SYNTHESIS AND REACTIONS OF 5-ACETYL-2-AMINO-3-CYANO-4-(5-X-2-FURYL)-6-METHYL-4*H*-PYRANS

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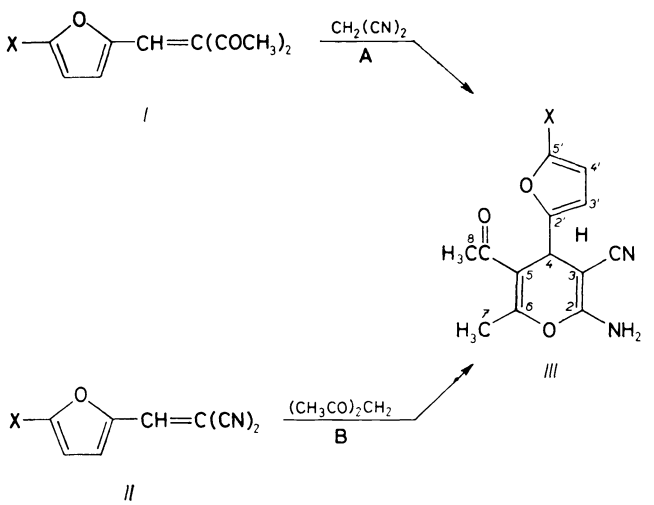
Received May 19, 1989
Accepted June 14, 1989

Substituted 2-amino-4-(5-X-2-furyl)-4*H*-pyrans *IIIa*—*IIIe* have been prepared by a cyclization reaction of 5-X-2-furylmethylenepropanedinitriles *IIa*—*IIe* with 2,4-pentanedione. In reaction of 3-(5-X-2-furyl)methylene-2,4-pentanediones *Ia*—*Ie* with propanedinitrile the formation of 4*H*-pyrans *IIIa*—*IIIe* is accompanied, depending on the catalyst type, by the formation of 5-X-2-furylmethylenepropanedinitriles *IIa*—*IIe*. 2-(4-Methylbenzylideneamino)-4*H*-pyran (*V*), 2-formylamino-4*H*-pyran (*VI*), and 3*H*,5*H*-pyrano[2,3-*d*]pyrimidine-4-one (*VII*) have been synthesized by functional modifications of the amino group in 4*H*-pyran *IIIa*. The transformation of 4*H*-pyran ring into pyridine ring gives — from 4*H*-pyran *IIIa* — 5-acetyl-3-cyano-4-(2-furyl)-6-methyl-3,4-dihydro-2(1*H*)-pyridone (*VIII*) and 5-acetyl-2-amino-3-cyano-4-(2-furyl)-6-methylpyridine (*IX*). The structure of synthesized compounds *III*—*IX* has been proved by means of IR, UV, and NMR spectra.

Substituted 2-amino-3-cyano-4*H*-pyrans are accessible either by cyclization reactions of arylalkylidenepropanedinitriles with α-methyleneketones[1-6] or α-arylalkylideneketones with propanedinitrile[1,3,7,8]. The authors[9] described a reaction of 3-benzylidene-2,4-pentanedione with propanedinitrile giving — in the presence of piperidine — 5-acetyl-2-amino-3-cyano-6-methyl-4-phenyl-4*H*-pyran. In context of studies of furylethylene derivatives carried out in our laboratory we tried to make use of the accessible 3-(5-X-2-furyl)methylene-2,4-pentanediones[10] *I* and 5-X-2-furylmethylenepropanedinitriles *II* in an analogous synthesis of new 4*H*-pyrane derivatives containing a 2-furyl residue at 4-position. The aim of the present communication was to find suitable conditions for synthesis of 4*H*-pyrans *III* and to examine their reactivity.

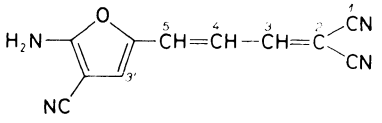
3-(5-X-2-Furyl)methylene-2,4-pentanediones *Ia*—*Ie* react with propanedinitrile in the presence of sodium ethoxide as a catalyst to give the corresponding 5-X-2-furylmethylenepropanedinitriles *IIa*—*IIe* in the yields of 50—79% (Scheme 1). Formation of 4*H*-pyrans *III* was not observed in any case. The reaction product, after elimination of 2,4-pentanedione anion, is the more conjugated and, hence, thermodynamically more stable 5-X-2-furylmethylenepropanedinitrile[11,12] (as compared with the starting derivative *I*).



