2-Phenyl-4-(4-methoxyphenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene (IIc) reacted similarly with hydroxylamine hydrochloride. The yields of oximes IIIc and IVc in this case were 29% and 45%, respectively.

2-Phenyl-5-oxo-5,6,7,8-tetrahydroquinoline (V). This compound was obtained in 85% yield by the method in [3] from 3 g (0.0123 mole) of 2-[3-phenyl-3-oxopropyl]cyclohexane-1,3-dione, 3.08 g (0.04 mole) of ammonium acetate, and 30 ml of glacial acetic acid.

5-Oxo-5,6,7,8-tetrahydroquinolines Va-d, f, h, i and VIa-d, f, g were obtained by the method in [3].

The characteristics of the newly obtained Vh, i and VIa-d, f, g are presented in Tables 2 and 3.

LITERATURE CITED

1. B. M. Mikhailov, Zh. Obshch. Khim., 7, 2950 (1937).
2. V. G. Kharchenko, L. I. Markova, T. D. Kazarinova, and L. M. Yudovich, Khim. Geterotsikl. Soedin., No. 6, 846 (1985).
3. V. G. Kharchenko, L. I. Markova, Yu. T. Struchkov, A. A. Espenbetov, T. D. Kazarinova, and N. T. Komyagin, Khim. Geterotsikl. Soedin., No. 8, 1085 (1987).
4. V. G. Kharchenko, L. I. Markova, T. D. Kazarinova, and L. Yu. Yudovich, Khim. Geterotsikl. Soedin., No. 7, 915 (1985).
5. A. Maouestian, Y. van Haverbeke, Z. Z. Van den Eynde, and N. de Paun, Bull. Soc. Chim. Belges, 89, 45 (1980).
6. L. I. Lelyukh, K. M. Korshunova, and V. G. Kharchenko, Izv. Vuzov. Khim. Khim. Tekhnol., 12, 1536 (1975).
7. V. G. Kharchenko, L. I. Markova, N. S. Smirnova, K. M. Korshunova, and G. I. Rybina, Zh. Org. Khim., 18, 2184 (1982).

ACETALS OF LACTAMS AND ACID AMIDES

55.* STUDY OF REACTION OF 3-OXOPYRIDINE AND ISOQUINOLIN-3-ONE DERIVATIVES WITH DIMETHYLFORMAMIDE DIETHYL ACETAL

L. T. Guss, L. V. Ershov,
G. A. Bogdanova, and V. G. Granik

UDC 547.833.7'824'421.
51.04:541.124

The reactions of 4-carbamoyl- and 4-cyanopyridin-3-one and 4-cyanoisoquinolin-3-one with DMFA diethyl acetal were studied, and hydrogenated di- and trimethylene derivatives of 2,7-naphthyridine-1,8-dione were synthesized. It was found that O- or N-alkylation reactions of the pyridone fragment of the starting bicyclic compounds take place together with the condensation of the DMFA acetal at the amide amino group or the active methylene unit.

4-Cyano-2,3,5,6-tetrahydro-7H-cyclopenta[1,2-c]pyridin-3-one (II) and 4-cyano-2,3,5,6,7,8-hexahydroisoquinol-3-one (III) have been synthesized previously [2] by reaction of cycloalkylidenecyanoacetamides with DMFA acetal (I). The aim of the present work was to study the properties of these bicyclic compounds further in order to synthesize condensed heterocyclic compounds from them. It was found that the alkaline hydrolysis of the nitrile group of compounds II, III proceeds very slowly, and is preparatively impractical. It was possible using

*For Communication 54, see [1].

