Heterocyclic β-Enamino Esters. 28. The Reaction of Heterocyclic β-Enamino Esters and Nitriles with Cyclic Amidines. A Simple Route to Azolopyrimidines (1)

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Whereas 2-amino-3-ethoxycarbonyl-4,5-dihydrofurans Ia-c condense with 5-membered amidine derivatives, *via* elimination of ethanol to afford the azolopyrimidines IIIa,b, XI, and XIVa,b, the 2-amino-3-cyano-4,5-dihydrofurans Id,e give with the same reagents, under elimination of ammonia, the novel ring systems of furo-azolopyrimidines XVIII and XXa,b. 2-Amino-3-ethoxycarbonyl-5,6-dihydro-4*H*-thiopyrane (XXI) reacts with 5-amino-1,2,4-triazole (II) to yield the triazolo[1,5-*a*]pyrimidine XXII, and with 2-aminobenzimidazole to XXIII. The mechanism of these reactions is discussed. XIVb and VIIb are cyclized in a secondary step to give the novel furo[2,3-*d*]benzimidazo[1,2-*a*]pyrimidine XXVI, and furo[2,3-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidine XXVIII respectively, besides the acetoxy derivatives XVII and XXIX.

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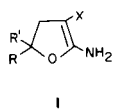
The considerable biological and medicinal activities of azolopyrimidines in the past times has stimulated considerable research in this field (3-5). As a part of a program directed for exploring the synthetic potential, scope and limitations of heterocyclic β-enamino esters and nitriles (6), we report here a novel synthesis of azolopyrimidines, *via* reaction of heterocyclic β-enamino esters with 5-membered cyclic amidines.

These investigations have resulted in a simple synthesis of several, otherwise difficultly accessible novel derivatives of known ring systems, as well as to a number of new ring systems.

Thus, the 2-amino-3-ethoxycarbonyl-4,5-dihydrofuranes Ia,b react with 5-amino-1,2,4-triazole (II) to give products of molecular formula corresponding to condensation of Ia,b with II, *via* elimination of ethanol. Five isomeric structures can be discussed as potential reaction products (*cf.* Chart 1).

Chart 1



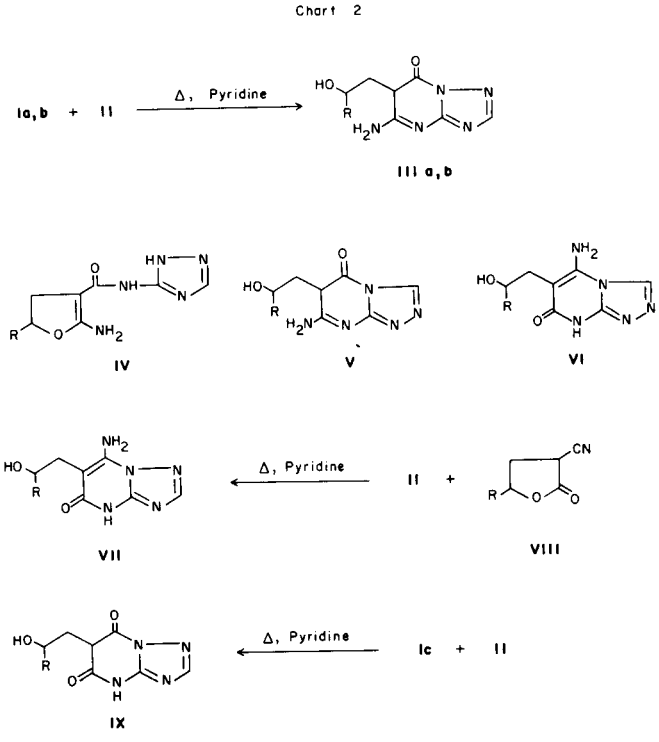
I

I	R	R'	X
a	H	H	$CO_2C_2H_5$
b	CH_3	H	$CO_2C_2H_5$
c	CH_3	CH_3	$CO_2C_2H_5$
d	H	H	CN
e	CH_3	H	CN

II

The enamino-amide structure IV can be excluded based on ^{1}H-nmr and ^{13}C-nmr of the reaction products. Thus, ^{1}H-nmr reveals the absence of two multiplets for the two sterically different furane 4-H and shows up these two protons as one multiplet, as required by the 1,2,4-triazolopyrimidine structures III, V, and VI. Moreover, the ^{13}C-nmr reveals additionally the absence of resonance for furan C-5, and shows a resonance for the terminal -$\overset{|}{\underset{|}{C}}$-OH group (7). With the aid of ^{1}H-nmr the 1,2,4-triazolo[3,4-*a*]-pyrimidine structures V and VI can also be ruled out as reaction products: the signals of the triazole proton (products from II and Ia,b) appear at higher field (δ = 8.15 ppm) than as expected for 1,2,4-triazolo[3,4-*a*]pyrimidines (δ = 8.7 - 9 ppm) (8).

