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CHARACTERISTICS OF HETEROCYCLIZATION OF TRIKETONES OF THE 2-(3-OXOPROPYL)CYCLOHEXANE-1,3-DIONE SERIES WITH HYDROXYLAMINE HYDROCHLORIDE

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A rearrangement that leads to the formation of mixtures of 2,4- and 2,3-diaryl-substituted 5-oxotetrahydroquinoline oximes was observed in the heterocyclization of oxo 1,5-diketones of the 2-(3-oxopropyl)cyclohexane-1,3-dione series, as well as in the recyclization of 5-oxotetrahydro-4H-chromenes, in the presence of excess hydroxylamine hydrochloride. It was established that the rearrangement proceeds only when electron-donor groups are present in the starting compounds.

According to the literature data [1], 2-(1,3-diphenyl-3-oxopropyl)cyclohexane-1,3-dione (Ia) on reaction with excess hydroxylamine hydrochloride is converted to 2,4-diphenyl-5-oxo-5,6,7,8-tetrahydroquinoline oxime (IIIa), which under acid-hydrolysis conditions (25% sulfuric acid) forms two tautomeric 5-oxotetrahydroquinolines. However, the character of the tautomerism was not ascertained.

We have reproduced this reaction in accordance with [1]. It was established that 2,3-diphenyl-5-oxo-5,6,7,8-tetrahydroquinoline oxime (IVa) [2] is formed along with the expected 2,4-diphenyl-5-oxo-5,6,7,8-tetrahydroquinoline oxime (IIIa). The acidic hydrolysis of oxime IVa gave 2,3-diphenyl-5-oxo-5,6,7,8-tetrahydroquinoline (VIa), which in [1] was erroneously assumed to be a tautomer of ketone Va. Thus, we have observed the previously unknown rearrangement of triketone Ia during its reaction with excess hydroxylamine hydrochloride.

In order to ascertain the general character of the observed rearrangement, as well as its possible mechanism, we made a systematic study of the reactions of oxo 1,5-diketones Ia-h and 5-oxotetrahydro-4H-chromenes IIa, c, h with hydroxylamine hydrochloride in absolute ethanol (see top of following page).

We found that the reaction of oxo 1,5-diketones Ia-g with a threefold molar excess of hydroxylamine hydrochloride is accompanied by heterocyclization with simultaneous oximation of the third carbonyl group. In each case oxo 1,5-diketones Ia-g react with hydroxylamine to give mixtures of two isomeric oximes – 2,4-diaryl- (IIIa, g) and 2,3-diaryl-5-oxo-5,6,7,8-tetrahydroquinolines (IVa-g).

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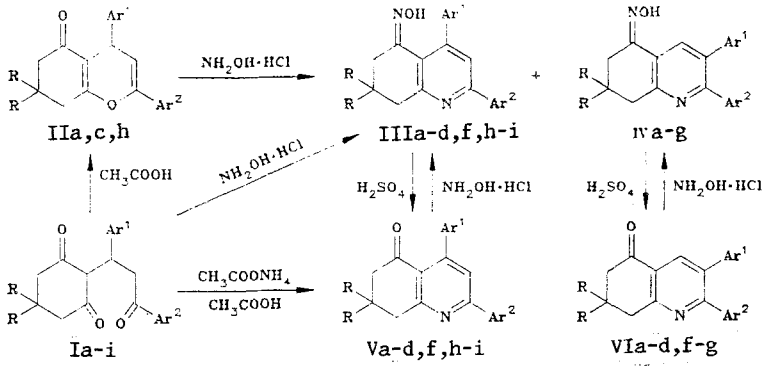


a,c,e,g,h,i R=H; b,d,f R=CH_3; a,b $Ar^1=Ar^2=C_6H_5$; c,d $Ar^1=C_6H_4OCH_3$-4, $Ar^2=C_6H_5$; e,f $Ar^1=Ar^2=C_6H_4OCH_3$-4; g $Ar^1=C_6H_5$, $Ar^2=C_6H_4OCH_3$-4; h $Ar^1=C_6H_4NO_2$-4, $Ar^2=C_6H_5$; i $Ar^1=H$, $Ar^2=C_6H_5$

The ratio of the isomers formed for oxo 1,5-diketones Ia, b is ~1:1. Oxo 1,5-diketones Ic-g, which contain methoxyphenyl groups as substituents, on reaction with hydroxylamine under similar conditions are converted primarily to rearrangement products — 2,3-diaryl-5-oxotetrahydroquinoline oximes IVc-g; in these cases the ratio of isomeric compounds IIIc-g and IVc-g is ~1:2.