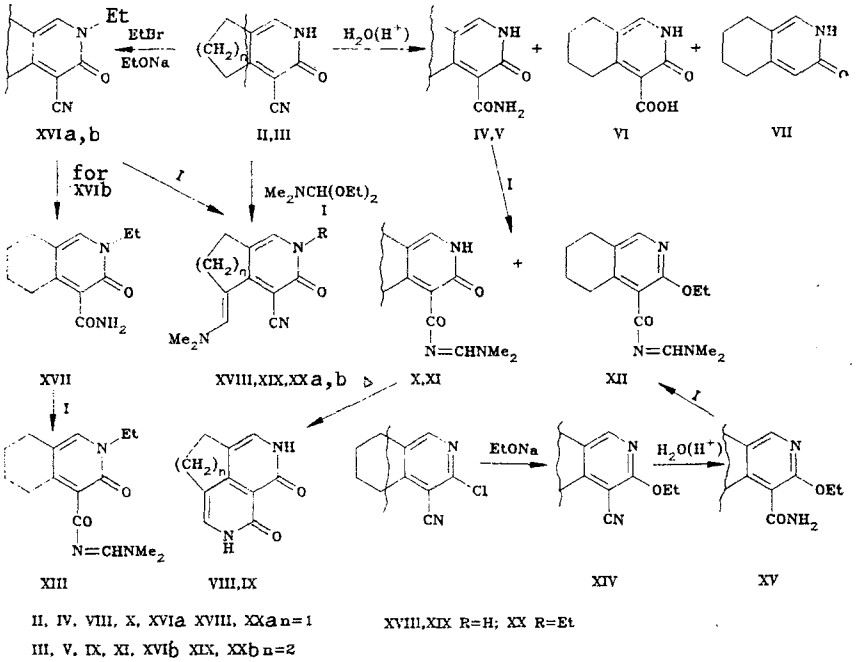
S. Ordzhonikidze All-Union Scientific Research Chemical Pharmaceutical Institute, Moscow 119815.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 215-220, February, 1990. Original article submitted July 4, 1988.

concentrated sulfuric acid to obtain the corresponding carbamido derivatives IV, V in high yields. Taking isoquinolin-3-one III as an example, it was found that the extent of hydrolysis is substantially dependent on the concentration of the sulfuric acid used: in 50% acid, 4-carboxy derivative VI is formed in a good yield, while in 75% acid, hexahydroisoquinolin-3-one VII is formed. A TLC control (Silufol UV-254, chloroform–ethanol, 15:85) showed that under equal conditions (concentrated H_2SO_4, 90-100°C) nitrile II hydrolyzes completely even after 10 min, while nitrile III is still present in the reaction mixture after 1 h of heating, i.e., the presence of a condensed five-membered ring leads to the acceleration of the hydrolysis, compared with the six-membered ring. Considering that the process proceeds in an acid medium, the difference in the electron-acceptor influence of these rings [3] can probably be neglected; the observed phenomenon is possibly due to the higher steric accessibility of the cyano group in the pyridine derivative.

Heating of amides IV, V obtained with acetal I leads to condensation, followed by cyclization and the formation of tricyclic naphthyridines VIII, IX. To determine the paths of formation of these tricyclic compounds, these reactions were carried out under milder conditions, so that it was possible to isolate intermediate N-dimethylamino-methylene derivatives X, XI, which cyclize on heating into naphthyridinediones VIII, IX.

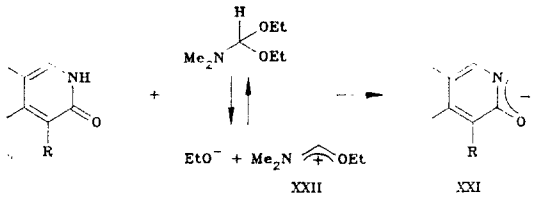
After the separation of amidine XI, from the mother reaction solution, a further compound was isolated, in the IR spectrum of which the absorption band of the pyridone carbonyl was not observed, while in the PMR spectrum the signals of an ethyl group appeared. To clarify the structure of the compound obtained, an alternate synthesis of the possible O- and N-ethyl derivatives XII, XIII was carried out. The ethoxy derivative XII was obtained from 3-chloro-4-cyano-5,6,7,8-tetrahydroisoquinoline [4] by converting it into a hydrogenated 3-ethoxy-4-cyanoisoquinoline (XIV), followed by the saponification of the CN group to the carbamide group and the reaction of the amide XV obtained with acetal I. The N-ethyl derivative XIII was obtained by ethylation of the sodium salt of III with ethyl bromide, followed by hydrolysis of the CN group in the N-ethyl derivative of cyanopyridone XVIb and the reaction of the carbamoyl compound XVIIb with acetal I. Comparison of samples of XII, XIII obtained with the above described compound of an unknown structure showed that in the reaction of amide V with DMFA acetal (I) O-ethylation takes place, as well as the formation of amidine XI. This result is very unexpected: while the N-alkylation by amide-acetals of the oxo derivatives of heterocycles (the 2-pyridones and their derivatives have not been studied previously) was described in the literature [5, 6], the O-alkylation process of these systems until the present work had not been observed.



