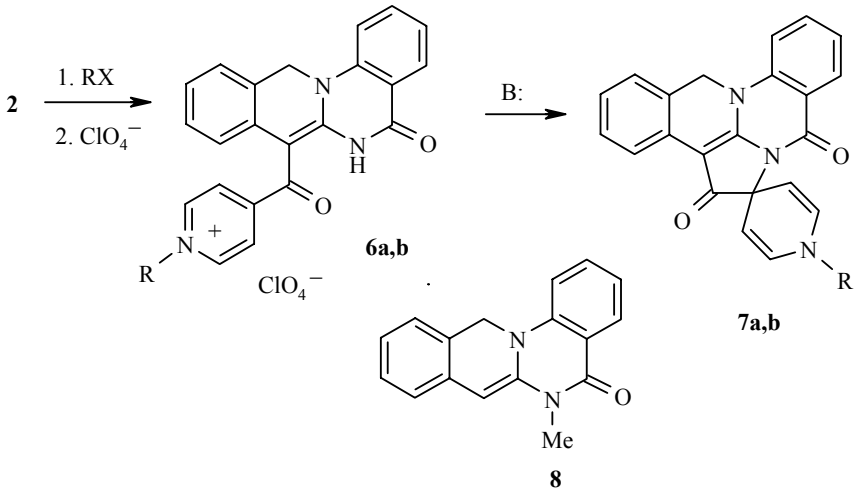
Taras Shevchenko Kiev National University, Kiev 01033, Ukraine; e-mail: vkovtunenko@univ.kiev.ua.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 113-122, January, 2006. Original article submitted January 23, 2004.




**3 a** R= Py-4, **b** R= Me, **c** R= $C_6H_4OMe$-4, **d** R= $C_6H_4F$-4

Analogous spirocyclization turned out to be possible when treated with other acylating agents besides isonicotinoyl chloride, which we showed for the examples of synthesis of 1'-acetyl-, 1'-(4-methoxybenzoyl)-, and 1'-(4-fluorobenzoyl)spiro[7H,12H-6a,11b-diazabenz[*e*]aceanthrylene-6(5H),4'(1'H)-pyridine]-5,7-diones **3b-d** by acylation of the isonicotinoyl derivative **2** by the corresponding acid chlorides in anhydrous pyridine medium. Furthermore, the proposed sequence of conversions in the spirocyclization under discussion is also supported by data obtained in alkylation of compound **2** by methyl tosylate and ethyl iodide. When solutions of these alkylating agents are heated with isoquinoquinazolone **2** in acetonitrile, quaternization of the latter occurs at the nitrogen atom of the pyridinium ring with formation of the 1-methyl- and 1-ethyl-4-[(5-oxo-6,12-dihydro-5H-isoquino[2,3-*a*]quinazolin-7-yl)carbonyl]pyridinium salts **6a,b**, characterized in the form of the perchlorates. Such a structure for the reaction products is indicated by the significant (0.5-0.7 ppm) downfield shift of the signals from the α- and β-pyridine protons in their $^1$H NMR spectra, observed as doublets with spin–spin coupling constant 6.5 Hz, compared with the signals for the corresponding protons of the starting compound **2**. The signals from the proton at the $N_{(6)}$ atom participating in the intramolecular hydrogen bond also proved to be shifted, but only upfield. This shift is due to the electronegative effect of the pyridinium ring on the carbonyl group and consequently the weakening of the chelate H bond.




**6**, **7 a** R= Me, **b** R= Et

The red-orange salts **6**, when their pyridine solutions are treated with triethylamine and then precipitated with water, are converted to pale-yellow compounds with a nonsalt structure, which is indicated by the absence of an anion according to elemental analysis data and the IR spectra. In the $^1$H NMR spectra of these compounds (Table 1), there is no signal from a proton, exchanging with the $D_2O$, on the $N_{(6)}$ atom, nor are there downfield signals for the pyridine ring. Moreover, we observe two two-proton doublets upfield with $J$ = 7.6 (**7a**) and $J$ = 7.2 Hz (**7b**), typical of *cis*-olefin protons [7], while the signals from the alkyl substituents on the pyridine nitrogen atom are shifted upfield, which provides a basis for assigning the structure 1'-methyl- and 1'-ethylspiro[7H,12H-6a,11b-diazabenz[*e*]aceanthrylene-6(5H),4'(1'H)-pyridine]-5,7-diones **7a,b** to the products obtained.