Oxo 1,5-diketone Ih, which contains a nitro group in the phenyl substituent, reacts with hydroxylamine to give only the expected 2,4-diaryl-5-oxotetrahydroquinoline oxime IIIh (65%). Rearrangement does not take place. It should be noted that in this case, in addition to oximation and heterocyclization, one observes a retro-Michael process, as a consequence of which a chalcone — 4-nitrobenzalacetophenone (~22%) — is present in the reaction products along with oxime IIIh.

Isomeric oximes IIIa-d and IVa-d were separated and obtained in the form of individual compounds by fractional crystallization from ethanol. It is interesting that oxime IIIc crystallized from the reaction mixture with three molecules of hydroxylamine to give clathrate VIIc, which decomposed with the liberation of oxime IIIc on refluxing in dimethylformamide.

In the case of oxo 1,5-diketones Ie-g from the mixtures of isomeric oximes formed as a result of the reaction we were able to isolate only rearrangement products — 2,3-diaryl-substituted 5-oxotetrahydroquinoline oximes IVe-g — by fractional crystallization. In order to identify the composition of the reaction mixture obtained 2,4-di(4-methoxyphenyl)-5-oxotetrahydroquinoline oxime (IIIf) was obtained by alternative synthesis from the corresponding 5-oxotetrahydroquinoline Vf [3] and hydroxylamine hydrochloride.

In addition to this we realized the hydrolysis of oximes IIIa-d, f, h and IVa-d, f, g with 25% sulfuric acid under conditions similar to those presented in [1]. The corresponding ketones — 5-oxo-5,6,7,8-tetrahydroquinolines Va-d, f, h and VIa-d, f, g — were obtained as a result of the hydrolysis. 2,4-Diaryl-5-oxotetrahydroquinolines Va-d, f, h were identical to the compounds obtained by the action of ammonium acetate on the corresponding oxo 1,5-diketones Ia-d, f, h [4].

5-Oxohydroquinolines Va-d, f, h and VIa-d, f, g on reaction with hydroxylamine hydrochloride are converted smoothly to the corresponding oximes IIIa-d, f, h and IVa-d, f, g.

Thus, isomerization does not occur in the step involving the reaction of 5-oxotetrahydroquinolines V and VI with hydroxylamine, and it also is not observed in the hydrolysis of oximes IIIa-d, f, h and IVa-d, f, g with 25% sulfuric acid.

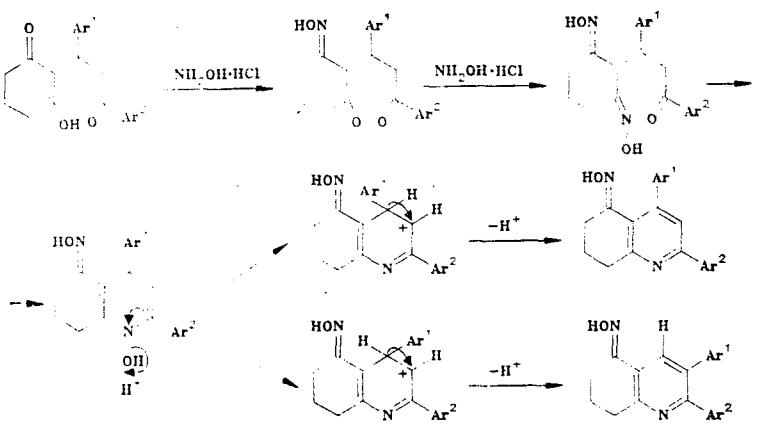
The facts presented above provide evidence that the reaction of hydroxylamine hydrochloride with oxo 1,5-diketones Ia-g, which contain electron-donor groups, is accompanied primarily by rearrangement, while the presence of an electron-acceptor nitro group in oxo 1,5-diketone Ih makes this arrangement impossible.