We also observed the O-alkylation process on another example — an ethoxycarbamoyl compound XV was isolated in a low yield from the mother liquor after the separation of the tri-

cyclic compound IX (on heating compound V with acetal I). Considering that in the case of amides IV, V, the alkylation reaction is complicated by the condensation of acetal I at the carbamoyl amino group and the cyclization into naphthyridinediones VIII, IX, an attempt was made to investigate this process on the example of nitriles II, III. However, it was found that acetal I readily condenses with the oxo-nitriles II, III at the 5-position with the formation of 5-dimethylaminomethylene derivatives XVIII, XIX. Examination of the mother liquors after the separation of enamines XVIII, XIX showed that an alkylation process takes place in this case also. However, in this case the isolated compounds were N-ethyl derivatives XXa, b, which in their spectral characteristics and physical properties were identical with those of compounds obtained independently by the reaction of nitriles XVIa, b* with acetal I.

Thus, the alkylation of carbamoyl compound V with DMFA acetal proceeds at the oxygen atom with the formation of an O-alkyl derivative XII, while that of nitriles II, III – at the nitrogen atom (the N-ethylpyridones XXa, b are obtained). To find out whether in fact the alkylation processes proceed so selectively, we studied the PMR spectra of mixtures obtained after the reaction of the acetal with amide V and nitrile III. The spectra were compared with the corresponding spectra of authentic O- and N-ethyl derivatives (XII and XIII, XIV† and XXb). It was found that in the mixture obtained in the reaction of amide V with acetal I, both O- (XII) and N-ethyl (XIII) derivatives are present in approximately equal ratios. On the contrary, the alkylation of nitrile III with the acetal proceeds regioselectively, and other than the nonalkylated compound XIX, only the N-ethyl derivative XXb is present in the mixture. The signals corresponding to the ethoxy derivative XIV are not observed in the spectrum. The ratio of compounds XXb and XIX is approximately 5-7:1. The explanation for the observed insufficient selectivity of the alkylation depending on the substituents can be attributed to the fact that a mesomeric anion, which is formed in the reaction of acetal I with substituted pyridones is subjected to alkylation: the ambidentate cation XXII that is formed is an electrophilic particle, which undergoes the reaction with the alkylating agent.



If R is a group with a small volume (for example the CN group), the hindrances to the solvation of the oxygen atom on which the excessive electron density is mainly concentrated, are small. The effective solvation of the anionic center on the oxygen atom impedes the O-alkylation, and the process is directed to the nitrogen atom. On the contrary, a bulky substituent (R = CON=CHNMe$_2$) hinders such a solvation and the alkylation process ceases to be regioselective.

EXPERIMENTAL

The IR spectra were run in KBr tablets on a Specord 75-IR spectrophotometer. The PMR spectra were recorded on a Tesla BS-497 (internal standard HMDS) and Varian XL-200 (internal standard TMS) spectrometers. The mass spectra were obtained on a Varian MAT-112 spectrometer.

The characteristics of the synthesized compounds are given in Table 1. The elemental analysis data for C, H, N correspond to the calculated values.

