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σ-COMPLEXES IN THE PYRIMIDINE SERIES. 13.* REACTION OF 7- AND 5-METHOXYFUROXANO-[3,4-*d*]PYRIMIDINES WITH SOME C-NUCLEOPHILES

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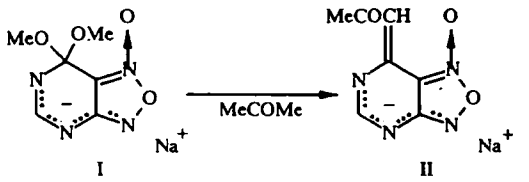
We have studied the reaction of isomeric 7- and 5-methoxyfuroxano[3,4-d]pyrimidines with carbanions of some CH acids. We have shown that regardless of the position of the substituent in the pyrimidine ring, nucleophilic attack occurs regioselectively at the $C_{(7)}$ atom. As a result, we have obtained the products of substitution at the methoxy group, and also anionic σ complexes and covalent σ adducts.

Annelation of a 1,2,5-oxadiazole ring to a pyrimidine ring significantly increases the π deficiency of the latter. Only a few examples are given in the literature for the formation of stable anionic σ complexes and covalent σ adducts in reaction of derivatives of furoxano[3,4-*d*]pyrimidine with N- and O-nucleophiles [2, 3]. In this case, nucleophilic attack generally occurs at the 7 position of the pyrimidine ring. At the same time, the reaction of furoxano[3,4-*d*]pyrimidines with ketones in alkaline medium is accompanied by transformation of the furoxan ring, and leads to di-N-oxides of pteridine (the Beirut reaction) [4-6]. The pyrimidine moiety in this case remains unaltered. The hemiacetal anionic σ complex I (which we described earlier in [3]) when dissolved in acetone is converted to the salt II (a Zimmerman [spelling unverified] salt).



I II

In the PMR spectrum of this compound (Table 1), the signals from the methine protons (6.15 ppm) and the methyl group (2.27 ppm) along with the singlet from the 5-H proton are clear evidence for the position of the acetonylidene residue. The difference between the absorption maxima in the electronic spectra of salt II recorded in acetone and methanol is explained by protonation of the pyrimidine nitrogen atom in methanol. Furthermore, the position of the vibrational band of the carbonyl group in the IR spectrum (Table 1) is evidence for conjugation of the ketone moiety with the heterocycle.

When activated derivatives of benzene and pyridine react with the carbanion of acetone, the nucleophilic attack occurs exclusively at the unsubstituted position of the ring, with formation of anionic Yanovskii σ complexes [7, 8]. Furthermore, in studying nucleophilic substitution in the series of 5-nitropyrimidine derivatives, it has been established that the orientation of attack depends considerably on the position of the substituents on the pyrimidine ring, and also on the nature of the carbanion. In this case, it was shown that carbanions of acetone and acetophenone selectively attack the unsubstituted positions of the 5-nitropyrimidine ring with formation of stable anionic Meisenheimer σ complexes, while the acetylacetone carbanion attacks the substituted position with formation of Zimmerman salts [9-11].

*For Communication 12 see [1].

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TABLE 1. PMR, IR, and UV Spectral Data for the Synthesized Compounds