To study the mechanism of the observed rearrangement we investigated the reactions of 5-oxotetrahydro-4H-chromenes IIa, c, h with hydroxylamine hydrochloride. It was found that the chromenes react with hydroxylamine hydrochloride in the same way as the corresponding oxo 1,5-diketones Ia, c, h. When 5-oxotetrahydrochromenes IIa, c undergo recyclization they form two isomeric oximes IIIa, c and IVa, c. In the case of 5-oxo-tetrahydrochromene IIIh, which contains a nitro group in the phenyl substituent, recyclization in the presence of hydroxylamine hydrochloride is not accompanied by rearrangement; as a result, only oxime IIIh develops.

TABLE 1. Physicochemical Characteristics of 5-Oxo-tetrahydroquinoline Oximes IIIa-d, f, h, i, IVa-g, and VIIc

Compound	Empirical formula	mp, °C	IR spectrum, cm^{-1}		^1H NMR spectrum, ppm	Yield, %	
			ν_{OH}	$\nu_{C=N}$	3-H (4-H)	isomer	III+IV
IIIa	$C_{21}H_{18}N_2O$	216...217	3250	1630	7,49	42	95
IIIb	$C_{23}H_{22}N_2O$	201...202	3280	1635	7,48	43	98
IIIc	$C_{22}H_{20}N_2O_2$	198...199	3260	1630	7,47	25	98
IIId	$C_{24}H_{24}N_2O_2$	180...181	3210	1640	7,45	22	84
IIIe+IVe	$C_{23}H_{22}N_2O_3$	193...200	—	—	—	—	90
IIIf	$C_{25}H_{26}N_2O_3$	185...187	3275	1610	7,36	10	97
IIIg+IVg	$C_{22}H_{20}N_2O_2$	188...199	—	—	—	—	69
IIIh	$C_{21}H_{17}N_3O_3$	252...253	3270	1640	7,46	65	65
IIIi	$C_{15}H_{14}N_2O$	185...187	3230	1630	7,55 (8,18)	—	72
IVa	$C_{21}H_{18}N_2O$	259...261	3160	1640	8,20	47	95
IVb	$C_{23}H_{22}N_2O$	256...257	3160	1630	8,20	49	98
IVc	$C_{22}H_{20}N_2O_2$	253...254	3155	1635	8,18	59	98
IVd	$C_{24}H_{24}N_2O_2$	264...266	3160	1640	8,18	55	97
IVe	$C_{23}H_{22}N_2O_3$	214...215	3160	1640	8,13	26	90
IVf	$C_{25}H_{26}N_2O_3$	233...235	3150	1615	8,13	42	97
IVg	$C_{22}H_{20}N_2O_2$	221...223	3150	1630	8,18	11	69
VIc	$C_{22}H_{29}N_3O_5$	211...212	—	—	—	30	—

Considering the facts that, first, the reaction of 2,4-diaryl-5-oxotetrahydroquinolines Va-d, f with hydroxylamine hydrochloride does not lead to isomerization, while the recyclization of 2,4-diaryltetrahydrochromenes IIa, c in the presence of the latter is accompanied by isomerization, second, one observes a pronounced effect of electron-donor substituents on the character of the transformation of oxo 1,5-diketones Ic-g in the direction of the primary formation of isomeric 2,3-diaryltetrahydroquinoline oximes IV, and, third, the heterocyclization of triketones Ia-g with ammonium acetate in acetic acid is not accompanied by rearrangement [4], the scheme of the process under discussion can probably be represented in the following way:



The structures of the compounds obtained were confirmed by the results of elementary analysis (Tables 1 and 2) and x-ray diffraction investigation [3], as well as by IR and NMR spectroscopic data (Tables 1-3). Absorption of a carbonyl group is absent in the IR spectra of oximes IIIa-d, f, h and IVa-g, while absorption bands at 3150-3280 cm^{-1}, which we assign to stretching vibrations of the hydroxy group in the =N—OH grouping, appear.