Chart 2



Spectroscopy, however, seems to be of little help for distinguishing between structures III and VII. Thus, samples of VIIa,b were prepared independently, *via* the reaction of II with the α-cyano-γ-butyrolactones VIIIa,b.

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Table I

List of Products of Reaction of Ia-e and XXI with Cyclic Amidines

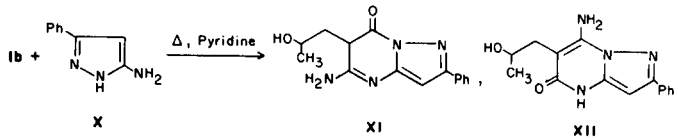
Compound	Solvent of Crystallization	Yield (%)	M.p. (°C)	Molecular formula (Molecular weight)	Found / Calcd. C	Analysis H	N
IIIa	Water	51	274-276	$C_7H_9N_5O_2$	43.07	4.67	35.89
				(195,17)	43.12	4.65	36.10
IIIb	Water	71	246-247	$C_8H_{11}N_5O_2$	45.56	5.31	33.50
				(209,07)	45.93	5.30	33.48
VIIa	Water	71	279-281	$C_7H_9N_5O_2$	43.07	4.67	35.89
				(195,17)	42.65	4.65	35.57
VIIb	Water	35	225	$C_8H_{11}N_5O_2$	45.93	5.30	
				(209,07)	45.56	5.30	
IX	Water	50	220	$C_9H_{12}N_4O_3$	48.21	5.39	25.44
				(224,22)	47.91	5.43	24.99
XI	Pyridine	71	285	$C_{15}H_{16}N_4O_2$	62.91	5.67	19.73
				(284,31)	63.36	5.58	19.70
XIVa	Pyridine	76	286	$C_{12}H_{12}N_4O_2$	59.05	4.96	22.61
				(244,25)	59.01	4.95	22.94
XIVb	Pyridine	82	261	$C_{13}H_{14}N_4O_2$	60.81	5.43	21.60
				(258,27)	60.45	5.46	21.70
XVII	Ethanol	41	262	$C_{13}H_{14}N_4O_2$	60.20	5.42	21.60
				(258,27)	60.45	5.46	21.70
XVIII	Water	30	273	$C_8H_9N_5O$	49.88	6.07	36.41
				(191,19)	50.25	5.74	36.63
XXa	Ethanol	50	275	$C_{14}H_{12}N_4O$	66.62	4.92	22.68
				(252,27)	66.65	4.79	22.21
XXb	Ethanol	48	251	$C_{15}H_{14}N_4O$	67.63	5.38	21.02
				(266,29)	67.65	5.30	21.04
XXII	Ethanol	85	286	$C_8H_{11}N_5OS$	42.19	4.77	31.10
				(225,27)	42.66	4.92	30.85
XXIII	Ethanol	25	197	$C_{13}H_{16}N_4O_2S$	53.21	5.10	19.12
				(292,29)	53.42	5.54	19.17
XXV	Water	5	295	$C_8H_8N_4O_2$	49.53	4.20	28.55
				(192,18)	49.99	4.20	29.16
XXVI	Ethanol	75	260	$C_{13}H_{11}N_3O_2$	65.04	4.57	17.28
				(241,27)	64.72	4.60	17.42
XXVII	Ethanol/Water	7	245	$C_{15}H_{16}N_4O_3$	60.28	5.27	18.23
				(300,31)	59.99	5.37	18.66
XXVIII	Water	30	275	$C_8H_9N_5O$	49.66	4.75	35.87
				(191,19)	50.25	4.74	36.63
XXIX	Ethanol	50	258	$C_9H_{11}N_5O_3$	45.22	4.67	29.40
				(237,22)	45.47	4.67	29.53

And in fact, these compounds proved to be completely different from reaction products of Ia,b with II. Consequently, the latter products were assigned structure III (and the alternate tautomeric structures respectively).