Compound	IR spectrum, cm^{-1}		UV spectrum, λ_{max}, nm (lgε) (methanol)	PMR* spectrum, δ, ppm, spin–spin coupling constant (*J*), Hz
	ν_{NH}†	$\nu_{C=O}$		
II	—	1650	383(3,77)‡	2,27 (3H s, CH_3); 6,15 (1H, s, CH); 7,84 (1H, s, 5-H)
Va	3430	1650	261(3,79) 384(3,77)	2,25 (3H, s, CH_3); 6,27 (1H, s, CH); 7,90 (1H, s, 5-H); 12,22 (1H, br.s, NH)
Vb	3440	1650	270(4,02) 395(4,21)	6,97 (1H, s, CH); 7,54–7,90 (5H, m, C_6H_5); 7,99 (1H, s, 5-H); 12,65 (1H, br.s, NH)
VI	3400	1700	216(3,77) 319(4,15)	2,32 (3H, s, CH_3); 2,65 (3H, s, CH_3); 7,92 (1H, d, *J* = 3,4, 5-H); 13,26 (1H, br.s, NH)
VII	—	—	266(3,58)	4,27 (3H, s, OCH_3); 8,65 (1H, s, 5-H)
IX a	3230	1715	242(3,85) 286(3,51)	2,26 (3H, s, CH_3); 2,72–3,53 (2H, m, CH_2); 3,92 (3H, s, OCH_3); 5,15, 5,09 (1H, dt, $^3J_{HCH}$ = 10,5, $^3J_{HNH}$ = 2,0, 7-H); 5,94 (1H, br.s, NH)
IX b	3300	1680	244(4,19) 287(3,57)	3,65 (2H, m, CH_2); 3,81 (3H, s, OCH_3); 5,28 (1H, m, 7-H); 7,52–7,98 (5H, m, C_6H_5); 8,33 (1H, br.s, NH)
XI a	—	1660	234(3,83) 328(4,25)	1,28 (9H, t, *J* = 7,2; $N(CH_2CH_3)_3$); 2,53 (3H, s, CH_3); 3,18 (6H, q, *J* = 7,2; $N(CH_2CH_3)_3$); 3,84 (3H, s, OCH_3); 6,37 (1H, s, CH)
XII a	3200	1670	333(4,17)	2,51 (3H, s, CH_3); 3,84 (3H, s, OCH_3); 6,37 (1H, s, CH); 11,20 (1H, br.s, NH)
XII b		1637	277(3,58) 392(3,73)	4,11 (3H, s, OCH_3); 7,12 (1H, s, CH); 7,49–8,00 (5H, m, C_6H_5); 12,43 (1H, br.s, NH)
XIV	—	1660	280(4,38)	1,04 (4H, s, $2CH_2$); 1,29 (9H, t, *J* = 7,2, $N(CH_2CH_3)_3$); 2,14 (6H, s, $2CH_3$); 3,18 (6H, q, *J* = 7,2, $N(CH_2CH_3)_3$); 3,83 (3H, s, OCH_3); 5,88 (1H, s, 7-H)
XV	—	1660	258(4,15)	1,21 (9H, t, *J* = 7,5, $N(CH_2CH_3)_3$); 2,23 (6H, s, $2CH_3$); 2,98 (6H, q, *J* = 7,5, $N(CH_2CH_3)_3$); 3,83 (3H, s, OCH_3); 5,78 (1H, br.s, 7-H)
XVI	3322	1660	288(4,13)	1,00 (4H, s, $2CH_2$); 2,24 (6H, s, $2CH_3$); 3,77 (3H, s; OCH_3); 5,82 (1H, s, 7-H); 8,19 (1H, br. s, OH); 11,70 (1H, br.s, NH)
XVII	3260	1690	248(4,17)	2,33 (3H, d, *J* = 1,3, $-C(OH)CH_3$); 2,38 (3H, s, $COCH_3$); 3,61 (3H, s, OCH_3); 5,53 (1H, *J* = 1,3, 7-H); 8,19 (1H, br.s, NH); 8,44 (1H, br.s, OH)
XVIII	—	1680	220(3,970) 310(4,00)	2,52 (3H, s, CH_3); 2,74 (3H, c, $COCH_3$); 7,58 (1H, s, 4-H)

*The PMR spectra of compounds II, Va, b, IXa, b, XIIa, b, XVI, XVII were taken for solutions in DMSO-D_6; for XIa, XIV, XV, in CD_3OD; for VI, VII, in $CDCl_3$.