It should be noted that the absorption of the hydroxy group of 2,4-diaryl-substituted oximes IIIa-d, f, h is found at 3210-3280 cm^{-1}, as compared with 3150-3170 cm^{-1} for oximes IVa-g. The presence of absorption bands of a conjugated carbonyl group at 1680-1690 cm^{-1} is characteristic for the IR spectra of 5-oxotetrahydroquinolines VIa-d, f, g.

The ^1H NMR spectra of 5-oxotetrahydroquinolines Va-d, f have been previously described [4]. Slight changes in the weak-field region of the spectrum are observed on passing to the corresponding oximes IIIa-g. Just as in the case of ketones V and VI, the principal differences in the ^1H NMR spectra of isomeric oximes III and IV were recorded in the aromatic-proton region. Whereas the 3-H proton resonates at 7.4 ppm in the case of III and V, a singlet at 8.2 ppm is observed in the spectra of the corresponding isomers IV and VI (Tables 1 and 2).

TABLE 2. Physicochemical Characteristics of 5-Oxo-5,6,7,8-tetrahydroquinolines Vh, i and VIa-d, f, g

Compound	Empirical formula	mp, °C	IR spectrum, cm^{-1}		^1H NMR spectrum, ppm	Yield, %
			$\nu_{C=O}$	$\nu_{C=N}$	4-H (3-H)	
Vh	$C_{21}H_{16}N_2O_3$	199...200	1680	1640	(7,55)	83
Vi	$C_{15}H_{13}NO$	128...128,5	1685	1635	8,18 (7,55)	85
VIa	$C_{21}H_{17}NO$	134...135	1690	1640	8,28	84
VIb	$C_{23}H_{21}NO$	132...133	1690	1630	8,26	98
VIc	$C_{22}H_{19}NO_2$	127...128	1680	1635	8,23	92
VId	$C_{24}H_{23}NO_2$	166...167	1685	1640	—	89
VIf	$C_{25}H_{25}NO_3$	149...149,5	1690	1630	8,18	87
VIg	$C_{22}H_{19}NO_2$	159...160	1680	1635	—	99

TABLE 3. Data from the ^{13}C NMR Spectra of 5-Oxo-5,6,7,8-tetrahydroquinolines Va-g, i and VIa-c, f

Compound	Chemical shift, ppm									
	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	R=CH
Va	157,99	121,03	151,80	196,68	39,35	20,94	33,24	164,21	124,20	—
Vb	158,78	121,24	151,81	197,04	53,38	32,09	47,47	163,04	123,50	27,92
Vc	158,55	121,66	152,05	197,46	39,95	21,38	33,77	164,67	124,76	—
Vd	158,82	121,48	151,54	197,58	53,58	32,19	47,51	163,19	123,59	27,94
Ve*	161,10	120,75	151,90	197,36	39,91	21,38	33,80	164,62	124,09	—
Vf	161,09	120,60	151,50	197,40	53,67	32,20	47,69	163,19	123,06	28,09
Vg*	160,92	120,41	151,95	197,04	39,58	21,20	33,52	164,61	123,77	—
Vi	159,89	118,21	135,16	197,06	38,03	21,41	32,32	163,19	126,02	—
VIa	160,57	134,67	136,00	197,65	38,39	21,74	32,19	161,85	126,25	—
VIb	160,15	134,25	136,29	197,23	51,67	32,54	45,83	160,54	125,01	27,96
VIc	160,26	134,10	136,56	197,45	38,22	21,57	32,00	161,28	126,04	—
VIf	159,93	133,63	136,25	197,51	51,86	32,67	46,01	160,25	124,75	28,07

*Compounds Ve, g were obtained by the reaction of oxo 1,5-diketones Ie, g with ammonium acetate [4].