4-Carbamoyl-2,3,5,6-tetrahydro-7H-cyclopenta[1,2-c]pyridin-3-one (IV). A mixture of 1 g (6.7 mmoles) of nitrile II and 10 ml of concentrated H_2SO_4 (d = 1.84 g/ml) was stirred for 1 h at 95-110°C. It was then cooled, made alkaline with a 20% solution of NaOH to pH ≈7-8, and amide IV was filtered off. IR spectrum: 1635 (C=O); 1670 (C=O); 3170, 3350 cm^{-1} (NH_2) PMR spectrum (CF_3COOD): 1.86 (2H, m, 6-CH_2); 2.90 (2H, m, 7-CH_2); 3.10 (2H, m, 5-CH_2); 7.8 ppm (1H, s, 1-H).

*Compound XVIb was obtained by an alternate synthesis by a scheme described above for the preparation of XVIa – by alkylation of nitrile II.

†It was preliminarily shown that under these conditions, the ethoxy-nitrile XIV does not undergo reaction with acetal I.

TABLE 1. Characteristics of Synthesized Compounds

Compound	Empirical formula	M+	mp, °C (solvent)	Yield, % (method)
IV	$C_9H_{10}N_2O_2$	—	>300 (ethanol-water)	88
V	$C_{10}H_{12}N_2O_2$	—	299...301 (water)	90
VI	$C_{10}H_{11}NO_3$	—	227...229 (AcOH+water)	87
VII	$C_9H_{11}NO$	—	201...203 (butyl acetate)	82
VIII	$C_{10}H_8N_2O_2$	188	>300 (AcOH+water)	48 (A); 82 (B)
IX	$C_{11}H_9N_2O_2$	200	>300 (water)	78 (A); 75 (B)
X	$C_{12}H_{14}N_3O_2$	—	173...175 (acetonitrile)	69
XI	$C_{13}H_{17}N_3O_2$	247	220...221 (acetonitrile)	91
XII	$C_{15}H_{21}N_3O_2$	275	163...165 (ethyl acetate)	22 (A); 77 (B)
XIII	$C_{15}H_{21}N_3O_2$	275	155...157 (ethyl acetate)	81
XIV	$C_{12}H_{14}N_2O$	202	78...79 (hexane)	71
XV	$C_{12}H_{16}N_2O_2$	—	174...176 (ethanol-acetonitrile)	70
XVI	$C_{11}H_{12}N_2O$	188	146...148 (2-propanol)	68
XVI	$C_{12}H_{14}N_2O$	200	171...172 (2-propanol)	60
XVII	$C_{12}H_{16}N_2O_2$	—	178...180 (ethyl acetate-ethanol)	54
XVIII	$C_{12}H_{13}N_3O$	215	>320 (DMFA)	52
XIX	$C_{13}H_{15}N_3O$	229	>310 (DMFA)	42
XX	$C_{14}H_{17}N_3O$	243	232...233 (DMFA)	16 (A); 68 (B)
XX	$C_{15}H_{19}N_3O$	255	177...179 (DMFA)	9 (A); 88 (B); 43 (C)

In a similar way, 4-carbamoyl-2,3,5,6,7,8-hexahydroisoquinol-3-one (V) was obtained from nitrile III, IR spectrum: 1630 (C=O); 1670 (C=O); 3200, 3280, 3310, 3410 cm^{-1} (NH_2). PMR spectrum (CF_3COOD): 1.67 (4H, m, 6-CH_2, 7-CH_2); 2.70 (4H, m, 5-CH_2, 8-CH_2); 7.72 ppm (1H, s, 1-H).

4-Carboxy-2,3,5,6,7,8-hexahydroisoquinol-3-one (VI). A solution of 8.9 g (50 mmoles) of nitrile II and 120 ml of 50% H_2SO_4 (d = 1.45 g/ml) was boiled for 3 h. The mixture was cooled, made alkaline with a 20% NaOH solution to pH ≈5-6, and acid VI was filtered off. IR spectrum: 1720 (C=O), 2700-3100 cm^{-1} (OH). PMR spectrum (CF_3COOD): 1.70 (4H, m, 6-CH_2, 7-CH_2); 2.67 (4H, m, 5-CH_2, 8-CH_2); 7.85 ppm (1H, s, 1-H).