From the reaction of Ic with II the dioxo derivative IX is the only isolable product. It seems that the amino group in this compound is very sensitive against moisture, so that the dioxo compound can only be isolated.

An analogous condensation product is obtained by reacting 5-amino-3-phenylpyrazole (X) with Ib. Based on spectroscopic and analytical data two structures can be discussed. Although available data cannot exclude structure XII completely, structure XI was considered most likely for this product, based on analogy to the well established structure of the reaction products of acyclic enamino esters (9) with X, and also by analogy to the behaviour of Ib toward II.

Chart 3



X XI XII

Compounds Ia,b are also capable of a similar condensation reaction with 2-aminobenzimidazole (XIII), *via* elimination of ethanol. Structure XIV was considered for this product based on ^{1}H-nmr, which reveals 6-H at lower

Table II

Spectroscopic Data of Products of Reaction of Ia-e and XXI with Cyclic Amidines and of Compounds XXIV-XXIX

Compound	m/e	Ir [cm^{-1}] (in potassium bromide)	^{1}H-Nmr δ ppm
IIIa	195	3320, ~3000 (NH and OH); 2970, ~2000 (CH and OH dimer); 1650 (CO)	2.55 (m, 2H, CH_2); 3.44 (m, 3H, CH_2OH) 6.31 (s, 2H, NH_2) and 8.08 (s, 1H, triazole CH)
IIIb	209	3320, 3180 (NH and OH); 2960, 2940, 2820 ~2300 (OH dimer) and 1670-1650 (CO and C=N)	1.11 (d, J = 6; 3H, CH_3); 2.50 (d, 2H, CH_3); 3.66-3.88 (m, br, 2H, >CHOH); 6.44 (s, 2H, NH_2 and 8.11 (s, 1H, triazole CH)
VIIa	195	3380, 3340~3250, 3200 (NH and OH); 2980 ~2960 (CH_2); 2850~2300 (OH dimer); 1670 ~1660 (CO and C=N)	2.55 (m, 2H, CH_2); 3.44 (m, 3H, CH_2OH); 7.11 (s, 2H, NH_2) and 8.08 (s, 1H, triazole CH)
VIIb	209	3440, 3340 3160 (OH and NH); 2990, 2920 (CH_2 and CH) 2760-2000 (OH dimer); 1670 (CO) and 1610 (C=N)	1.08 (d, J = 6, 3H, CH_3); 2.55 (d, J = 5, CH_2); 3.66 (br, 1H, OH); 3.82 (m, 1H, >CH); 7.11 (s, 2H, NH_2) and 8.08 (s, 1H, triazole CH)
IX	-	3400-2300 (NH and OH dimer); 1730 (CO)	1.00 (d, J = 6, 3H, CH_3); 1.22 (d, J = 6, 3H, CH_3); 2.66 ~3.66 (m, 3H, >CH-CH-); 5.00 (m, 1H, CH) and 7.93 (s, 1H, triazole CH)
XI	285	3330, 3180 (NH and OH); 2990, 2900~2840 (CH_2, CH_3 and CH); 1650 (CO)	1.13 (d, J = 6, 3H, CH_3); 2.55 (d, 2H, CH_2); 3.88 (m, 1H, CH); 4.77 (br, 1H, OH); 6.29 (s, 3H, NH_2 and pyrazole 4-H); 7.40 ~7.88 (m, 5H, aromatic protons) and 11.35 (br, 1H, NH)
XIVa	244	3490, 3360 3240 (NH and OH); 2960, 2860 (CH_2 and CH); 1670 (CO); 1630 (C=C and C=N)	2.55 (m, 2H, CH_2); 3.44 (m, 3H, CH_2 and OH); 4.55 (br, 1H, ring CH); 6.28 (s, 2H, NH_2); 7.16-7.80 (m, 3H, 7-H, 8-H and 9-H); 8.33 (dd, 1H, 6-H)
XIVb	258	3480, 3360-2000 (chelated NH and OH); 1670 (CO) and 1630 (C=C and C=N)	1.15 (d, J = 6; 3H, CH_3); 2.60 (m, 2H, CH_2); 3.95 and 4.55 (m, 2.74 CHOH and 74% of CH proton); 6.30 (s, 2H, NH_2); 7.11-7.44 (m, 3H, 7-H, 8-H, 9-H); 8.22 (dd, 1H, 6-H) and 12.33 (s, 0.26 proton; 26% of NH proton)