In order to identify the synthesized III-VI we obtained 2-phenyl-5-oxo-5,6,7,8-tetrahydroquinoline (Vi) and the corresponding oxime IIIi and recorded their spectra. The resonance signals of the 3-H and 4-H protons in these compounds are located at 7.5 and 8.2 ppm (J = 8.2 and 8.4 Hz), respectively, on the basis of which it might be assumed that the aryl substituents in oximes IVa-g and oxoquinolines VIa-d, f-g are attached to the $C_{(2)}$ and $C_{(3)}$ atoms. In this case one should expect strong steric interaction between the aryl substituents, which is reflected in a change in the character of the absorption of the aromatic protons.

To confirm the structures of the compounds obtained we recorded the ^{13}C NMR spectra of 5-oxotetrahydroquinolines V and VI (Table 3). Isomeric quinolines V and VI have the same number of signals. In particular, ketones Va and VIa have 17 peaks each, from which by means of the spectra with incomplete decoupling of the protons one can isolate three peaks corresponding to the methylene carbon atoms [$C_{(6)}$, $C_{(7)}$, $C_{(8)}$], four intense peaks of the o- and m-carbon atoms of the phenyl substituents, three low-intensity peaks of methylidyne carbon atoms (the para carbon atoms of the phenyl substituents and the unsubstituted carbon atom of the pyridine ring), and seven peaks related to the quaternary carbon atoms [$C_{(2)}$, $C_{(3)}$ or $C_{(4)}$, $C_{(5)}$, $C_{(9)}$, $C_{(10)}$, and the ipso-carbon atoms of the phenyl substituents]. In the case of the other ketones the number of signals changes in conformity with the number of substituting groups (CH_3, OCH_3).

The doublets in the spectra with incomplete decoupling of the protons at 120 ppm for Va-g and at 136 ppm for ketones VIa-c, f are a convenient diagnostic test for ascertaining the character of the substitution in the 5-oxo-5,6,7,8-tetrahydroquinoline system. Data from the ^{13}C NMR spectra of the compounds obtained are presented in Table 3. The assignments were made with the aid of the literature data [5] and by taking into account the effect of the substituents.

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil and perchlorinated 1,3-butadiene were recorded with a UR-20 spectrometer. The ^1H and ^{13}C NMR spectra of the com-

pounds obtained were recorded with a Varian FT-80A spectrometer with a resonance frequency of 80 MHz for the hydrogen nuclei and 20 MHz for the carbon nuclei; solutions of the compounds with a concentration of 0.1 mole/liter were used for the ^1H NMR spectra, while solutions with a concentration of 0.5 mole/liter were used for the ^{13}C NMR spectra with tetramethylsilane (TMS) as the internal standard.

The course of the reactions was monitored by TLC on Silufol-254 plates in a hexane–ether–chloroform system (2:1:1) with development by iodine vapors.

2-[1-(4-Nitrophenyl)-3-phenyl-3-oxopropyl]cyclohexane-1,3-dione (Ih, $C_{21}H_{19}NO_5$). This compound was obtained by the method in [6] from 9.5 g (0.083 mole) of cyclohexane-1,3-dione, 18.1 g (0.086 mole) of 4-nitrobenzalacetophenone, and a solution of 0.08 g (3 mmole) of sodium in 100 ml of ethanol–dioxane (5:1). Workup gave 17.2 g (~59%) of a product with mp 172-173°C (from ethanol). IR spectrum: 1680 (CO), 1630 cm^{-1} (C=C).

2-Phenyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene (IIh, $C_{21}H_{17}O_4$). This compound was obtained by the method in [7] from 4 g (0.01 mole) of 2-[1-(4-nitrophenyl)-3-phenyl-3-oxopropyl]cyclohexane-1,3-dione, 40 ml of glacial acetic acid, and 5 ml of acetic anhydride. Workup gave 2.1 g (57%) of a product with mp 135-136°C (from ethanol). IR spectrum: 1680 (CO), 1640 cm^{-1} (C=N).