In formulae *I* – *III*: *a*, X = H *b*, X = CO_2CH_3 *c*, X = C_6H_5S *d*, X = CH_3 *e*, X = C_6H_5O

SCHEME 1

The reaction of 3-(2-furyl)methylene-2,4-pentanedione (*Ia*) with propanedinitril catalyzed with piperidine gives the 4*H*-pyran derivative *IIIa* (yield 70%) along with a violet substance *IV* melting at 222–225°C. The latter was separated from *IIIa* by fraction crystallization from acetone. The elemental analysis and spectral data obtained for compound *IV* agree with the suggested structure of 5-(5-amino-4-cyano--2-furyl)-2-cyano-2,4-pentadienenitrile. The IR spectrum of compound *IV* exhibits an intensive absorption band at 2 200 cm^{-1} typical of a conjugated CN group as well as absorption maxima at 3 330, 3 255, and 3 190 cm^{-1} of the N—H valence vibrations. Its NMR spectrum shows five signals, the assignment to the individual olefinic protons H-3, H-4, and H-5 being carried out by the analysis of this three-spin system AMX. The formation of compound *IV* can be explained by the transformation of the starting 3-(2-furyl)methylene-2,4-pentanedione (*Ia*) into 2-furylmethylene-propanedinitrile (*IIa*) which reacts with another propanedinitrile molecule. This compound *IV* was prepared by Čepec[13] for the first time.



IV

Also in the case of the other 3-(5-X-2-furyl)methylene-2,4-pentanediones *Ib–Ie* the formation of 4*H*-pyrans *IIIb–IIIe* in the presence of piperidine is accompanied by the formation of the corresponding 5-X-2-furylmethylenepropanedinitriles *IIb–IIe*. The presence of compounds *IIb–IIe* was identified by the ^{1}H NMR spectrum of the raw reaction product. The 4*H*-pyrans were isolated by crystallization and obtained in average yield of 47–70% (method *A*, Table I).

The piperidine catalyzed cyclization of 5-X-2-furylmethylenepropanedinitriles *IIa–IIe* with 2,4-pentanedione (method *B*) provides the corresponding 2-amino-5--acetyl-3-cyano-6-methyl-4*H*-pyrans *IIIa–IIIe* in very good yields 67–94% (Table I). Compared with the method *A*, this method is more advantageous for syntheses of 4*H*-pyrans *III*, because it not only gives higher yields but also it devoid of any side reactions of the starting substrate. The unsubstituted derivative *IIIa* and other 2-amino-3-cyano-4*H*-pyrans with various substituents were described recently by Ibrahim[14].

The physico-chemical characteristics found by us for compound *IIIa* do not agree with the constants given in ref.[14]. The structure of synthesized 2-amino-3-cyano-4--(5-X-2-furyl)-4*H*-pyrans *IIIa–IIIe* was confirmed by elemental analysis and spectral methods. The IR spectra show typical absorption maxima of valence vibrations of a cyclic enaminonitrile grouping at 2 185–2 200 cm^{-1} (C≡N) and 3 307 to

TABLE I

5-Acetyl-2-amino-3-cyano-4-(5-X-2-furyl)-6-methyl-4*H*-pyrans *IIIa–IIIe*

Compound	Formula (M.w.)	M.p., °C	Yield, %		Calculated/Found		
			A[a]	*B*[a]	% C	% H	% N
IIIa	$C_{13}H_{12}N_2O_3$ (244·3)	159–161[b]	70	82	63·92 64·00	4·96 5·19	11·47 11·58
IIIb	$C_{15}H_{14}N_2O_5$ (302·3)	152–154	69	94	59·59 59·77	4·68 4·84	9·27 9·35
IIIc	$C_{19}H_{16}N_2O_3S$ (352·4)	132–133	61	85	64·75 64·60	4·59 4·87	7·95 8·07
IIId	$C_{14}H_{14}N_2O_3$ (258·3)	84–85	55	80	65·09 65·35	5·47 5·51	10·85 10·79
IIIe	$C_{19}H_{16}N_2O_4$ (336·4)	123–125	47	67	67·84 67·55	4·80 4·77	8·33 8·21

[a] For details of the syntheses of compounds *III* by procedures *A* and *B* see Experimental; [b] ref.[14] gives m.p. 220°C.