In a similar way, 2,3,5,6,7,8-hexahydroisoquinol-3-one (VII) was obtained in a 75% H_2SO_4 with alkalination to pH ≈8. IR spectrum: 1660 cm^{-1} (C=O). PMR spectrum (DMSO-D_6): 1.63 (4H, m, 6-CH_2, 7-CH_2); 2.52 (4H, m, 5-CH_2, 8-CH_2); 6.01 (1H, s, 4-H); 7.05 ppm (1H, s, 1H).

1,2,7,8-Tetrahydro-4,5-dimethylene-2,7-naphthyridine-1,8-dione (VIII). A. A mixture of 1 g (5.6 mmoles) of amide IV, 5 ml of acetal I and 10 ml of DMFA was stirred for 3 h at 100°C. The mixture was then cooled, the precipitate was filtered off, boiled in 10 ml of DMFA, and filtered hot to yield 0.5 g of naphthyridinedione VIII.

B. A solution of 0.5 g (22 mmoles) of amidine X and 5 ml of DMFA was boiled for 2 h 30 min. The mixture was cooled and 0.34 g of compound VIII was filtered off. IR spectrum: 1660 (C=O); 1690 cm^{-1} (C=O). PMR spectrum (CF_3COOD): 3.37 (4H, s, 7-CH_2, 8-CH_2); 7.74 ppm (2H, s, 1-H, 6-H).

1,2,7,8-Tetrahydro-4,5-trimethylene-2,7-naphthyridine-1,8-dione (IX). A. A mixture of 0.97 g (5 mmoles) of amide V, 3 ml of acetal I and 3 ml of absolute ethanol was boiled for 30 min at 140°C. It was then cooled, ground with a 1:1 ether–absolute ethanol mixture, and 0.78 g of compound IX was filtered off.

B. A solution of 1.65 g (6.7 mmoles) of amidine XI in 20 ml of DMFA was boiled for 1 h 30 min, and then evaporated. The residue was ground with water, and 1.02 g of compound IX was filtered off. IR spectrum: 1650 (C=O); 1690 cm^{-1} (C=O). PMR spectrum (CF_3COOD): 1.87 (2H, m, 8-CH_2); 2.76 (4H, m, 7-CH_2, 9-CH_2); 7.67 ppm (2H, s, 1-H, 6-H).

4-[N-(N,N,-Dimethylaminomethylene)carbamoyl]-2,3,5,6,7,8-hexahydroisoquinol-3-one (XI). A 7.2 ml portion of acetal I and 20 ml of absolute ethanol were added to 3.72 g (20 mmoles) of amide V and the mixture was boiled for 1 h. It was then cooled and 4.48 g of compound XI was filtered off. IR spectrum: 1630 (C=O); 1660 cm^{-1} (C=O). PMR spectrum (DMSO-D_6): 1.62

(4H, m, 6-CH_2, 7-CH_2); 2.51 (2H, m, 8-CH_2); 2.59 (2H, m, 5-CH_2); 3.00 (3H, s, NMe_2); 3.17 (3H, s, NMe_2); 7.22 (1H, s, 1-H); 8.39 ppm (1H, s, -N=CH).

In a similar way, 0.9 g of 4-[N-(N,N-dimethylaminomethylene)carbamoyl]-2,3,5,6-tetrahydro-7H cyclopenta[1,2-a]pyridin-3-one (X) was obtained from 1 g (5.6 mmoles) of amide IV. IR spectrum: 1640 (C=O); 1660 cm^{-1} (C=O). PMR spectrum (DCOOD): 1.98 (2H, m, 6-CH_2); 2.70 (2H, m, 7-CH_2); 3.27 (2H, m, 5-CH_2); 3.30 (3H, s, NMe_2); 3.50 (3H, s, NMe_2) 7.65 (1H, s, 1-H); 8.80 ppm (1H, s, -N=CH).