†For compounds XIa, XIV, and XV, the band at 2700 cm^{-1} belongs to $\nu_{(N-H)}$ for the HN^+Et_3 cation.

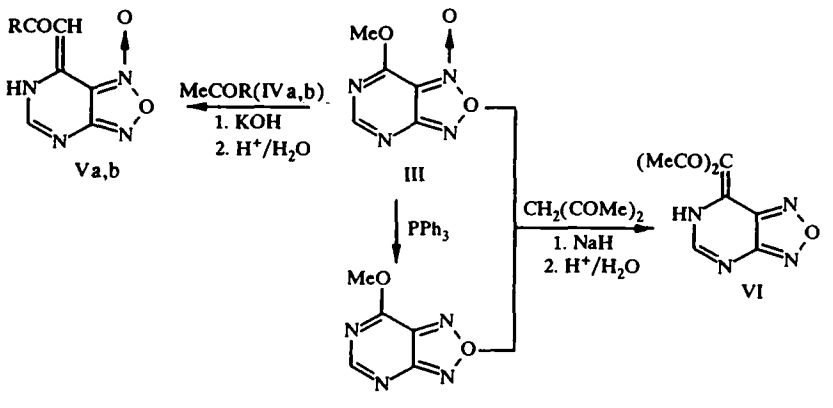
‡The UV spectrum of salt II in acetone was 472 nm (3.77).

Considering that the anionic σ complex I is found in solution in equilibrium with the starting 7-methoxyfuroxano[3,4-*d*]pyrimidine, we may hypothesize that salt II is formed as a result of nucleophilic attack by the acetone carbanion at the substituted position of the pyrimidine ring. So in this work, we have studied the reaction of 7- and 5-methoxyfuroxano[3,4-*d*]pyrimidines, in which we consider two possible combinations of substituted and unsubstituted positions of the pyrimidine ring with the carbanions formed from CH acids of different strengths (acetone, acetophenone, α-bromoacetophenone, acetylacetone, dimedone, and nitroacetone).

In fact, by reaction of 7-methoxyfuroxano[3,4-*d*]pyrimidine (III) with acetone (IVa) (pK_a 20.0 [12]) in the presence of an equimolecular amount of potassium hydroxide, followed by neutralization of the reaction mixture, we obtained 7-acetonylidenefuroxano[3,4-*d*]pyrimidine (Va); while we obtained ketone (Vb) from compound III and the carbanion of acetophenone (IVb) (the pK_a of acetophenone is 15.8 [12]). The presence in the PMR spectra of singlet signals from the methine protons of the ketone moieties (6.27 and 6.97 ppm respectively) allows us to unambiguously assign the pyrimidinylidene structure to compounds Va, b. Evidence for this also comes from the position of the absorption band for the carbonyl group

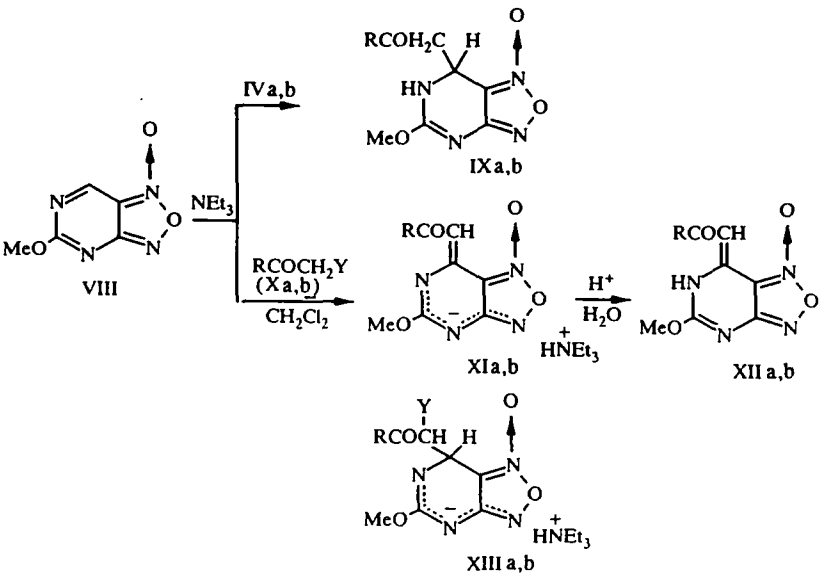
in the IR spectrum (see Table 1), indicating its conjugation with the C=C bond of the pyrimidinylidene moiety. Thus these conversions are the first example of nucleophilic *ipso*-substitution in activated aromatic systems when treated with the carbanion of acetone (or acetophenone). Such an orientation of the reaction is obviously determined by the high electron-deficiency of the 7 position of the pyrimidine ring in compound III.