3 412 cm^{-1} (N—H) and of 4*H*-pyran and furane skeleton in the region of 1 500 to 1 700 cm^{-1} (Table II). The ^1H NMR spectra of compounds *III* (Table III) exhibit a characteristical signal of methine group at 4-position (δ = 4·58–4·71). The signals of methyl groups have close chemical shifts and are observed as a single signal in compounds *IIIa*, *IIIc*, and *IIId*. In the ^{13}C NMR spectra these groups are well distinguished and are observed at δ = ~29 (CH_3CO) and δ = ~19 (CH_3 at C-6). Their assignment was carried out by comparing with the ^{13}C NMR spectrum of 5-acetyl--2-amino-3-cyano-6-methyl-4-phenyl-4*H*-pyran and other 4*H*-pyrans[15] containing a 6-methyl group. The quaternary carbon atoms C-2 and C-6 have very close chemical shifts (Table IV), and their relative assignment was determined on the basis of geminal interactions of the protons of methyl group with the C-6 atom in the non-decoupled spectrum. The signal of the tertiary carbon atom C-4 lies at δ = = 32·6–33·1. The C-3 atom exhibits the resonance at a very high field δ = 54·0 to 55·1, which can be interpreted by the electron-donor efects of —O— and NH_2 groups.

The formylation of 4*H*-pyrane *IIIa* with the mixed anhydride of formic and acetic acids gave the 2-formylamino-4*H*-pyran *VI* (yield 83%), and the reaction of 2-amino-

TABLE II

UV and IR spectra of 2-amino-3-cyano-4-(5-X-2-furyl)-4*H*-pyrans *IIIa*–*IIIe*

Compound	UV[a]		IR, $\tilde{\nu}$, cm^{-1}				
	λ_{max}, nm	log ε[b]	N–H	C≡N	C=O and C=C		C–O–C
IIIa	239	3·31	3 373	2 190	1 700	1 660	1 205
	293 sh	2·31	3 307		1 667	1 647	
IIIb[c]	243	3·32	3 410	2 200	1 700	1 588	1 210
	263	3·30			1 668	1 440	
	337	2·78					
IIIc	212	3·09	3 410	2 200	1 700	1 588	1 220
	242	3·42			1 668	1 480	
	400	2·15					
IIId	238	3·57	3 412	2 200	1 700	1 640	1 208
	278 sh	2·92	3 340		1 670	1 603	
	351	2·73					
IIIe	203	3·10	3 400	2 185	1 700	1 603	1 208
	237	3·32	3 330		1 670	1 490	
					1 645		

[a] Concentration 1 . 10^{-4} mol l^{-1}, methanol; [b] in m^2 mol^{-1}; [c] 1 730 ν(C=O) of the $COOCH_3$ group.

-4*H*-pyran *IIIa* with 4-methylbenzaldehyde gave 2-(4-methylbenzylidene)amino-4*H*--pyran *V*. These reactions represent further evidence for the 2-amino group in 4*H*-

TABLE III

^{1}H NMR spectra (δ, ppm) of 2-amino-4-(5-X-2-furyl)-4*H*-pyrans *IIIa*—*IIIe*

Compound	CH_3[a]	H-4	H-3′	H-4′	NH_2	X
IIIa	2·21 s	4·63 s	6·16 m	6·37 m	6·98 s	7·56 m
IIIb	2·19 s 2·21 s	4·71 s	6·38 d[b]	7·19 d	7·07 s	3·71 s
IIIc	2·18 s	4·66 s	6·30 d[c]	6·83 d	7·03 s	7·00—7·49 m
IIId	2·21 s	4·58 s	5·98 m	5·98 m	6·95 s	2·21 s
IIIe	2·20 s 2·24 s	4·58 s	6·18 d[d]	5·65 d	7·00 s	6·92—7·55 m

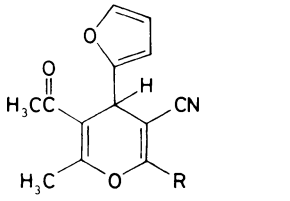
[a] The CH_3CO and CH_3 group at C-6; [b] $J(3', 4') = 3{\cdot}5$ Hz; [c] $J(3', 4') = 3{\cdot}4$ Hz; [d] $J(3', 4') = 3{\cdot}5$ Hz.