3-Ethoxy-4-[N-(N,N-dimethylaminomethylene)carbamoyl]-5,6,7,8-tetrahydroisoquinoline (XII). A. A 2.6 g portion of acetal I was added to 2.6 g (13.5 mmoles) of amide V and the mixture was stirred for 7 h at 135-140°C. It was then cooled, and amidine XI was filtered off. The mother liquor was evaporated, and after adding 25 ml of water, was extracted with 120 ml (4 × 30) of ethyl acetate. The extracts were dried over Na_2SO_4, filtered, and evaporated to yield 0.8 g of compound XII.

B. A solution of 1 g (4.5 mmoles) of amide XV, 3 ml of acetal I and 10 ml of absolute toluene was boiled for 45 min. It was then cooled and 0.61 g of compound XII was filtered off. The mother liquor was evaporated, whereby another 0.36 g of compound XII was obtained. IR spectrum: 1650 cm^{-1} (C=O). PMR spectrum (DMSO-D_6): 1.22 (3H, t, CH_2CH_3), 1.69 (4H, m, 6-CH_2, 7-CH_2); 2.57 (2H, m, 5-CH_2); 2.65 (2H, m, 8-CH_2); 2.99 (3H, s, NMe_2); 3.17 (3H, s, NMe_2); 4.24 (2H, q, OCH_2CH_3); 7.79 (1H, s, 1-H); 8.42 ppm (1H, s, -N=CH).

N-Ethyl-4-[N-(N,N-dimethylaminomethylene)carbamoyl]-2,3,5,6,7,8-hexahydroisoquinol-3-one (XIII). A 1 ml portion of acetal I and 4 ml of DMFA were added to 0.69 g (3.2 mmoles) of amide XVII and the mixture was stirred for 1 h at 70°C. The mixture was evaporated, the residue was ground with ether, and 0.71 g of compound XIII was filtered off. IR spectrum: 1640 (C=O); 1660 cm^{-1} (C=O). PMR spectrum (DMSO-D_6): 1.20 (3H, t, CH_2CH_3), 1.63 (4H, m, 6-CH_2, 7-CH_2); 2.50 (2H, m, 5-CH_2, 8-CH_2); 2.98 (3H, s, NMe_2); 3.15 (3H, s, NMe_2); 3.84 (2H, q, NCH_2CH_3); 7.37 (1H, s, 1-H); 8.32 ppm (1H, s, -N=CH).

3-Ethoxy-4-cyano-5,6,7,8-tetrahydroisoquinoline (XIV). Sodium ethylate (prepared from 1.5 g of sodium and 30 ml of absolute ethanol) was added to a mixture of 3.38 g (15.6 mmoles) of 3-chloro-4-cyano-5,6,7,8-tetrahydroisoquinoline and 15 ml of DMFA, and the mixture was stirred for 1 h at 100°C. It was then cooled, 25 ml of water was added, and 2.42 g of the ethoxy derivative XIV was filtered off. IR spectrum: 2240 cm^{-1} (CN). PMR spectrum (DMFA-D_7): 1.38 (3H, t, CH_2CH_3); 1.80 (4H, m, 6-CH_2, 7-CH_2); (2H, t, 8-CH_2); 2.86 (2H, t, 5-CH_2); 4.44 (2H, q, OCH_2CH_3); 8.15 ppm (1H, s, 1-H).

3-Ethoxy-4-carbamoyl-5,6,7,8-hexahydroisoquinoline (XV). A 10 ml portion of concentrated H_2SO_4 was added to 1.1 g (5 mmoles) of nitrile XIV, and the mixture was stirred for 1 h at 100°C. It was then cooled, made alkaline to pH ≈9-10 with a 25% NH_4OH solution, and 0.78 g of amide XV was filtered off. IR spectrum: 1645 (C=O); 3200, 3420 cm^{-1} (NH_2). PMR spectrum (CF_3COOD): 1.20 (3H, t, OCH_2CH_3), 1.51 (4H, m, 6-CH_2, 7-CH_2); 2.57 (4H, m, 5-CH_2, 8-CH_2); 4.20 (2H, q, OCH_2CH_3); 7.55 ppm (1H, s, 1-H).