When furoxanopyrimidine III is reacted with acetylacetone (pK_a 8.9 [12]) in DMSO in the presence of sodium hydride, we obtain 7-diacetylmethylidenefurazano[3,4-*d*]pyrimidine (VI). In this case, nucleophilic substitution of the methoxy group also occurs, while the presence of sodium hydride leads to reduction of the furoxan ring (in analogy with the data in [6]).



IV, Va = Me, b = Ph

The structure of product VI was confirmed by spectral data (see Table 1), the results of elemental analysis (Table 2), and also independent synthesis from 7-methoxyfurazano[3,4-*d*]pyrimidine (VII).

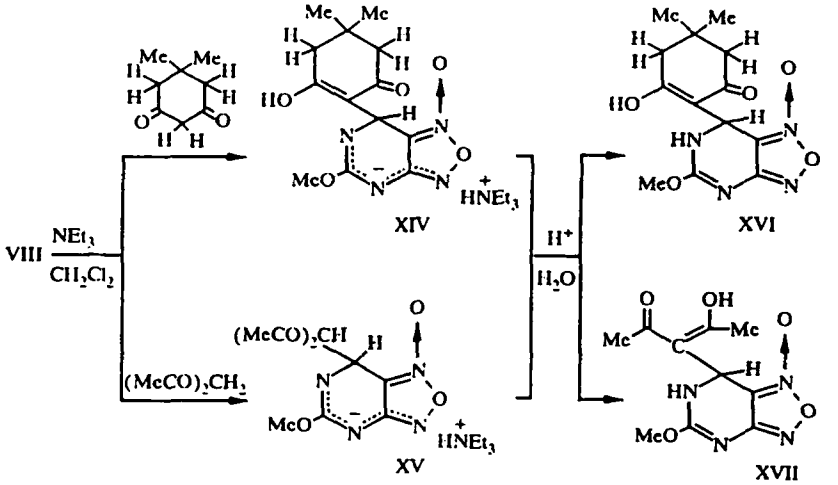


IX–XIII a R = Me, b R = Ph; XI a Y = NO_2, b Y = Br

In 5-methoxyfuroxano[3,4-*d*]pyrimidine (VIII), the unsubstituted position of the ring is the most electron-deficient. When this compound is reacted with acetone (or acetophenone) in the presence of triethylamine, nucleophilic attack occurs at the $C_{(7)}$ atom with formation of 7-acetonyl-(phenacyl)-5-methoxyfuroxano[3,4-*d*]-6,7-dihydro-pyrimidines (IXa, b) respectively. In the PMR spectrum of the covalent σ adduct IXa, the methine proton appears as a doublet of triplets (in the 5.15-5.09 ppm region), while the protons of the methylene group (due to nonequivalence) appear as the AB part of an ABX system. This proves the presence of a geminal acetonyl moiety in the 7 position, and allows us to assign the 6,7-dihydropyrimidine structure to compound IXa. Similar features are observed in the PMR spectrum of the σ adduct IXb. When the furoxanopyrimidine VIII is reacted with the carbanion of nitroacetone (pK_a of nitroacetone is 5.1 [12]), the Zimmerman salt XIa is formed. Acidification of its aqueous solution leads to 7-acetonylidene-5-methoxyfuroxano[3,4-*d*]pyrimidine (XIIa). This reaction, owing to the pre-

