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SYNTHESIS OF *C*-GLYCOPYRANOSYLFURAN DERIVATIVES BY REACTION OF DIALDEHYDES WITH CYANOACETAMIDE*

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ABSTRACT

The reaction of diglycol- and thiodiglycol-aldehyde (**1a,b**) with cyanoacetamide yields *cis*-3,5-diacetoxy-4-carbamoyl-4-cyano-tetrahydropyran (**2a**) and -tetrahydrothiopyran (**2b**). When this reaction is applied to (2*S*)-2-(3-ethoxycarbonyl-2-methyl-5-furyl)-3,5-dihydroxy-1,4-dioxane (**1c**), (2*S*)-3,5-dihydroxy-2-(3-methoxycarbonyl-2-methyl-5-furyl)-1,4-dioxane (**1d**), and (2*S*,3*R*,5*S*)-2-(3-acetyl-2-methyl-5-furyl)-3,5-dihydroxy-1,4-dioxane (**1e**), 5-(3-carbamoyl-3-cyano-3-deoxy-β-D-*xylo*-pentopyranosyl)-3-ethoxycarbonyl-2-methylfuran (**2c**), 5-(2,4-di-*O*-acetyl-3-carbamoyl-3-cyano-3-deoxy-β-D-*xylo*-pentopyranosyl)-3-methoxycarbonyl-2-methylfuran (**2e**), and 3-acetyl-5-(2,4-di-*O*-acetyl-3-carbamoyl-3-cyano-3-deoxy-β-D-*xylo*-pentopyranosyl)-2-methylfuran (**2f**), respectively, are formed with (4*S*,5*S*)-4-carbamoyl-4-cyano-2-(3-ethoxycarbonyl-2-methyl-5-furyl)-5-hydroxy-5,6-dihydropyran (**3a**) and (4*S*,5*S*)-4-carbamoyl-4-cyano-5-hydroxy-2-(3-methoxycarbonyl-2-methyl-5-furyl)-5,6-dihydropyran (**3b**) as minor products. The dehydration of **2a,b**, 5-(2,4-di-*O*-acetyl-3-carbamoyl-3-cyano-3-deoxy-β-D-*xylo*-pentopyranosyl)-3-ethoxycarbonyl-2-methylfuran (**2d**), **2e**, and **2f** yields *cis*-3,5-diacetoxy-4,4-dicyano-tetrahydropyran and -tetrahydrothiopyran (**2l,m**), and the 5-(2,4-di-*O*-acetyl-3,3-dicyano-3-deoxy-β-D-*erythro*-pentopyranosyl) derivatives (**2n–p**) of 3-ethoxycarbonyl-2-methylfuran, 3-methoxycarbonyl-2-methylfuran, and 3-acetyl-2-methylfuran, respectively.

INTRODUCTION

The reaction of active methylene compounds with 1,5-dialdehydes [diglycolaldehyde (**1a**), thiodiglycolaldehyde (**1b**), (2*S*)-2-(3-ethoxycarbonyl-2-methyl-5-furyl)-3,5-dihydroxy-1,4-dioxane (**1c**), (2*S*)-3,5-dihydroxy-2-(3-methoxycarbonyl-2-methyl-5-furyl)-1,4-dioxane (**1d**) and (2*S*,3*R*,5*S*)-2-(3-acetyl-2-methyl-5-furyl)-3,5-dihydroxy-1,4-dioxane (**1e**)] has been studied extensively[1–6] and we now report on the reaction of the less active[7] methylene compound cyanoacetamide with **1a–e**.

*Derivatives of 3-hetero-1,5-dialdehydes, Part XV. For Part XIV, see ref. 4.

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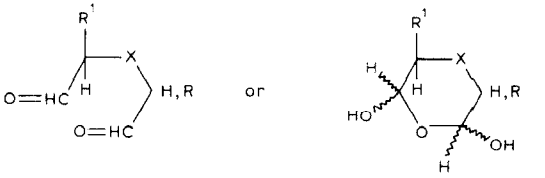
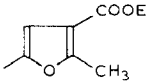
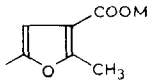