An analogous pattern is observed in the $^1$H NMR spectra of acyl-substituted spiropyridines **3**, except that the acyl group causes a downfield shift of the doublets from the α-dihydropyridine protons toward the aromatic absorption region. This makes it difficult to observe them, but the position of these signals (in the 7.2-7.5 ppm region) was established from the change in the multiplicity under double resonance conditions when irradiated at the resonant frequency of the β-protons. Furthermore, in the spectrum of the 1-acetyl derivative **3b** when saturated under NOE conditions at the resonant frequencies of the protons in the 1-$COCH_3$ group and the β-pyridine protons, the integrated intensity of the signal from the α-pyridine protons increases by 37% and 22% respectively. A characteristic feature of the spectra of acylspiropyridines **3** turned out to be the effect of the nature of the radical R on the absorption pattern for the protons of the dihydropyridine moiety. In the spectra of 1'-isonicotinoyl and 1'-acetyl derivatives **3a,b**, recorded at 25°C, we observe a broadened multiplet at 5.02 ppm (**3a**) and two broadened multiplets for the β-pyridine protons at 5.00 ppm and 4.92 ppm (**3b**), while the resonance for the α-pyridine protons is observed as two poorly resolved multiplets with a large difference in chemical shifts (Table 1). As the temperature of the solutions is raised, the signals from the β-pyridine protons coalesce; and at 80°C their resonance is observed as doublets with spin–spin coupling constant 6.8 Hz (**3a**) and 7.6 Hz (**3b**), while the signals from the α-pyridine protons are observed as broadened multiplets. An analogous observation in the spectra of structurally similar systems was described previously in [4, 5], and we agree with the authors of those papers that such a pattern is due mainly to a dynamic equilibrium between the hindered conformations of the acyl group, as a result of hindrance to rotation about the amide C–N bond. Nevertheless, we also do not rule out the possibility of a contribution from hindered conformational conversions of the dihydropyridine ring.