N-Ethyl-4-cyano-2,3,5,6,7,8-hexahydroisoquinol-3-one (XVIb). Sodium ethylate (prepared from 0.23 g of sodium and 7 ml of absolute ethanol) was added to a solution of 2 g (10 mmoles) of nitrile III in 15 ml of absolute ethanol, and the mixture was heated to 55-60°C, 6.5 g (60 mmoles) of ethyl bromide was then added dropwise in the course of 1 h, and the mixture was allowed to stand for 30 min. After evaporating off 7 ml of ethanol, the mixture was cooled, and compound XVIb filtered off. IR spectrum: 1660 (C=O); 2230 cm^{-1} (CN). PMR spectrum (DCOOD): 1.17 (3H, t, CH_2CH_3); 1.56 (4H, m, 6-CH_2, 7-CH_2); 2.40 (2H, m, 8-CH_2); 2.73 (2H, m, 5-CH_2); 3.96 (2H, q, NCH_2CH_3); 7.60 ppm (1H, s, 1-H).

In a similar way, N-ethyl-4-cyano-5,6-dihydro-7H-cyclopenta[1,2 c]pyridin-3-one (XVIa) was obtained from nitrile II, IR spectrum: 1660 (C=O); 2225 cm^{-1} (CN). PMR spectrum ($CDCl_3$): 1.32 (3H, t, CH_2CH_3); 2.15 (2H, m, 6-CH_2); 2.90 (4H, m, 5-CH_2, 7-CH_2); 3.95 (2H, q, NCH_2CH_3); 7.39 ppm (1H, s, 1H).

N-Ethyl-4-carbamoyl-2,3,5,6,7,8-hexahydroisoquinol-3-one (XVII). A solution of 1.5 g (7.4 mmoles) of nitrile XVIb in 15 ml of concentrated H_2SO_4 was stirred for 1 h at 100-110°C. The mixture was cooled, made alkaline to pH ≈10 with a 10% solution of NaOH, and 0.75 g of amide XVII was filtered off. IR spectrum: 1660, 1670 (C=O); 3200, 3370 cm^{-1} (NH_2). PMR spectrum (CF_3COOD): 1.14 (3H, t, CH_2CH_3); 1.51 (4H, m, 6-CH_2, 7-CH_2); 2.45, (2H, m, 8-CH_2), 2.77 (2H, m, 5-CH_2); 4.03 (2H, q, NCH_2CH_3); 7.61 ppm (1H, s, 1-H).

4-Cyano-5-N,N-dimethylaminomethylene-2,3,5,6-tetrahydro-7H-cyclopenta[1,2-c]pyridin-3-one (XVIII). A mixture of 4 g (25 mmoles) of nitrile II, 12 ml of acetal I and 10 ml of absolute ethanol was boiled for 3 h 30 min, was then cooled, the precipitate was filtered off, and washed with 20 ml of hot chloroform. Yield, 2.6 g of compound XVIII. IR spectrum: 1640 (C=O); 2202 cm^{-1} (CN). PMR spectrum (CF_3COOD): 2.30 (2H, m, 7-CH_2); 2.78 (2H, m, 6-CH_2); 3.40 (3H, s, NMe_2, NMe_2); 3.70 (3H, s, NMe_2); 7.55 (1H, s, 1-H); 8.17 ppm (1H, s, =C<u>H</u>-NMe_2).

In a similar way, 4-cyano-5-N,N-dimethylaminomethylene-2,3,5,6,7,8-hexahydroisoquinol-3-one (XIX) was prepared from nitrile III, IR spectrum: 1640 (C=O); 2205 cm^{-1} (CN). PMR spectrum (DMFA-D_7): 1.66 (2H, q, 7-CH_2); 2.35 (2H, t, 8-CH_2); 2.70 (2H, t, 6-CH_2); 3.18 (6H, s, NMe_2); 7.16 (1H, s, 1-H); 7.22 ppm (1H, s, =C<u>H</u>-NMe_2).