TABLE IV

^{13}C NMR chemical shifts (δ, ppm) of 2-amino-3-cyano-4*H*-pyrans *IIIa*—*IIIe*

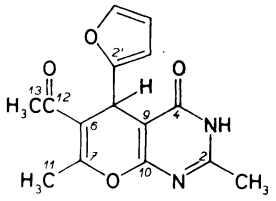
Carbon	*IIIa*	*IIIb*	*IIIc*	*IIId*	*IIIe*
C-2	159·6 s	159·6 s	160·9 s	159·8 s	159·8 s
C-3	54·5 s	53·6 s	54·0 s	55·1 s	54·6 s
C-4	32·6 d	32·9 d	33·1 d	32·9 d	33·0 d
C-5	113·0 s	112·5 s	112·7 s	113·4 s	113·1 s
C-6	155·9 s	156·7 s	156·0 s	155·9 s	155·9 s
CN	119·7 s	119·5 s	119·5 s	120·1 s	119·9 s
CO	197·9 s	197·4 s	197·7 s	198·5 s	198·5 s
C-7	18·6 q	18·8 q	18·7 q	18·8 q	18·8 q
C-8	29·5 q	29·8 q	29·6 q	29·9 q	29·7 q
C-2′	155·8 s	158·1 s	159·5 s	154·4 s	148·6 s
C-3′	105·7 d	108·5 d	108·4 d	106·8 d	107·4 d
C-4′	110·5 d	119·5 d	121·4 d	106·8 d	90·5 d
C-5′	142·4 d	143·0 s	140·4 s	151·4 s	156·5 s
X	—	160·8 s	136·2 s	13·6 q	154·8 s
		51·7 q	129·3 d		130·3 d
			126·4 d		124·4 d
			126·4 d		116·6 d

-pyrans giving characteristic reactions of amines[7,16]. The reaction of compound *IIIa* with acetanhydride gives 5*H*-pyrano[2,3-*d*]pyrimidine *VII* which is a cyclization product of the primary N-acetyl derivative. This reaction enables a simple synthesis of 5*H*-pyrano[2,3-*d*]pyrimidine skeleton[17].



V R = N = CH–C$_6$H$_3$(9,10,11,12,13)–CH$_3$

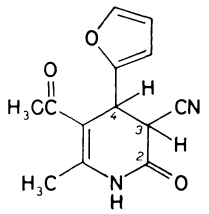
VI R = NHCHO



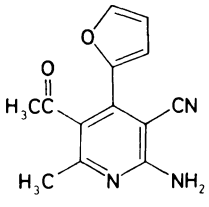
VII

The reactions of ring opening and recyclization of 2-amino-4*H*-pyrans were studied by Soto et al.[18]. In accordance with their findings, heating of 4*H*-pyran *IIIa* with acetic acid gives 2-pyridone *VIII*. The transformation of 2-amino-4*H*-pyran *IIIa* into the pyridine *IX* containing the same ring substituents as those in *IIIa* was carried out by treatment with ammonium acetate in acetic acid.

Elemental analysis, IR, UV, NMR (^{1}H, ^{13}C), and mass spectra confirm the structures of the 4*H*-pyrane derivatives *V*–*IX* synthesized.



VIII



IX

EXPERIMENTAL

The melting temperatures were determined with a Boetius apparatus and are not corrected. The IR spectra were measured with a UR 70 (Zeiss Jena) apparatus in KBr, the wavenumbers are given in cm^{-1}; the UV spectra were measured with a Specord UV VIS (Zeiss Jena) apparatus in methanol. The λ_{max} values are given in nm, the log ε values correspond to the dimension of m^2 mol^{-1}. The ^{1}H NMR spectra were measured with a Tesla BS 487 apparatus (80 MHz, CW mode) at 25°C in hexadeuteriodimethyl sulfoxide with hexamethyldisiloxane as the internal standard. The ^{13}C NMR spectra were measured in hexadeuteriodimethyl sulfoxide at 25°C using a JEOL FX-100 apparatus (25·04 MHz, FT mode), the chemical shifts are related to the solvent signal δ = 39·50. The reaction courses and purity of the substances produced were fol-

lowed by TLC (Silufol, detection by UV light and by iodine vapours). The furylmethylene-2,4-pentanediones *Ia*—*Ie* were prepared by the Knoevenagel condensation of the corresponding 5-X-2-furanecarbaldehydes with 2,4-pentanedione according to ref.[10]. The 5-X-2-furylmethylenepropanedinitriles were obtained by condensations of 5-X-2-furanecarbaldehydes with propanedinitrile[19].

5-X-2-Furylmethylenepropanedinitriles *IIa*—*IIe*

A mixture of 5 mmol 3-(5-X-2-furylmethylene)-2,4-pentanedione *Ia*—*Ie* and 5 mmol propanedinitrile in 5 ml anhydrous ethanol was stirred and treated with two drops of 5% sodium ethoxide in ethanol. The mixture was stirred at room temperature 4 h. The separated solid was collected by suction and recrystallized from ethanol.