XVII	258	3430, 3330, 3220 (NH and OH); 2990~2900 (CH_2 and CH); 1690 (CO); 1650 (C=N)	1.11 (d, J = 6, 3H, CH_3); 2.55 (m, 2H, CH_2); 3.88 (m, 1H, CH); 5.11 (br, 1H, OH); 6.33 (s, 1H, NH, CH); 6.77 (s, 1H, NH); 7.11-7.55 (m, 3-H, 7-H, 8-H, 9-H); 8.22 (dd, 1H, 9-H)
XVIII	191	3410~3300, 3100~3000 (chelated NH); 2990, 2820 (CH_3 and CH_2); 1680 (δ NH_2) 1650 (C=N)	1.39 (d, J = 6, 3H, CH_3); 2.55 (m, 1H, normal furan 4-H; 3.22 (m, 1H, deshielded furan 4-H); 5.00 (m, 1H, furan 5-H); 7.82 (s, 2H, NH_2); 8.97 (s, 1H, triazole CH)
XXa	-	3320, 3250, 3000 (NH_2); 2990, 2920 (CH_3CH_2 and CH_3); 1660 (δNH_2); 1620 (C=N)	3.11 (t, J = 6, 2H, CH_2); 4.66 (t, J = 6, 2H, CH_2); 6.55 (s, 1H, pyrazole CH); 7.40~7.55 (m, 5H, 3 aromatic protons and NH_2); 8.00~8.08 (m, 2H, aromatic protons)
XXb	266	3320~3190, 3160 (NH_2); 1670 (δ NH_2); 1620 (C=N)	1.31 (d, J = 6, 3H, CH_3); 2.55 (m, 1H, normal furan 4-H); 3.22 (m, 1H, deshielded furan 4-H); 5.00 (m, 1H, furan 5-H); 6.50 (s, 1H, pyrazole CH); 7.40~7.60 (m, 5H, three aromatic protons and NH_2); 8.0~8.08 (m, 2H, two deshielded aromatic protons)
XXII	-	3440, 3300, 3100 (NH_2, NH); 2960 (CH_2), 1670 (CO); 1620 (C=N)	1.66-2.4 (m, 8H, $3CH_2$, CH, SH); 6.33 (s, 2H, NH_2); 8.08 (s, 1H, triazole CH); 12.0 (br, 1H, NH)
XXIII	-	3400~3300 (NH); 2990~2800 (CH_2); 1670 (CO)	1.77~4.0 (m, 7H, $3CH_2$, CH and SH); 5.66 (s, 2H, NH_2); 7.11~7.77 (m, 3H, 3 aromatic protons); 8.20 (m, H, phenyl, 4-H)
XXV	-	3110 (NH); 2990~2940 (CH_3 and CH_2); 1710 ~1680 (CO)	1.44 (d, J = 6, 3H, CH_3); 2.55 (m, 1H, normal furan 4-H); 3.22 (m, 1H, deshielded furan 4-H); 5.22 (m, 1H, furan 5-H); 8.73 (s, 1H, triazole CH)
XXVI	-	3480~3420, 3320 (NH); 2990~2900 (CH_3, CH_2); 1700, 1670 (CO)	1.44 (d, J = 6, 3H, CH_3); 2.55 (m, 1H, normal furan H-4); 3.22 (m, 1H, deshielded furan CH); 5.22 (m, 1H furan H-5); 7.31~7.44 (m, 3H, benzene 7-H, 8-H, 9-H); 8.22 (dd, 1H, benzene 6-H)
XXVII	-	3490, 3370 (NH_2), 2990~2200 (CH_2, CH_3 and chelated NH); 1710 (acetyl CO); 1670 (ring CO); 1630 (δ NH_2)	1.44, 1.55 (two doublets both from one CH_3 (normal and deshielded CH_3)); 2.00 (s, 3H, acetyl CH_3); 5.22 (m, 1H, >CHOH); 2.55-3.22 (m, 3H, CH_2, CH); 6.2 (s, 2H, NH_2); 7.30-7.40 (m, 3H, 7-H, 8-H, 9-H); 8.20 (dd, 1H, 6-H)
XXVIII	191	3420, 3400, 3035 (NH); 2990, 2996 (CH_3, CH_2); 1690 (CO); 1640 (C=N, C=C)	1.44 (d, J = 6, 3H, CH_3); 2.55 (m, 1H, normal furan 4-H); 3.22 (m, 1H, deshielded furan 4-H); 5.22 (m, 1H, furan 5-H); 7.11 (s, 2H, NH_2); 8.22 (s, 1H, triazole CH)
XXIX	-	3390, 3340, 3200 (NH_2, NH); 2980, 2920 (CH_2, CH_3); 1720 (acetyl CO); 1660 (ring CO); 1630 (δNH_2); 1610 (C=N, C=C)	2.00 (s, 1H, acetyl CH_3); 2.50~2.85 (m, 2H, CH_2); 4.01 (m, 2H, CH_2); 7.30 (s, 1H, NH_2); 8.08 (s, 1H, triazole CH); 12.26 (br, 1H, NH)