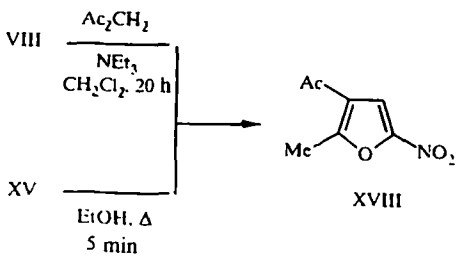
sence of a good leaving group in the carbanion, obviously occurs according to a "vicarious nucleophilic substitution of hydrogen" mechanism (VNS^H) [13, 14]. The anionic σ complex (XIIIa), formed in the first step as a result of cleavage of nitric acid, is converted to the salt XIa. The reaction of compound VIII with the carbanion of α-bromoacetophenone occurs similarly according to a VNS^H mechanism, but without liberation of the salt XIb.

Based on the PMR spectra, we can assign the pyrimidinylidene structure to compounds XIIa, b. Thus the carbanions of nitroacetone and bromoacetophenone, formed from CH acids of different strengths, owing to the presence of good leaving groups react with furoxanopyrimidine VIII according to the same mechanism. For compounds XIIa, b, in contrast to 6,7-dihydropyrimidines IXa, b, absorption in the longer wavelength region of the UV spectrum is characteristic (see Table 1). This obviously is determined by the lengthening of the π-electron conjugation chain, including the ketone component. The carbanion of dimedone, which is a CH acid comparable in strength with nitroacetone (the pK_a of dimedone is 5.21 [12]), forms a stable anionic Meisenheimer σ complex XIV with compound VIII under analogous conditions.



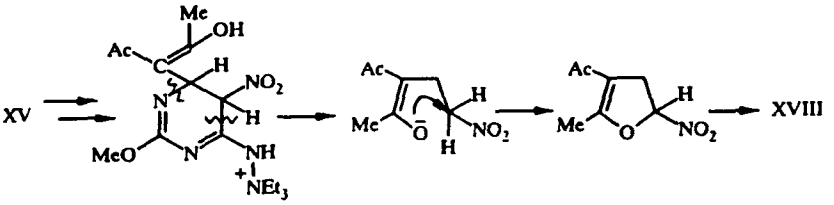
In the case of diacetylmethanide, an anionic σ complex (XV) is isolated. Neutralization of aqueous solutions of the anionic σ complexes XIV and XV leads to furoxano[3,4-*d*]-6,7-dihydropyrimidines XVI and XVII respectively. According to the PMR spectrum of the covalent σ adduct XVII, the methyl groups of its acetylacetone moiety are nonequivalent (they appear as a three-proton singlet and a doublet at 2.38 and 2.33 ppm respectively), which suggests an enol form for the indicated moiety. This is consistent with literature data [15] for the σ adduct of 4,6-dinitrobenzofuroxan with acetylacetone.

Our investigations allow us to draw the following basic conclusions. The furoxan ring in compounds III and VIII activate the $N_{(6)}=C_{(7)}$ double bond of the azadiene moiety to a significant degree, which leads to nucleophilic attack by the carbanions at the 7 position. Furthermore, increasing the total π deficiency of the furoxanopyrimidine ring (compared with 5-nitropyrimidines [9-11]) allows us to expand the range of CH acids whose carbanions are capable of nucleophilic attack on a pyrimidine ring, and to bring their lower limit to the pK_a values of conjugate acids whose anions form σ complexes with 1,3,5-trinitrobenzene [16]. We have shown in [17] that the furoxanopyrimidine VIII, when treated with carbanions of methyl and ethyl esters of acetoacetic acid, undergoes recyclization to the corresponding esters of 2-methyl-5-nitro-3-furancarboxylic acid. Similarly, when compound VIII is reacted with acetylacetone in methylene chloride in the presence of a five-fold excess of triethylamine for 20 h (method A), 3-acetyl-2-methyl-5-nitrofuran (XVIII) is formed.