2-*Furylmethylenepropanedinitrile* (IIa): yield 62%, m.p. 69—70°C (ref.[20] gives m.p. 71—72°C). ^{1}H NMR: 6·73—6·88 m, 1 H (H-4'); 7·28—7·43 m, 1 H (H-3'); 8·08—8·28 m, 2 H (H-5' and H-α).

5-*Methoxycarbonyl*-2-*furylmethylenepropanedinitrile* (IIb): not yet described; yield 79%, m.p. 192—194°C. For $C_{10}H_6N_2O_3$ (202·2) calculated: 59·40% C, 3·00% H, 13·86% N; found: 59·35%C, 2·91% H, 13·77% N. ^{1}H NMR: 3·83 s, 3 H (CH_3); 7·38—7·50 m, 2 H (H-3' and H-4'); 8·34 s, 1 H (H-α).

5-*Phenylthio*-2-*furylmethylenepropanedinitrile* (IIc): yield 50%, m.p. 89—90°C (ref.[21] gives m.p. 85°C). ^{1}H NMR: 6·85 d, 1 H (H-4', J(3', 4') = 3·9); 7·35—7·50 m, 6 H (H_{arom} and H-3'); 8·11 s, 1 H (H-α).

5-*Methyl*-2-*furylmethylenepropanedinitrile* (IId): yield 57%, m.p. 89—91°C (ref.[20] gives m.p; 91—92°C). ^{1}H NMR: 2·39 s, 3 H (CH_3); 6·54 d, 1 H (H-4', J(4', 3') = 4·0); 7·34 d, 1 H (H-3'). 8·08 s, 1 H (H-α).

5-*Phenoxy*-2-*furylmethylenepropanedinitrile* (IIe): not yet described; yield 55%, m.p. 94—95°C. For $C_{14}H_8N_2O_2$ (236·2) calculated: 71·17% C, 3·42% H, 11·86% N; found: 71·05% C, 3·22% H, 11·61% N. ^{1}H NMR: 5·85 d, 1 H (H-4', J(4', 3') = 4·0); 7·32—7·44 m, 5 H (H_{arom}); 7·46 d, 1 H (H-3'); 7·98 s, 1 H (H-α).

5-Acetyl-2-amino-3-cyano-4-(5-X-2-furyl)-6-methyl-4*H*-pyrans (*IIIa*—*IIIe*)

Procedure A. Two drops of piperidine were added to a mixture of 5 mmol 3-(5-X-2-furylmethylene)-2,4-pentanedione *Ia*—*Ie* and 5 mmol propanedinitrile in 5 ml anhydrous ethanol with stirring. The mixture was stirred 4 h and left to stand at room temperature 12 h. The separated solid was collected by suction and recrystallized from ethanol. The yields of the products *IIIa*—*IIIe* are given in Table I.

In the synthesis of 4-(2-furyl)-4*H* pyran (*IIIa*) the separated solid was collected by suction, and the mixture of compound *IIIa* and furane derivative *IV* was separated by fraction crystallization from acetone. The more soluble violet substance with m.p. 222—225°C (ref.[13] gives m.p. 222—224°C) is 5-(5-amino-4-cyano-2-furyl)-2-cyano-2,4-pentadienenitrile (*IV*), the less soluble product is 4*H*-pyrane *IIIa*. Compound *IV*: yield 5%, for $C_{11}H_6N_4O$ (210·2) calculated: 62·85% C, 2·88% H, 26·66% N; found: 62·70% C, 2·76% H, 26·49% N. IR spectrum: 3 330, 3 255, 3 190 (NH_2); 2 220 (CN); 1 640, 1 600, and 1 570 (C=C_{arom}). ^{1}H NMR: 6·53 dd, 1 H (H-4, J(3, 4) = = 12, J(4, 5) = 14); 7·20 d, 1 H (H-5); 7·40 s, 1 H (H-3'); 8·08 d, 1 H (H-3); 8·86 br. s, 2 H (NH_2).

Procedure B. Two drops of piperidine were added to a mixture of 5 mmol 5-X-2-furylmethylenepropanedinitrile *IIa*—*IIe* and 5 mmol 2,4-pentanedione in 5 ml anhydrous ethanol with stirring.

The mixture was stirred 4 h and then was left to stand 12 h. The separated solid was collected by suction and recrystallized from ethanol. A survey of the 4*H*-pyrans *III* synthesized together with their physical characteristics are given in Table I.