TABLE 1 Spectral Characteristics of Compounds **3a-d**, **7a,b**

| Compound | IR spectrum, $\nu_{C=O}$, $cm^{-1}$ | $^1H$ NMR spectrum, δ, ppm. (*J*, Hz) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 6a,11b-Diazabenz[*e*]aceanthrylene moiety | | | | | | | | Dihydropyridine moiety | | |
| | | H-4, 1H, d | H-8, 1H, d | H-10, 1H, t | H-11, 1H, d | H-9, 1H, t | H-1, H-2, 2H, m | H-3, 1H, t | $C_{(13)}H_2$, 2H, c | H-2', H-6', 2H, d | H-3', H-5', 2H, d | 1'-R |
| **3a** | 1700, 1660 | 8.08 ($^3J$ = 7.2) | 7.97 ($^3J$ = 7.2) | 7.84 ($^3J$ = 8.0) | 7.56* (3H, m) | 7.40 (2H, m, H-9, $H_A$-2',6') | 7.26-7.20 (3H, m, H-1,2, $H_B$-2',6') | 7.11 ($^3J$ = 7.2) | 5.41 | —*[2] (7.25 (m, 80°C)) | 5.02 (m), (5.10 (d, $^3J$ = 6.8, 80°C)) | 8.77 (2H, d, $^3J$ = 5.2, H-2",6"), 7.56 (3H, m, H-11,3",5") |
| **3b** | 1700, 1665 | 8.04 ($^3J$ = 7.2) | 7.98 ($^3J$ = 7.6) | 7.85 ($^3J$ = 8.0) | 7.57 ($^3J$ = 8.2) | 7.40 ($^3J$ = 7.6) | 7.27-7.25 | 7.13 ($^3J$ = 7.2) | 5.41 | 7.51 (1H, m, $H_A$), 7.34 (1H, m, $H_B$) [7.43 (m, 80°C)] | 5.00 (1H, m, $H_A$), 4.92 (1H, m, $H_B$) [4.96 (d, $^3J$ = 7.6, 80°C)] | 2.36 (3H, s, $CH_3$) |
| **3c** | 1700, 1667 | 8.08 ($^3J$ = 7.2) | 7.96 ($^3J$ = 7.6) | 7.87 ($^3J$ = 8.0) | 7.57 ($^3J$ = 8.0) | 7.50 ($^3J$ = 7.6) | 7.28-7.23 | 7.13* (3H, m.) | 5.41 | 7.33 ($^3J$ = 8.0) | 5.01 ($^3J$ = 8.0) | 7.62 (2H, d, $^3J$ = 8.0, H-2",6"), 7.13 (3H, m, H-3,3",5"), 3.85 ($OCH_3$) |
| **3d** | 1700, 1665 | 8.07 ($^3J$ = 7.2) | 7.97 ($^3J$ = 8.4) | 7.88 ($^3J$ = 7.6) | 7.58 ($^3J$ = 7.6) | 7.43* (3H, m) | 7.28-7.23 | 7.13 ($^3J$ = 7.2) | 5.41 | 7.32, (2H, m) | 5.06 ($^3J$ = 8.0) | 7.71 (2H, m., H-2",6"), 7.43 (3H, m, H-9,3",5") |
| **7a** | 1690 | 8.03 ($^3J$ = 8.0) | | 7.79 ($^3J$ = 8.0) | 7.52 ($^3J$ = 8.0) | 7.35 ($^3J$ = 8.0) | 7.23 | 7.08 ($^3J$ = 7.6) | 5.39 | 6.51 ($^3J$ = 7.6) | 4.28 ($^3J$ = 7.6) | 3.26 (3H, s, $CH_3$) |
| **7b** | 1700 | 8.04 ($^3J$ = 7.6) | | 7.78 ($^3J$ = 7.6) | 7.51 ($^3J$ = 8.0) | 7.35 ($^3J$ = 7.6) | 7.22 | 7.07 ($^3J$ = 7.6) | 5.39 | 6.56 ($^3J$ = 7.2) | 4.27 ($^3J$ = 7.2) | 3.47 (2H, q, $^3J$ = 7.5, $CH_2$), 1.31 (3H, t, $^3J$ = 7.5, $CH_3$) |

* Overlap of signals, see column 13.

*[2] Overlap of signals, see columns 7, 8.

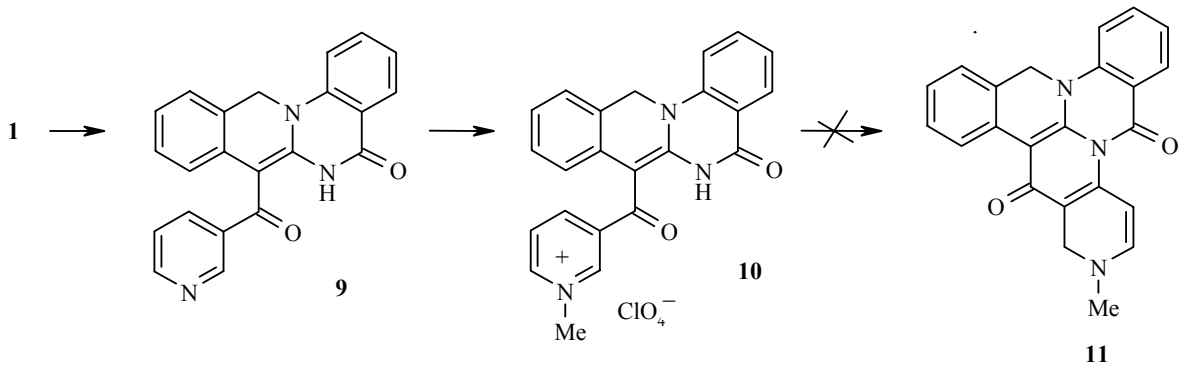
Hindrance of the conformational conversions of the dihydropyridine ring and rotation about the amide C–N bond also leads to splitting of the signals from the α and β carbon atoms in the $^{13}C$ NMR spectra of compounds **3a,b** recorded at 25°C: $C_\alpha$ (129.06, 125.58 ppm) and $C_\beta$ (105.40, 103.85 ppm) in the spectrum of **3b**, $C_\alpha$ (broadened, 128.0 ppm) and $C_\beta$ (broadened, 105.7 ppm) in the spectrum of **3a** (Table 2). The signal at 68 ppm with low intensity is assigned to resonance of the spiro carbons, and the more intense signals at 49 ppm and 88 ppm are assigned to resonance of $C_{(12)}$ and $C_{(4b)}$ respectively, based on comparison of these spectra with the spectrum of the structurally similar compound 6-methyl-5,6-dihydro-12H-isoquino[2,3-*a*]quinazolin-5-one (**8**) [2] and the starting isonicotinoyl derivative **2**, in which the corresponding signals are observed at 48 ppm ($C_{(12)}$) and 82-94 ppm ($C_{(7)}$, Table 2).