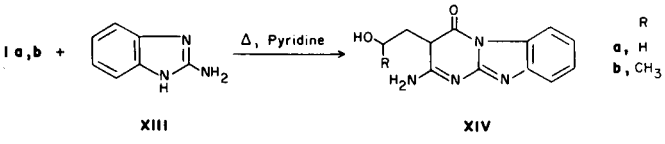
Table III

^{13}C-Nmr Spectra of Compounds IIIa,b, VIIb, XXII

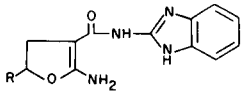
Compound	C-2	C-5	C-6	C-7	C-9	C-1′	C-2′	C-3
IIIa	148.09	153.49	85.28	156.53	148.76	26.72	59.92	
IIIb	148.15	153.98	85.89	156.98	148.91	32.76	66.50	22.87
VIIb	146.76	162.17	87.28	151.28	148.49	32.76	66.26	22.87
XXII	148.45	152.89	86.89	156.35	148.06	27.78	21.68	23.26

frequency than 7-H, 8-H and 9-H. This downfield shift can only be rationalized for in terms of a deshielding effect by the anisotropy of the adjacent carbonyl group, as in XIV (10). The structures XV or XVI would be difficult to account for this downfield shift. In turn, the isomeric compound XVII could be synthesized *via* reaction of XIII with α-cyano-γ-valerolactone (VIIIb).

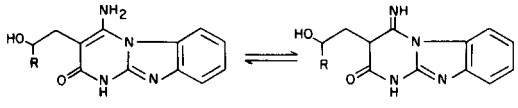
Chart 4



XIII XIV



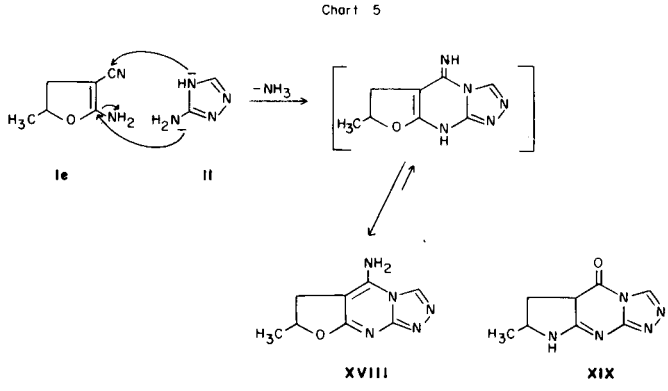
XV



XVI XVII

The enamino nitrile derivatives Id,e behave differently upon treatment with II and X. Thus, the condensation product resulting from II and Ib, *via* elimination of ammonia is isolated. Once again, the ^{1}H-nmr reveals the triazole proton at a lower field than as observed for II, III, and VII indicating the presence of a 1,2,4-triazolo[3,4-*a*]pyrimidine moiety in this compound. Two one-proton multiplets at δ = 2.55 and 3.22 ppm are observed, indicating the presence of a five membered ring with methyl rest at C-5, which affects, by anisotropy, a proton at C-4. Two structures, *cf.* XVIII and XIX, could be formed, and there is a logical mechanism for the reaction. XVIII is established for the reaction product, due to the absence of a carbonyl vibration in the ir showing instead an amino group both in the ir and the ^{1}H-nmr spectra.