5-Acetyl-3-cyano-4-(2-furyl)-6-methyl-2-(4-methylbenzylideneamino)-4*H*-pyran (*V*)

A mixture of 2·44 g 4*H*-pyran *IIIa* and 1·32 g 4-methylbenzaldehyde in 30 ml anhydrous toluene with catalytic amount of 4-methylbenzenesulfonic acid was refluxed 6 h. After concentrating the mixture to a half volume and cooling to 0°C, the separated product *V* was collected by suction and recrystallized from ethanol. Yield of 4*H*-pyran *V* is 2·4 g (69%), m.p. 187—188°C. For $C_{21}H_{18}N_2O_3$ (346·4) calculated: 72·81% C, 5·25% H, 8·09% N; found: 73·03% C, 5·38% H, 8·23% N. UV spectrum (λ_{max}(log ε)): 229 (3·20), 293 (3·32), 333 (3·20). IR spectrum: 2 220 (CN); 1 699, 1 661, 1 622, 1 593, and 1 567 (CO and C=C_{arom}). ^{1}H NMR: 2·24 s, 3 H (CH_3CO); 2·36 s, 3 H (CH_3–C(6)); 2·40 s, 3 H (CH_3); 5·06 s, 1 H (H-4); 6·35 m, 1 H (H-3′); 6·44 m, 1 H (H-4′); 7·39 d, 2 H (H-11, J(10, 11) = 7·8); 7·63 m, 1 H (H-5′); 7·90 d, 2 H (H-10); 8·92 s, 1 H (N=CH). ^{13}C NMR: 18·5 q (C-7), 21·6 q (C-13), 29·5 q (C-8), 34·2 d (C-4), 85·3 s (C-3), 107·5 d (C-3′), 110·8 d (C-4′), 111·7 s (C-5), 116·7 s (CN), 129·8 d (C-10), 130·1 d (C-11), 131·8 s (C-9), 143·3 d (C-5′), 144·4 s (C-12), 153·6 s (C-2′), 156·4 s (C-6), 157·4 s (C-2), 163·9 d (N=CH), 197·5 s (C=O).

5-Acetyl-3-cyano-2-formylamino-4-(2-furyl)-6-methyl-4*H*-pyran (*VI*)

A mixture of 4·6 g 99·7% formic acid and 10·2 acetanhydride was stirred at 50°C 1 h, cooled to room temperature, and treated with 4·88 g 4*H*-pyran *IIIa* and 15 ml formic acid. The mixture was stirred at room temperature 16 h and then poured into 100 ml ice water. The separated solid was collected by suction, thoroughly washed with water, and recrystallized from ethanol. Yield of compound *VI* was 4·5 g (83%), m.p. 144—146°C. For $C_{14}H_{12}N_2O_4$ (272·3) calculated: 61·75% C, 4·45% H, 10·29% N; found: 61·68% C, 4·36% H, 10·35% N. UV spectrum (λ_{max}(log ε)): 237 (3·36), 273 sh (2·86). IR spectrum: 3 210 (NH), 2 220 (CN), 1 710 (C=O), 1 690, 1 675, 1655, 1 605, 1 504 (CO and C=C_{arom}). ^{1}H NMR: 2·24 s, 6 H (2 × CH_3); 4·89 s, 1 H (H-4); 6·20 to 6·48 m, 2 H (H-3′ and H-4′); 7·55 m, 1 H (H-5′); 8·56 s, 1 H (CH=O); 11·05 br. s, 1 H (NH).

5-Acetyl-4-(2-furyl)-2,7-dimethyl-3*H*,5*H*-pyrano[2,3-*d*]pyrimidin-4-one (*VII*)

A mixture of 2·44 g 4*H*-pyran *IIIa* and 10 ml acetanhydride was refluxed 7 h and then was left to stand 12 h. The separated solid was collected by suction, thoroughly washed with water, and recrystallized from ethanol. Yield of product *VII* was 1·2 g (42%), m.p. 228—230°C. For $C_{15}H_{14}N_2O_4$ (286·3) calculated: 62·92% C, 4·94% H, 9·79% N; found: 62·93% C, 5·11% H, 9·99% N. UV spectrum (λ_{max} (log ε)): 210 (3·14), 256 (3·05), 348 (2·10). IR spectrum: 3 440 (NH); 1 692, 1 673, 1 654, 1 600 (C=O and C=C_{arom}). ^{1}H NMR: 2·27 s, 9 H (3 × CH_3); 5·04 s, 1 H (H-4); 6·14 m, 1 H (H-3′); 6·31 m, 1 H (H-4′); 7·46 m, 1 H (H-5′); 12·54 s, 1 H (NH). ^{13}C NMR: 18·8 q (C-11), 20·9 q (CH_3), 29·6 q (C-13), 29·9 d (C-5), 97·9 s (C-9), 106·2 d (C-3′), 110·5 d (C-4′), 113·4 s (C-6), 142·0 d (C-5′), 154·8 s (C-2′), 157·0 s (C-7), 158·8 s (C-10), 160·5 s (C-2), 161·8 s (C-4), 197·8 s (C-12).