In the IR spectra of spiropyridines **3**, **7**, we observe a complex set of strong bands in the 1650-1680 $cm^{-1}$ region, obviously corresponding to stretching vibrations of the C=O and C=C groups.

The mass spectra of all the spiropyridines are characterized by the presence of a molecular ion peak with the theoretically expected value of *m*/*z*. Its intensity for compounds **7** reaches 100%. In the case of the N-acylspiropyridines **3**, as should be expected [8], the most intense peaks correspond to the fragmentary ions $[R'CO]^+$ and $[M–R'CO]^+$, while in the spectrum of the isonicotinoyl derivative **3a** we additionally see the pyridinium ion (81%). In the spectrum of the acetylspiropyridine **3b**, the most intense peak (100%) corresponds to the fragmentary ion formed as a result of the rearrangement with ejection of a ketene molecule that is typical of acetyl derivatives. In the spectra of the alkylspiropyridines **7a,b**, we observe signals from the fragmentary ions formed due to α,β-cleavage relative to the pyridine nitrogen atom ($[M–H]^+$ with intensity 46% and 56% respectively and cleavage at the R–N bond ($[M–R]^+$). The intense signals (46%-47%) with *m*/*z* 93 (**7a**) and 107 (**7b**) are assigned to signals from alkylpyridinium radical ions.

Spiropyridines **3, 7** proved to be quite unstable in acid medium. We should note that this property of a spirodihydropyridine system has also be pointed out by other authors [9]. When we tried to recrystallize acyl derivatives **3** from acetic acid, in all cases we obtained the same compound **2** regardless of the nature of the acyl substituent R. When spiropyridines **3, 7** are treated with perchloric acid, in addition to cleavage of the pyrrole ring, deacylation also occurs with formation of the known perchlorate compound **1** [10]. The hydrolytic instability of 7-acyl-substituted isoquinoquinazolones **2**, but in basic media, has been noted earlier in [11].

A conversion similar to that described above was also used in [4] in synthesis of condensed [1,6]naphthyridines. In this case, enamines of the β-carbolinyl series were treated with excess nicotinoyl chloride. We tried to realize such a scheme with isoquinoquinazolone **1**. But we found that when it was treated with a two-fold excess of nicotinoyl chloride, the only reaction product was 7-nicotinoyl-6,12-dihydro-5H-isoquino[2,3-*a*]quinazolin-5-one (**9**) [2], which does not tend toward further acylation under the conditions for synthesis of spiropyridines **3.**




Like isonicotinoyl-substituted **2**, this compound is quaternized by methyl tosylate at the pyridine nitrogen atom, with formation of the quaternary salt **10**. However, we were unable to accomplish its cyclization to form the corresponding (considering [4]) condensed naphthyridine **11**: when its solutions in pyridine or DMF