The stable anionic σ complex XV also undergoes recyclization to form nitrofuran XVIII when boiled in ethanol (method B); the structure of XVIII has been confirmed by the spectral characteristics and elemental analysis data (see the Experimental section and Table 2).

The type of transformation of the furoxanopyrimidine ring to nitrofuran derivatives considered here has not been described in the literature. So we can say that these transformations are a new type of recyclization for such a heterocyclic system. The mechanism and limits for application of the reaction require further study. But based on the established structure of nitrofuran derivatives, we may hypothesize the following mechanism for their formation:



Undoubtedly in the first step of the reaction, the carbanion attacks the most electron-deficient 7 position of the pyrimidine ring with formation of the anionic σ complex XV, which when treated with excess triethylamine is transformed to the unstable 5-nitro-4,5-dihydropyrimidines as a result of opening of the furoxan ring. Rupture of the pyrimidine ring at the $N_{(3)}-C_{(4)}$ and $C_{(5)}-C_{(6)}$ bonds followed by cyclization of the nitroenols formed by the Feist–Benary method [18, 19] leads to the 5-nitrofuran XVIII. Furthermore, as follows from the scheme given, a necessary condition for recyclization to occur is the presence at the geminal center of a substituent or part of a substituent in enol form. Evidence for this comes from the fact that the covalent σ adduct IXb (containing a ketone moiety at the geminal center) does not undergo recyclization under the conditions of method B, but rather as a result of aromatization is converted to 7-phenacylidenefuroxano[3,4-*d*]pyrimidine XIIb.

EXPERIMENTAL

The PMR spectra were recorded on a Bruker WP-200 spectrometer in $CDCl_3$, DMSO-D_6, and CD_3OD solutions, internal standard TMS. The UV spectra were taken on a Specord M-40 (in ethanol). The IR spectra were recorded on a Specord M-80 (in KBr pellets) (for compounds II, V, IX, XI, XII, XIV-XVII, the presence of a "furoxan" absorption band in the 1600-1640 cm^{-1} region is characteristic, see [6]).

The course of the reactions and the purity of the synthesized compounds were monitored by TLC on Silufol UV-254 in a 50:1 chloroform–methanol solvent system (visualization in UV light). The products VI, VII, IXa, b, XIIb, and XVIII were purified by column chromatography on silica gel, using chloroform as the eluent. The anionic σ complex I and also furoxano[3,4-*d*]pyrimidines III and VIII were obtained according to the procedures described in [3]. The spectral data for the synthesized compounds are presented in Table 1; the characteristics of these products are presented in Table 2.

7-Methoxyfurazano[3,4-*d*]pyrimidine (VII). Triphenylphosphine (0.5 g, 1.9 mmoles) was added to a solution of 0.3 g (1.78 mmoles) compound III in 10 ml methylene chloride. After 40 min, the reaction mixture was evaporated to dryness. Product VII was isolated from the residue using chromatography.

Sodium Salt of the 7-Acetonylidenefuroxano[3,4-*d*]pyrimidine Anion (II, $C_7H_5NaN_4O_3$). A solution of 0.7 g (3.15 mmoles) of σ complex I in 30 ml acetone was held at room temperature for 1 h. The solvent was evaporated to dryness under reduced pressure, and the residue was treated with absolute ether (3 × 50 ml). The red crystalline salt II was obtained, which was dried under vacuum. Yield: 0.59 g (84%).