2,4-Diphenyl-5-oxo-5,6,7,8-tetrahydroquinoline Oxime (IIIa) and 2,3-Diphenyl-5-oxo-5,6,7,8-tetrahydroquinoline Oxime (IVa). A) A mixture of 10 g (0.031 mole) of 2-(1,3-diphenyl-3-oxopropyl)cyclohexane-1,3-dione (Ia), 6.51 g (0.093 mole) of hydroxylamine hydrochloride, and 80 ml of absolute ethanol was refluxed for 20 h, after which it was cooled and poured into 300 ml of 2% aqueous potassium hydroxide solution. The resulting precipitate was separated, washed successively with water to pH 7.0 and ethanol (50 ml), and dried. Workup gave 9.32 g (95%) of a mixture of oximes IIIa and IVa, which was recrystallized from ethanol to give 4.12 g (42%) of 2,4-diphenyl-5-oxo-5,6,7,8-tetrahydroquinoline oxime (IIIa). The solid material that did not dissolve on refluxing in ethanol was recrystallized from DMF to give 4.61 g (47%) of 2,3-diphenyl-5-oxo-5,6,7,8-tetrahydroquinoline oxime (IVa).

5-Oxotetrahydroquinoline oximes IIIb, d, f, h, i and IVb, d-g were similarly obtained (Table 1).

B) A mixture of 0.63 g (2 mmole) of 5-oxohydroquinoline VIa, 0.42 g (6 mmole) of hydroxylamine hydrochloride, and 15 ml of absolute ethanol was refluxed for 8 h, after which it was cooled, and the resulting precipitate was separated, washed with water to pH 7.0, and dried. It was then recrystallized from DMF to give 0.58 g (88%) of 2,3-diphenyl-5-oxo-5,6,7,8-tetrahydroquinoline oxime (IVa).

Oximes IIIa-d, f, h (recrystallized from ethanol) and oximes IVb-d, f were similarly obtained.

C) A mixture of 5.7 g (0.019 mole) of 2,4-diphenyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene (IIa), 4.0 g (0.057 mole) of hydroxylamine hydrochloride, and 50 ml of absolute ethanol was refluxed for 10 h, after which it was cooled and poured into 300 ml of 25% aqueous potassium hydroxide solution. The resulting precipitate was separated, washed successively with water to pH 7.0 and ethanol (50 ml), and dried to give 5.64 g (94%) of a mixture of oximes IIIa and IVa, which was recrystallized from ethanol to give 2.1 g (35%) of 2,4-diphenyl-5-oxo-5,6,7,8-tetrahydroquinoline oxime (IIIa). The solid material that did not dissolve on refluxing in ethanol was recrystallized from DMF to give 2.4 g (40%) of 2,3-diphenyl-5-oxo-5,6,7,8-tetrahydroquinoline oxime (IVa).

Oxime IIIh was similarly obtained.

2-Phenyl-4-(4-methoxyphenyl)-5-oxo-5,6,7,8-tetrahydroquinoline Oxime (IIIc) and 2-Phenyl-3-(4-methoxyphenyl)-5-oxo-5,6,7,8-tetrahydroquinoline Oxime (IVc). A mixture of 10 g (0.027 mole) of 2-[1-phenyl-3-(4-methoxyphenyl)-3-oxopropyl]cyclohexane-1,3-dione (Ic), 5.6 g (0.081 mole) of hydroxylamine hydrochloride, and 80 ml of absolute ethanol was refluxed for 20 h, after which it was cooled, and the resulting yellow precipitate of the clathrate (VIIc) was separated and dried. The yield was 3.8 g (30%). The filtrate was poured into 300 ml of 2% aqueous potassium hydroxide solution, and the resulting precipitate was separated, washed successively with water to pH 7.0 and ethanol (50 ml), and dried to give 5.6 g (47%) of oxime IVc. The clathrate (VIIc) was heated in 10 ml of DMF and cooled, and the resulting precipitate of oxime IIIc was separated, dried, and recrystallized from ethanol to give 3.32 g (28%) of oxime IIIc.

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.

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ACETALS OF LACTAMS AND ACID AMIDES

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

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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].

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