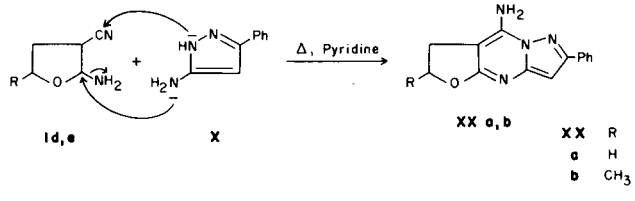
Chart 5



Ie II XVIII XIX

Similar to the behaviour of Ib toward II, the enaminonitriles Id,e with 5-amino-3-phenylpyrazole (X) give reason for the formation of furo[2,3:5,6]pyrazolo[1,5-*a*]pyrimidines XXa,b. The structures of these derivatives follow from analytical and spectroscopic data.

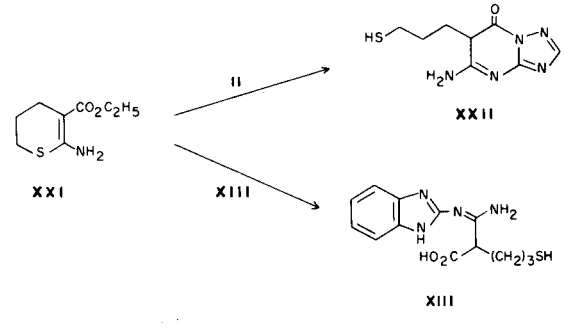
Chart 6



Id,e X XX a,b

Unlike the reactivities depicted above, 2-aminopyridine, 2-aminothiazole, and 2-aminopyrimidine do not react with Ia-e under conditions employed previously. Moreover, 2-amino-3-ethoxycarbonyl-4,5-dihydrothiophene did not

Chart 7

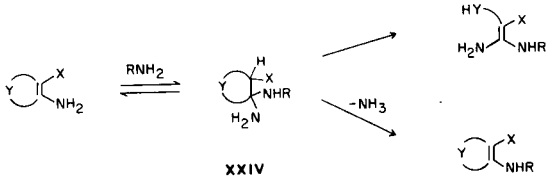


XXI XXII XIII

condense with cyclic amidines, whereas 2-amino-3-ethoxycarbonyl-5,6-dihydro-4*H*-thiopyrane (XXI) reacts with II to give the 1,2,4-triazolo[1,5-*a*]pyrimidine XXII, and with XIII to yield the benzimidazole XXIII.

It seems most likely that the reaction of Ia-e and XXI with cyclic amidines proceeds *via* initial Michael type addition of the primary amino moiety of the cyclic amidines to afford the intermediate Michael adduct XXIV. The latter one either undergoes ring cleavage and recyclization, *via* elimination of ethanol, or losing ammonia or the added amine. This assumption explains our observation that the reactivity of cyclic amidines toward Ia-e and XXI is independent on their pK_b. Furthermore, enamino esters with aromatic double bond character were found stable toward the action of cyclic amidines. It occured to us that all three possible pathways might be operating at the same time. Thus, more than one product might result from the reaction.

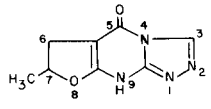
Chart 8



XXIV

Consequently we tried to work up completely the individual reaction mixtures, but only in one case have we succeeded to isolate another side product, as the mother liquors usually consist of polymeric materials. By reacting Ib and II, we have been able to separate by fractional crystallization 5% of XXV resulting *via* of condensation with ammonia elimination.

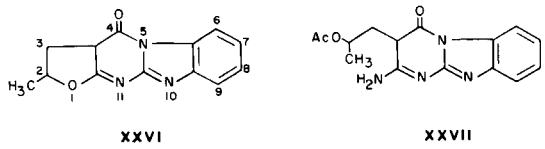
Chart 9



XXV

The presence of a hydroxyalkyl group in III, VII, and XIV neighboring to a potential hydroxyl or amino group prompted us to cyclize these derivatives into their pyrrolo-, or furoazolopyrimidine derivatives. Several cyclization procedures were attempted, but all failed to provide good yields of the desired products. However, when XIV is refluxed in a mixture of acetic and sulfuric acid, a furo[2,3:2′,3′]benzoimidazo[1,2-*a*]pyrimidine XXVI is formed in 30% yield by internal condensation. Additionally the acetyl derivative of XIV is isolated. Although XIV has more than one site for acylation the reaction product is assigned the acetyloxy structure XXVII based on spectroscopic data (*cf.* Table II).