7-Acetonylidenefuroxano[3,4-*d*]pyrimidine (Va). Finely ground potassium hydroxide (0.1 g, 1.78 mmoles) was added to a solution of 0.3 g (1.78 mmoles) of compound III in 5 ml acetone with rapid stirring. The reaction mixture was stirred for 1 h, then 0.1 g (1.78 mmoles) more potassium hydroxide was added and stirring was continued for 45 min. Then the solution was filtered. The filtrate was evaporated under reduced pressure, and the residue was treated with absolute ether (3 × 50 ml). The red crystalline residue obtained was dissolved in 5 ml water and the solution was neutralized with a 0.6 N H_2SO_4 solution. The product Va was extracted with chloroform (500 ml). The extract was dried over $MgSO_4$, the solvent was driven off under vacuum, and the residue was crystallized.

TABLE 2. Characteristics of Synthesized Compounds

Compound	Empirical formula	Found, % / Calculated, %			T_{mp} °C*	Yield, %
		C	H	N		
Va	$C_7H_6N_4O_3$	43,4 / 43,3	3,1 / 3,1	29,1 / 28,9	237...238	34
Vb	$C_{12}H_8N_4O_3$	56,0 / 56,2	3,0 / 3,1	21,7 / 21,9	205...207	27
VI	$C_9H_8N_4O_3$	49,3 / 49,1	3,7 / 3,6	25,2 / 25,4	178...180	12†
VII	$C_5H_4N_4O_2$	39,5 / 39,5	2,7 / 2,7	36,8 / 36,6	51...52	81
IXa	$C_8H_{10}N_4O_4$	42,6 / 42,5	4,4 / 4,4	24,7 / 24,8	184...185	61
IXb	$C_{13}H_{12}N_4O_4$	54,2 / 54,2	4,1 / 4,2	19,4 / 19,4	194...196	57
XIIa	$C_8H_8N_4O_4$	42,8 / 42,9	3,6 / 3,6	24,8 / 25,0	198...199	73
XIIb	$C_{13}H_{10}N_4O_4$	54,6 / 54,5	3,6 / 3,5	19,4 / 19,6	223...225	59
XIV	$C_{13}H_{16}N_4O_5$	50,5 / 50,7	5,2 / 5,2	18,1 / 18,2	168...170	73
XVII	$C_{10}H_{12}N_4O_5$	44,7 / 44,8	4,5 / 4,5	20,6 / 20,9	172...174	72
XVIII	$C_7H_7NO_4$	49,7 / 49,7	4,0 / 4,1	8,3 / 8,3	78...80	51

*After recrystallization from ethanol; all products melt with decomposition.
†The product was synthesized from compound III.

7-Phenacylidenefuroxano[3,4-*d*]pyrimidine (Vb) was obtained similarly to compound Va, from compound III and acetophenone.

7-Diacetylmethylidenefurazano[3,4-*d*]pyrimidine (VI). Sodium hydride (0.06 g, 2.50 mmoles) was added in portions to a solution of 0.26 ml (2.53 mmoles) acetylacetone in 2 ml DMSO. Two hours later, after evolution of hydrogen was complete, a solution of 0.3 g (1.78 mmoles) compound III in 5 ml DMSO was added to the reaction mass. The mixture was held at room temperature for 20 h, diluted with water (100 ml), neutralized with a 0.6 N H_2SO_4 solution, and extracted with ethylacetate. The extract was dried over $MgSO_4$, the solvent was evaporated, and product VI was isolated from the residue using chromatography.

Compound VI was also obtained according to the procedure described above from furazanopyrimidine VII, 80% yield.

7-Acetonyl-5-methoxyfuroxano[3,4-*d*]-6,7-dihydropyrimidine (IXa). Compound VIII (0.1 g, 0.59 mmoles) was added to a solution of 0.27 ml (1.94 mmoles) triethylamine in 5 ml dry acetone. After 18 h, the reaction mass was evaporated under reduced pressure, and product IXa was isolated from the residue using chromatography.