TABLE 2. $^{13}C$ NMR Spectra of Compounds **3a-d**

| Compound | Chemical shifts, δ, ppm (*J*, Hz) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 6a,11b-Diazabenz[*e*]aceanthrylene moiety | | | | | | | | Dihydropyridine moiety | | | |
| | $C_{(5)}$ | $C_{(11c)}$ | $C_{(7)}$ | $C_{(11a)}$ | $C_{(1)}$–$C_{(4a)}$, $C_{(7a)}$–$C_{(11)}$ | $C_{(12a)}$ | $C_{(4b)}$ | $C_{(12)}$ | $C_{(2')}$, $C_{(6')}$ | $C_{(3')}$, $C_{(5')}$ | $C_{(4')}$ ($C_{(6)}$) | 1'-R |
| **3a** | 187.64 | 157.70 | 155.53 | 140.04 | 135.94, 128.49, 127.94, 127.61, 126.36, 125.74, 125.06, 124.76, 121.68, 114.88 | 118.90 | 88.32 | 49.30 | 128.00 br. | 105.70 br. | 67.60 | 165.88 (C=O), 151.14 ($C_{(2'',6'')}$) 141.22 ($C_{(4'')}$), 122.70 ($C_{(3'',5'')}$) |
| **3b** | 188.22 | 157.67 | 155.57 | 140.03 | 135.87, 128.45, 127.84, 126.48, 125.68, 124.99, 124.89, 121.68, 114.83 | 119.09 | 88.27 | 49.26 | 129.06, 125.58 | 105.40, 103.85 | 68.03 | 167.81 (C=O), 22.09 ($CH_3$) |
| **3c** | 188.29 | 157.62 | 155.64 | 140.01 | 135.88, 128.45, 127.97, 127.79, 126.47, 125.68, 125.00, 124.87, 121.68, 114.79 | 119.07 | 88.06 | 49.28 | 129.05 | 104.43 | 68.06 | 167.60 (C=O), 162.60 ($C_{(4'')}$), 131.62 ($C_{(2'',6'')}$), 125.35 ($C_{(1'')}$), 114.79 ($C_{(3'',5'')}$), 56.18 ($OCH_3$) |
| **3d** | 188.04 | 157.65 | 155.65 | 140.02 | 135.90, 128.44, 127.95, 127.75, 126.48, 125.71, 125.01, 124.88, 121.68, 114.84 | 119.05 | 88.40 | 49.29 | 128.62 | 105.21 | 67.84 | 166.95 (C=O), 130.08 ($C_{(1'')}$), 164.49 (d, $^1J_{CF}$ = 237.8, $C_{(4'')}$), 131.98 (d, $^3J_{CF}$ = 16, $C_{(2'',6'')}$), 116.65 (d, $^2J_{CF}$ = 22, $C_{(3'',5'')}$) |

TABLE 3. Constants for Synthesized Compounds

| Compound | Empirical formula | Found, % / Calculated, % | | | | mp, °C* | Yield, % |
|---|---|---|---|---|---|---|---|
| | | C | H | Cl | N | | |
| **3a** | $C_{28}H_{18}N_4O_3$ | 73.27 / 73.35 | 3.89 / 3.96 | | 12.24 / 12.22 | 276 | 69 |
| **3b** | $C_{24}H_{17}N_3O_3$ | 72.86 / 72.90 | 4.26 / 4.33 | | 10.70 / 10.63 | 265 | 72 |
| **3c** | $C_{30}H_{21}N_3O_4$ | 73.87 / 73.91 | 4.30 / 4.34 | | 8.65 / 8.62 | 237 | 70 |
| **3d** | $C_{29}H_{18}FN_3O_3$ | 73.16 / 73.26 | 3.85 / 3.88 | | 8.86 / 8.84 | 266 | 71 |
| **6a** | $C_{23}H_{18}ClN_3O_6$ | 58.93 / 59.04 | 3.71 / 3.88 | 7.60 / 7.58 | 9.00 / 8.98 | 249 | 83 |
| **6b** | $C_{24}H_{20}ClN_3O_6$ | 59.75 / 59.82 | 4.04 / 4.18 | 7.41 / 7.36 | 8.81 / 8.72 | 226 | 78 |
| **7a** | $C_{23}H_{17}N_3O_2$ | 75.01 / 75.19 | 4.59 / 4.66 | | 11.49 / 11.44 | 288 | 55 |
| **7b** | $C_{24}H_{19}N_3O_2$ | 75.43 / 75.57 | 4.91 / 5.02 | | 11.12 / 11.02 | 262 | 56 |
| **10** | $C_{23}H_{18}ClN_3O_6$ | 58.95 / 59.04 | 3.80 / 3.88 | 7.61 / 7.58 | 9.01 / 8.98 | 220 | 60 |

* Solvent for recrystallization: nitromethane (**3a-c**), DMF (**3d, 7a,b**).

are treated with bases (triethylamine, aqueous solutions of bases, an alcoholic solution of sodium methoxide), a complex mixture of unidentified products is formed. Obviously this is connected with the possibility of an alternative direction of cyclization occurring (at the α-position of the pyridine ring) and realization of various routes for hydride transfer.