5-Acetyl-3-cyano-4-(2-furyl)-6-methyl-3,4-dihydro-2(1*H*)pyridone (*VIII*)

A mixture of 1·22 g 4*H*-pyran *IIIa* and 15 ml glacial acetic acid was refluxed 7 h, cooled to room temperature, left to stand 24 h, and decomposed with 50 ml ice water. After three days of standing

at room temperature, the product *VIII* was collected by suction and recrystallized from ethanol. Yield 0·75 g (61%), m.p. 168—170°C. For $C_{13}H_{12}N_2O_3$ (244·3) calculated: 63·93% C, 4·95% H, 11·47% N; found: 63·68% C, 4·75% H, 11·40% N. UV spectrum (λ_{max}(log ε)): 216 (2·92), 292 (3·01). IR spectrum: 3 290 (NH); 2 268 (CN); 1 718, 1 708 (C=O); 1 666, 1 580, and 1 487 (C=C_{arom}). ^{1}H NMR: 2·24 s, 3 H (CH_3CO); 2·34 s, 3 H (CH_3); 4·57 d, 1 H (H-4); 4·78 d, 1 H (H-3, J(3, 4) = 6); 6·32—6·50 m, 2 H (H-3′ and H-4′); 7·50 m, 1 H (H-5′); 9·31 s, 1 H (NH). ^{13}C NMR: 18·7 q (C-7), 29·7 q (C-8), 35·4 d (C-4), 39·1 d (C-3), 107·9 d (C-3′), 110·5 d (C-4′), 112·4 s (C-5), 115·1 s (CN), 143·2 d (C-5′), 146·9 s (C-6), 151·1 s (C-2′), 162·8 s (C-2), 195·6 s (C=O).

5-Acetyl-2-amino-3-cyano-4-(2-furyl)-6-methylpyridine (*IX*)

A mixture of 0·74 g 4*H*-pyran *IIIa* and 0·92 g ammonium acetate in 15 ml glacial acetic acid was refluxed 4 h and then was left to stand at room temperature 12 h, and decomposed by pouring into 50 ml ice water. The product *IX* was collected by suction and recrystallized from ethanol. Yield 0·30 t (40%), m.p. 238—239°C. For $C_{13}H_{11}N_3O_2$ (241·3) calculated: 64·72% C, 4·60% H, 17·42% N; found: 64·47% C, 4·75% H, 17·60% N. UV spectrum (λ_{max}(log ε)): 216 (3·06), 265 (3·22), 299 (3·03), 349 (2·85). IR spectrum: 3 395, 3 340 (NH); 2 200 (CN); 1 702 (CO); 1 664, 1 567, 1 540 (C=C, C=N). ^{1}H NMR: 1·94 s, 3 H (CH_3CO); 2·28 s, 3 H (CH_3); 6·74 m, 1 H (H-4′); 7·11 m, 1 H (H-3′); 7·23 br. s, 2 H (NH_2); 7·93 m, 1 H (H-5′).

Mass Spectra (*m*/*z* (Relative Abundances))

IIIa: 244 ($M^{\ddagger}$, 11), 216 (18), 201 (29), 178 (6), 173 (4), 159 (4), 144 (36), 121 (13), 116/115 (9/12), 100 (18), 93 (5), 89 (9), 85 (23), 77 (4), 66/65 (12/9), 64 (5), 51 (5), 44 (5), 43 (100).

V: 346 ($M^{\ddagger}$, 57), 347 (15), 331 (5), 318/317 (17/65), 305/304 (7/30), 303 (82), 276/275 (6/26), 261/260 (6/23), 231 (8), 227/226 (6/30), 225 (10), 214 (5), 210 (5), 209 (6), 184 (6), 182 (6), 168 (9), 157 (6), 149 (6), 146 (17), 130/129 (6/11), 120/119 (11/11), 118/117 (10/11), 105/104 (36/6), 103 (17), 93 (5), 91/90 (22/7), 89 (6), 78/77 (10/18), 71 (6), 69 (6), 65 (16), 63 (10), 57 (10), 55 (8), 51 (7), 44 (18), 43 (100).