7-Benzoylmethyl-5-methoxyfuroxano[3,4-*d*]-6,7-dihydropyrimidine (IXb) was obtained from furoxanopyrimidine VIII and acetophenone according to the procedure described for compound IXa.

7-Acetonylidene-5-methoxyfuroxano[3,4-*d*]pyrimidine (XIIa). Triethylamine (0.43 ml, 3.08 mmoles) was added to a mixture of 0.16 g (0.95 mmoles) compound VIII and 0.13 g (1.26 mmoles) nitroacetone in 5 ml dry, ethanol-free methylene chloride. After 30 min, the crystalline precipitate of the triethylammonium salt of the 7-acetonylidene-5-methoxyfuroxano[3,4-*d*]pyrimidine anion (XIa) was filtered out. Yield, 0.26 g (84%); mp 175-177°C (decomp.). Compound XIa (0.16 g, 0.49 mmoles) was dissolved in 5 ml water and neutralized with a 0.6 N H_2SO_4 solution. The precipitate was filtered out and crystallized.

7-Phenacylidene-5-methoxyfuroxano[3,4-*d*]pyrimidine (XIIb). Triethylamine (0.43 ml, 3.08 mmoles) was added to a mixture of 0.16 g (0.95 mmoles) compound VIII and 0.2 g (1.00 mmoles) bromoacetophenone in 5 ml dry, ethanol-free methylene chloride. After 20 h, the reaction mass was evaporated to dryness, and product XIIb was isolated from the residue using chromatography.

Triethylammonium Salt of the 7-(5′,5′-Dimethyl-3′-hydroxycyclohexan-1′-on-2′-yl)-5-methoxyfuroxano-[3,4-*d*]pyrimidine Anion (XIV, $C_{19}H_{31}N_5O_5$). The salt XIV was obtained from compound VIII and dimedone according to the procedure for synthesis of the salt XIa. Yield, 85%; mp 163-165°C (decomp.).

Triethylammonium Salt of the 7-Diacetylmethyl-5-methoxyfuroxano[3,4-*d*]pyridine Anion (XV, $C_{16}H_{27}N_5O_5$). The salt XV was obtained from compound VIII and acetylacetone according to the procedure used to obtain the salt XIa. Yield, 78%; mp 95-97°C (decomp.)

7-(5′,5′-Dimethyl-3′-hydroxycyclohexan-1′-on-2′-yl)-5-methoxyfuroxano[3,4-*d*]-6,7-dihydropyrimidine (XVI). Product XVI was obtained by neutralization of an aqueous solution of the salt XIV, as described for compound XIIa.

7-Diacetylmethyl-5-methoxyfuroxano[3,4-*d*]-6,7-dihydropyrimidine (XVII) was obtained by neutralization of an aqueous solution of the salt XVI, as described for compound XIIa.

3-Acetyl-2-methyl-5-nitrofuran (XVIII). A. Triethylamine (1.1 ml, 7.88 mmoles) was added to a mixture of 0.37 g (2.20 mmoles) compound VIII and 0.37 ml (3.60 mmoles) acetylacetone in 5 ml dry, ethanol-free methylene chloride. After 20 h, the reaction mass was evaporated to dryness under reduced pressure, and product XVIII was isolated from the residue using chromatography. IR spectrum: 1510, 1360 (NO_2). ^{13}C NMR spectrum ($CDCl_3$): 191.98 (CO); 160.73 ($C_{(8)}$); 150.08 ($C_{(3)}$); 123.48 ($C_{(5)}$); 111.08 ($C_{(4)}$); 28.94 ($CO\underline{C}H_3$); 14.68 (CH_3).

B. A solution of 0.24 g (0.65 mmoles) of the σ complex XV was boiled in 5 ml ethanol for 5 min, the solvent was driven off under vacuum, and product XVIII was isolated from the residue as described in procedure A. Yield, 0.05 g (45%).

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