Note that the spirocyclic pyridines **3, 7** described above are derivatives of a heterocyclic system for which no information was available in the literature before our work.

## EXPERIMENTAL

The IR spectra were recorded on an SP3-300 Pye Unicam, KBr disks. The $^1H$ and $^{13}C$ NMR spectra of solutions of the compounds were obtained on a Mercury 400 (Varian) (400 MHz and 100 MHz respectively) in DMSO-$d_6$, internal standard TMS. The mass spectra were recorded on a Finnigan MAT-8200 (ionization by electron impact). The melting points were determined on a Boetius heating stage.

Compounds **2** and **9** were obtained by the procedure given in [2].

**7-Isonicotinoyl-6,12-dihydro-5H-isoquino[2,3-*a*]quinazolin-5-one (2).** The $^{13}C$ NMR spectrum, δ, ppm: 188.44 (7-CO), 162.87 ($C_{(5)}$), 158.91 ($C_{(6a)}$), 155.55 ($C_{(2')}$, $C_{(6')}$), 141.25 ($C_{(4')}$), 132.49 ($C_{(12b)}$), 136.36, 127.97, 127.69, 126.62, 126.36, 126.23, 125.30, 124.55, 116.63 ($C_{(1)}$-$C_{(4a)}$, $C_{(7a)}$-$C_{(11)}$), 123.32 ($C_{(3')}$, $C_{(5')}$), 118.74 ($C_{(11a)}$), 94.10 ($C_{(7)}$), 48.23 ($C_{(12)}$).

**1'-Acylspiro[7H,12H-6a,11b-diazabenz[*e*]aceanthrylene-6(5H),4'(1'H)-pyridine]-5,7-diones 3a-d.** A. 7-Isonicotinoyl derivative **2** (0.35 g, 1 mmol) was dissolved in pyridine (10 ml) with heating. The corresponding acylating reagent (1.2 mmol) was added to the cooled solution. The mixture was boiled for 15 min, cooled, and then water (100 ml) was added. The precipitate formed after 30 min was filtered out and then carefully washed with water and then alcohol.

**1'-Isonicotinoylspiro[7H,12H-6a,11b-diazabenz[*e*]aceanthrylene-6(5H),4'(1'H)-pyridine]-5,7-dione (3a).** Mass spectrum, *m/z* ($I_{rel}$, %): 458 $[M]^{+\cdot}$ (45), 352 $[M - COPy]^+$ (58), 336 (14), 322 (19), 106 $[COPy]^+$ (100), 78 $[Py]^+$ (81), 51 (35).

**1'-Acetylspiro[7H,12H-6a,11b-diazabenz[*e*]aceanthrylene-6(5H),4'(1'H)-pyridine]-5,7-dione (3b).** Mass spectrum, *m*/*z* ($I_{rel}$, %): 395 $[M]^+$ (16), 353 $[M - O{=}C{=}CH_2]^+$ (100), 352 $[M - COCH_3]^+$ (70), 324 (30), 275 (56), 43 $[COCH_3]^+$ (98).

**1'-(4-Methoxybenzoyl)spiro[7H,12H-6a,11b-diazabenz[*e*]aceanthrylene-6(5H),4'(1'H)-pyridine]-5,7-dione (3c)**. Mass spectrum, *m*/*z* ($I_{rel}$, %): 487 $[M]^+$ (6), 352 $[M - COC_6H_4OCH_3]^+$ (4), 322 (5), 135 $[COC_6H_4OCH_3]^+$ (100), 107 $[C_6H_4OCH_3]^+$ (5), 77 $[C_6H_5]^+$ (10).