VI: 273 (8), 272 ($M^{\ddagger}$, 37), 244/243 (10/17), 230/229 (5/25), 227 (15), 218/217 (11/10), 216/215 (47/8), 211 (8), 202/201 (13/71), 200/199 (7/9), 198/197 (9/6), 190/189 (8/5), 187 (6), 185/184 (8/11), 183 (5), 177 (5), 175/174 (7/10), 173/172 (16/5), 160/159 (7/15), 158/157 (11/11), 156/155 (12/7), 148 (5), 146/145 (10/15), 135 (6), 132/131 (7/9), 130/129 (9/5), 128 (8), 121 (10), 119/118 (8/6), 117 (5), 103/102 (8/6), 101 (5), 91/90 (8/9), 89 (5), 81 (5), 77/76 (12/7), 75 (6), 68/67 (7/12), 65/64 (13/8), 63 (13), 55 (5), 53/52 (5/7), 51/50 (12/5), 45 (5), 44 (13), 43 (100).

VIII: 245 (5), 244 ($M^{\ddagger}$, 28), 229 (5), 218/217 (11/71), 215 (6), 202/201 (17/34), 189/188 (16/5), 185/184 (11/4), 176/175 (14/27), 174/173 (13/12), 162/161 (10/10), 160 (5), 158 (5), 149/148 (6/6), 147/146 (9/8), 145 (6), 134 (13), 132 (5), 130 (5), 121 (11), 118 (5), 106/105 (6/5), 91 (5), 81 (5), 77 (9), 65 (12), 63 (7), 58/57 (20/6), 55 (6), 52/51 (5/7), 44 (18), 43 (100).

The authors are indebted to Mrs E. Kaisová for technical assistance, to Dr M. Hroboňová for the spectral measurements, to Dr V. Mlynárik, for valuable interpretation of the NMR *spectra, and to Mrs M. Ondrejkovičová (Department of Analytical Chemistry) for the elemental analyses.*

REFERENCES

1. Kuthan J.: Adv. Heterocycl. Chem. *34*, 145 (1983).
2. Abdelrazek F. M., Kandeel Z. E., Himly K. M. H., Elnagdi M. H.: Synthesis *1985*, 432.
3. Heinisch G., Holzer W., Nawwar G. A. M.: Monatsh. Chem. *117*, 247 (1986).
4. Sharanina L. G., Nesterov V. N., Klokol G. V., Rodinovskaya L. A., Shklover V. E., Sharanin Y. A., Strutchkov Y. T., Promonenkov V. K.: Zh. Org. Khim. *22*, 1315 (1986).
5. Heinisch G., Holzer W., Nawwar G. A. M.: J. Heterocycl. Chem. *23*, 93 (1986).
6. Klokol G. V., Sharanina L. G., Nesterov V. N., Shklover V. E., Sharanin Y. A., Strutchkov Y. T.: Zh. Org. Khim. *23*, 412 (1987).
7. Elgemeie G. E. H., Elkerim A., Gohar M., Regaila H. A., Elfahham H. A.: Arch. Pharm. (Weinheim) *321*, 131 (1988).
8. Marchalín Š., Kuthan J.: Collect. Czech. Chem. Commun. *48*, 3123 (1983).
9. Soto J. L., Seoane C., Martín N., Quinteiro M.: Heterocycles *22*, 1 (1984).
10. Marchalín Š., Ilavský D., Kováč J.: Z. Chem. *27*, 406 (1987).
11. Patai S., Rappoport Z in: *The Chemistry of Alkenes* (S. Patai, Ed.), p. 558. Wiley, New York 1964.
12. Rappoport Z., Ladkani D.: J. Chem. Soc., Perkin Trans. 1, *1974*, 2595.
13. Čepec P., Považanec F., Kováč J.: Unpublished results.
14. Ibrahim N. S.: Heterocycles *24*, 935 (1986).
15. Pascual C., Martín N., Seoane C.: Magn. Resonance Chem. *23*, 793 (1985).
16. Seoane C., Soto J. L., Quinteiro M.: J. Prakt. Chem. *328*, 35 (1986).
17. Marchalín Š., Kuthan J.: Collect. Czech. Chem. Commun. *49*, 2309 (1984).
18. Seoane C., Soto J. L., Zamorano P., Quinteiro M.: J. Heterocycl. Chem. *18*, 309 (1981).
19. Corson B. B., Stoughton R. W.: J. Am. Chem. Soc. *50*, 2825 (1928).
20. Musumarra G., Ballistreri F. P.: Chem. Scr. *18*, 209 (1981).
21. Kada R., Knoppová V., Kováč J.: Collect. Czech. Chem. Commun. *40*, 1563 (1975).

Translated by J. Panchartek.