Chart 10

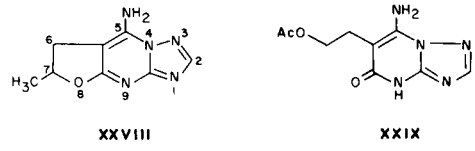


XXVI XXVII

Similarly VIIb cyclized into the furo[2,3:5′,6′]-1,2,4-triazolo[1,5-*a*]pyrimidine XXVIII on refluxing in acetic acid/sulfuric acid. However, the acetyloxy derivative was the only obtainable product when VIIa was treated similarly.

The procedures described above were found satisfactory, thus opening new pathways for the synthesis of several new azolopyrimidine derivatives. Accordingly, XVIII, XX, XXV, XXVI, and XXVIII, to our knowledge, are the first reported examples for these ring systems.

Chart 11



XXVIII XXIX

EXPERIMENTAL

All melting points are uncorrected. Ir-spectra were obtained (potassium bromide pellets) on a Perkin-Elmer Model 157 G. ^{1}H-nmr were measured in DMSO-d_6 with a Bruker Model WH-90 (internal standard: TMS, δ = 0 ppm). ^{13}C-nmr spectra were taken on a Bruker Model WP-80 (internal standard: TMS).

Reaction of Ia-e and VIIIa,b with Cyclic Amidines. General Procedure.

A solution each of Ia-e or VIIIa,b (20 mmoles) in pyridine (30 ml) was treated with the appropriate heterocyclic amidine (II, X, XIII - 20 mmoles). The reaction mixture was then refluxed for a period of 3-12 hours (the progress of the reaction was followed by tlc). After completion the solvent was evaporated and the remaining product was washed several times with petroleum ether. Trituration with ethanol and recrystallization from the proper solvent lead to the final product (physical data *cf.* list I; ir and ^{1}H-nmr *cf.* list II; ^{13}C-nmr data see table III).

7-Methyl-5-oxo-6,7-dihydro-5*H*,9*H*-furo[2,3-*d*]-1,2,4-triazolo[3,4-*a*]pyrimidine (XXV).

Method A.

A solution of 20 mmoles of Ib in pyridine (30 ml) was treated with II (20 mmoles) and the reaction mixture was refluxed for 6 hours. The solvent was evaporated and the residue was treated directly with a solution of 5 ml concentrated hydrochloric acid in 20 ml of water and refluxed for 30 minutes. After cooling the solution was neutralized with sodium bicarbonate, and the crystals formed on cooling were collected and recrystallized from water (*cf.* Tables I and II).

Method B.

The solution obtained after filtration of IIIb was evaporated and the remaining oil was treated as described above to give at least XXV after working up.

2-Methyl-4-oxo-2,3-dihydro-3a*H*,4*H*-furo[2,3-*d*]benzimidazo[1,2-*a*]pyrimidine (XXVI).

A suspension of XIVb (2.0 g, 8 mmoles) in acetic acid (30 ml) was treated with concentrated sulfuric acid (1.0 ml). After refluxing for 5 hours and evaporation, the residue was neutralized with sodium bicarbonate and the resulting solid product was crystallized from ethanol to give an analytically pure sample (*cf.* Tables I and II).

3-(2'-Acetyloxypropyl)-2-amino-4-oxo-3*H*,4*H*-benzimidazo[1,2-*a*]pyrimidine (XXVII).

The solution obtained on filtration of XXVI was evaporated *in vacuo* and the remaining product was purified by 2 times crystallization from ethanol/water (1:1).

5-Amino-7-methyl-6,7-dihydro-furo[2,3-*d*]-1,2,4-triazolo[1,5-*a*]pyrimidine (XXVIII).

A solution of VIIb (2.0 g, 10 mmoles) in acetic acid (30 ml) was treated with sulfuric acid (1.0 ml) and the solution was refluxed for 5 hours and evaporated *in vacuo*. The residue was dissolved in a little water and neutralized with sodium bicarbonate. The solid product, formed on standing was collected by filtration and crystallized from water.

5-Amino-6(2'-acetyloxyethyl)-7-oxo-7*H*,8*H*-1,2,4-triazolo[1,5-*a*]pyrimidine (XXIX).

VII was treated with acetic acid/sulfuric acid and the resulting product wass collected after working up as described above by filtration and crystallization from ethanol.

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