B. **1'-Isonicotinoylspiro[7H,12H-6a,11b-diazabenz[*e*]aceanthrylene-6(5H),4'(1'H)-pyridine]-5,7-dione 3a** was also obtained by the procedure described above, using as the starting materials the isoquinoquinazoline **1** (0.24 g, 1 mmol) and a 2.5-fold excess of isonicotinoyl chloride (0.35 g, 2.5 mmol). Yield 0.39 g (85%).

**1-Methyl-4-[5-oxo-6,12-dihydro-5H-isoquino[2,3-*a*]quinazolin-7-yl)carbonyl]pyridinium Perchlorate (6a).** A mixture of 7-nicotinoyl isoquinoquinazoline **2** (0.35 g, 1 mmol) and methyl tosylate (0.3 g, 1.6 mmol) in nitromethane (5 ml) was boiled for 4 h. The solvent was evaporated and the oily residue was dissolved in water (10 ml). A saturated $NaClO_4$ solution (3 ml) was added to the solution obtained, then the precipitate formed was filtered out and washed with water and then alcohol. IR spectrum, ν, $cm^{-1}$: 1685 br. (C=O), 3460 (NH). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 14.26 (1H, s, NH); 9.00 (2H, d, $^3J$ = 7.2, H-2',6'); 8.14 (3H, d, $^3J$ = 7.2, H-3',5',4); 8.09 (1H, d, $^3J$ = 8.2, H-1); 7.91 (1H, t, $^3J$ = 8.0, H-2); 7.48 (1H, t, $^3J$ =8.0, H-3); 7.41 (1H, d, $^3J$ = 8.2, H-11); 7.06 (1H, t, $^3J$ = 8.0, H-10); 6.96 (1H, t, $^3J$ = 8.0, H-9); 6.45 (1H, d, $^3J$ = 8.0, H-8); 5.39 (2H, s, $C_{(12)}H_2$), 4.38 (3H, s, $CH_3$).

**1-Ethyl-4-[(5-oxo-6,12-dihydro-5H-isoquino[2,3-*a*]quinazolin-7-yl)carbonyl]pyridinium Perchlorate (6b)** was obtained as salt **6a**, using ethyl iodide. IR spectrum, ν, $cm^{-1}$: 1687 br. (C=O), 3460 (NH). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 14.28 (1H, s, NH); 9.11 (2H, d, $^3J$ = 6.4, H-2',6'); 8.18 (2H, d, $^3J$ = 6.4, H-3',5'); 8.17 (1H, d, $^3J$ = 8.0, H-4); 8.12 (1H, d, $^3J$ = 8.2, H-1); 7.93 (1H, t, $^3J$ = 8.0, H-2); 7.50 (1H, t, $^3J$ = 8.0, H-3); 7.42 (1H, d, $^3J$ = 8.0, H-11); 7.07 (1H, t, $^3J$ = 8.0, H-10); 6.96 (1H, t, $^3J$ = 8.0, H-9); 6.46 (1H, d, $^3J$ = 8.0, H-8); 5.41 (2H, s, $C_{(12)}H_2$); 4.66 (2H, q, $^3J$ = 7.5 ($C\underline{H}_2CH_3$); 1.60 (3H, t, $^3J$ = 7.5, $CH_2C\underline{H}_3$).

**1'-Alkylspiro[7H,12H-6a,11b-diazabenz[*e*]aceanthrylene-6(5H),4'(1'H)pyridine]-5,7-diones 7a,b.** Triethylamine (4 ml) was added to a hot solution of the salt **6a,b** (1 mmol) in pyridine (5 ml). The precipitate falling out of the cooled solution was filtered out, washed with water and then acetone. The precipitate was recrystallized from DMF and light-yellow crystals of **7a,b** were obtained.

**1'-Methylspiro[7H,12H-6a,11b-diazabenz[*e*]aceanthrylene-6(5H),4'(1'H)-pyridine]-5,7-dione (7a).** Mass spectrum, *m*/*z* ($I_{rel}$, %): 367 $[M]^+$ (100), 366 $[M–H]^+$ (46), 352 $[M–CH_3]^+$ (6), 338 (49), 322 (15), 184 (16), 169 (56), 93 $[CH_3 – Py]^+$ (46).