N-Ethyl-4-cyano-5-N',N'-dimethylaminomethylene-2,3,5,6-tetrahydro-7H-cyclopenta[1,2-c]-pyridin-3-one (XXa). A. The reaction filtrate and the chloroform washes formed during the preparation of compound XVIII were combined and allowed to stand for 24 h at −2°C. Compound XXa was filtered off.

B. A 1 ml portion of acetal I and 4 ml of absolute toluene were added to 0.37 g (2 mmoles) of compound XVIa. The mixture was boiled for 4 h, then evaporated, and the residue was ground with ether to yield 0.33 g of compound XXa. IR spectrum: 1660 (C=O); 2200 cm^{-1} (CN). PMR spectrum (CF_3COOD): 1.00 (3H, t, $CH_2C\underline{H}_3$); 1.24 (2H, m, 7-CH_2); 2.79 (2H, m, 6-CH_2); 3.48 (3H, s, NMe_2); 3.65 (3H, s, NMe_2); 3.82 (2H, q, $NC\underline{H}_2CH_3$); 7.60 (1H, s, 1-H); 8.15 ppm (1H, s, =C<u>H</u>-NMe_2).

N-Ethyl-4-cyano-5-N',N'-dimethylaminomethylene-2,3,5,6,7,8-hexahydroisoquinol-3-one (XXb). A. In a similar manner as described in procedure A (in the preparation of compound XXa), compound XXb was isolated from the wash solutions from the preparation of compound XIX.

B. Compound XXb was synthesized from compound XVIb in a similar manner as described in procedure B (in the preparation of compound XXa).

C. A 4 ml portion of acetal I and 0.5 g of $AlCl_3$ were added to a solution of 1 g (5.6 mmoles) of nitrile III in 10 ml of dry xylene. The mixture was boiled for 6 h, 3 ml of acetal I and 0.2 g of $AlCl_3$ were then added, and boiling was continued for another 8 h. The mixture was filtered off (from $AlCl_3$), the filtrate was evaporated, the residue was ground with petroleum ether, and 0.5 g of compound XXb was filtered off. IR spectrum: 1660 (C=O); 2210 cm^{-1} (CN). PMR spectrum (DMFA-D_7): 1.23 (3H, t, $CH_2C\underline{H}_3$); 1.66 (2H, q, 7-CH_2); 2.36 (2H, t, 8-CH_2); 2.67 (2H, t, 6-CH_2); 7.23 ppm (1H, s, =C<u>H</u>-NMe_2); 7.43 (1H, s, 1-CH_2); 3.18 (6H, s, NMe_2); 3.88 ppm (2H, q, $NC\underline{H}_2CH_3$).

The physical constants, the analytical and mass spectrometric characteristics, and the yields of the compounds synthesized are given in Table 1.

LITERATURE CITED

1. A. V. Kadushkin, T. V. Golovko, and V. G. Granik, Khim. Geterotsikl. Soedin., No. 6, 830 (1989).
2. V. G. Granik, N. I. Smetskaya, N. A. Mukhina, I. V. Persianova, and V. G. Klimenko, Khim. Geterotsikl. Soedin., No. 3, 1279 (1983).
3. V. G. Granik, Usp. Khim., 11, 207 (1982).
4. V. A. Azimov, V. G. Granik, S. I. Grizik, L. V. Ershov, N. I. Smetskaya, S. D. Yuzhakov, and M. D. Mashkovskii, Khim.-farm. Zh., No. 8, 947 (1979).
5. R. F. Abdulla and R. S. Brinkmayer, Tetrahedron, 35, 1675 (1979).
6. K. D. Philips and J. P. Horwitz, J. Org. Chem., 40, 1856 (1975).