**1'-Ethylspiro[7H,12H-6a,11b-diazabenz[*e*]aceanthrylene-6(5H),4'(1'H)pyridine[-5,7-dione (7b).** Mass spectrum, *m*/*z* ($I_{rel}$, %): 381 $[M]^+$ (100), 380 $[M–H]^+$ (56), 352 $[M–C_2H_5]^+$ (59), 322 (33), 191 (21), 176 (23), 162 (26), 107 $[C_2H_5 – Py]^+$ (47), 79 (23).

**1-Methyl-3-[(5-oxo-6,12-dihydro-5H-isoquino[2,3-*a*]quinazolin-7-yl)carbonyl]pyridinium Perchlorate (10).** A mixture of 7-nicotinoyl isoquinoquinazoline **9** (0.35 g, 1 mmol) and methyl tosylate (0.3 g, 1.6 mmol) in nitromethane (5 ml) was boiled for 5 h. The solvent was evaporated. The oily residue was carefully washed with hexane and then acetone (5 ml) was added. A saturated $NaClO_4$ solution (3 ml) was added to the solution formed, the precipitate was filtered out and washed with acetone. IR spectrum, ν, $cm^{-1}$: 1690 broad (C=O), 3460 (NH). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 14.18 (1H, s, NH); 9.30 (1H, s, H-2'); 9.03 (1H, d, 3*J* = 6.0, H-6'); 8.50 (1H, d, $^3J$ = 8.0, H-4'); 8.15 (1H, d, $^3J$ = 8.0, H-4); 8.11 (1H, d, $^3J$ = 8.2, H-1); 7.97 (1H, m, H-5'); 7.91 (1H, t, $^3J$ = 8.0, H-2); 7.48 (1H, t, $^3J$ = 8.0, H-3); 7.42 (1H, d, $^3J$ = 8.2, H-11); 7.06 (1H, t, $^3J$ = 8.0, H-10); 6.95 (1H, t, $^3J$ = 8.0, H-9); 6.60 (1H, d, $^3J$ = 8.0, H-8); 5.39 (2H, s, $C_{(12)}H_2$); 4.43 (3H, s, $CH_3$).

We would like to thank Z. V. Voitenko (lecturer in the Department of Organic Chemistry, Taras Shevchenko Kiev National University) for providing technical assistance in taking the NMR and mass spectra.

**REFERENCES**


1. L. M. Potikha, N. V. Shkilna, V. M. Kisil, and V. A. Kovtunenko, *Khim. Geterotsikl. Soedin.*, 1362 (2004).
2. V. M. Kisel, V. A. Kovtunenko, L. M. Potikha, A. K. Tyltin, V. S. Nikitchenko, and F. S. Babichev, *Ukr. Khim. Zh.*, **58**, 790 (1992).
3. V. A. Kovtunenko, V. M. Kisil, L. M. Potikha, A. V. Turov, F. S. Babichev, *Ukr. Khim. Zh.*, **59**, 1070 (1993).
4. M. Sainsbury and N. L. Uttely, *J. Chem. Soc., Perkin Trans.*, 2109 (1977).
5. T. Naito, O. Miyata, and I. Ninomiya, *J. Chem. Soc., Chem. Commun.*, **11**, 517 (1979).
6. T. Naito and I. Ninomiya, *Heterocycles*, **15**, 735 (1981).
7. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy* [Russian translation], Mir, Moscow (1968).
8. P. B. Terentiev and A. P. Stankevicius, *Mass Spectroscopic Analysis of Biologically Active Nitrogen Bases* [in Russian], Mokslas, Vilnius (1987), p. 86.
9. D. D. Weller and G. R. Luellen, *Tetrahedron Lett.*, **22**, 4381 (1981).
10. V. M. Kisel, V. A. Kovtunenko, A. V. Turov, A. K. Tyltin, and F. S. Babichev, *Dokl. Akad. Nauk*, **306**, 628 (1989).
11. V. M. Kisel, L. M. Potikha, A. V. Turov, and V. A. Kovtunenko, *Khim. Geterotsikl. Soedin.*, 1258 (2001).