1a X = O, R = R^1 = H

1b X = S, R = R^1 = H

1c X = O, R = HetA =  , R^1 = H

1d X = O, R = HetB =  , R^1 = H

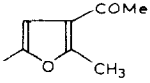
1e X = O, R = HetC =  , R^1 = H

TABLE I

PRODUCTS OF THE REACTION OF **1a–e** AND CYANOACETAMIDE

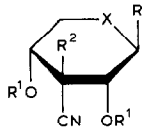
Starting products (g)	*Cyanoacetamide (g)*	*1,4-Dioxane–water (2.1, mL)*	*Time (h)*	*Yield (g, %)*
1a[14,15] [a]	1.2	15	90	**2a** (0.52, 26.3)[b]
1a[a]	1.2	15	90	**2a** (0.76, 38.5)[c]
1b[16] (1.0)	1.2	15	96	**2b** (1.05, 49.2)[b]
1c[17] (1.0)	0.62	15	84	**2c** (0.55, 44.0); **4a** (0.06, 5.0)
1d[5,18] (1.0)	0.65	15	72	**2e** (0.68, 43.0)[b]; **4b** (0.07, 6.0)
1e[19] (1.5)	1.1	21	72	**2f** (1.2, 47.2)[b]

[a]Prepared in the polymeric state from the bis(dimethyl acetal)[14] (1.42 g, 7.32 mmol) or bis(di-isopropyl acetal)[15] (2.24 g, 7.32 mmol). [b]The crude product was acetylated by using acetic acid–acetic anhydride–acetyl chloride. [c]The crude product was acetylated by using acetic anhydride–pyridine.

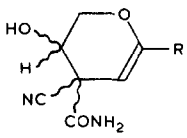
RESULTS AND DISCUSSION

The reactions of **1a–e** with cyanoacetamide were carried out in aqueous 1,4-dioxane at room temperature for 72–96 h, using piperidine as catalyst. The products from **1c** and **1d** were isolated by column chromatography, and those from **1a, 1b**, and **1e** by column chromatography after acetylation. The yields are given in Table I.

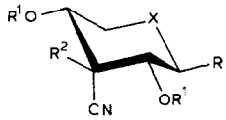
The sole products from **1a, 1b**, and **1e** were the pyran and thiopyran derivatives **2a, 2b**, and **2f**, respectively. The major products from **1c** and **1d** were the *C*-pyranosyl furan derivatives **2c** and **2e**, respectively, and the minor products were the 2,3-dihydropyran derivatives **3a** and **3b**, respectively. The formation of only one pyran derivative in each of these reactions reflects high stereoselectivity in



2a X = O, R = H, R^1 = Ac, R^2 = $CONH_2$
2b X = S, R = H, R^1 = Ac, R^2 = $CONH_2$
2c X = O, R = HetA, R^1 = H, R^2 = $CONH_2$
2d X = O, R = HetA, R^1 = Ac, R^2 = $CONH_2$
2e X = O, R = HetB, R^1 = Ac, R^2 = $CONH_2$
2f X = O, R = HetC, R^1 = Ac, R^2 = $CONH_2$
2g X = O, R = H, R^1 = Ac, R^2 = CONHAc
2h X = S, R = H, R^1 = Ac, R^2 = CONHAc
2i X = O, R = HetA, R^1 = Ac, R^2 = CONHAc
2j X = O, R = HetB, R^1 = Ac, R^2 = CONHAc
2k X = O, R = HetC, R^1 = Ac, R^2 = CONHAc
2l X = O, R = H, R^1 = Ac, R^2 = CN
2m X = S, R = H, R^1 = Ac, R^2 = CN
2n X = O, R = HetA, R^1 = Ac, R^2 = CN
2o X = O, R = HetB, R^1 = Ac, R^2 = CN
2p X = O, R = HetC, R^1 = Ac, R^2 = CN



3a R = HetA
3b R = HetB



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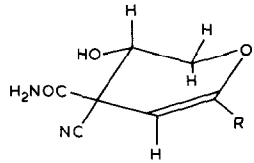

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contrast to the reaction of these dialdehydes with other active methylene compounds[4,5].

The structures of **2a–f** were established on the basis of elemental analyses and spectroscopic data (Tables II, III, and IV). Thus, **2a–f** show characteristic i.r. bands[8] for amide and ester groups. The cyano band[9] at ~2250 cm^{-1} is not observed for **2a,c–f** and was very weak for **2b** as found[10] for cyano groups near to oxygenated functions. The configuration at C-2 and C-4 in **2a–f** and the preferred $^4C_1$(D) conformation **4** in chloroform were deduced from the ^{1}H-n.m.r. data (especially $J_{1,2}$ and $J_{4,5a}$ 9.3–10.7 Hz) (see also Tables III and IV). The configuration at C-3 is tentatively assigned on the basis of the expected higher stability of the equatorial carbamoyl group and the axial cyano group in this conformation with the furan ring and the two hydroxyl or acetoxyl groups occupying equatorial positions.

TABLE II

TYPICAL I.R. ABSORTION BANDS FOR **2a–k**[a]

Compound	ν_{N-H}	$\nu_{C=O}$	ν_{N-H}	ν_{C-O}
2a	3470, 3370, 3250	1780, 1722, 1700	1670	1223, 1210, 1060
2b	3420, 3225, 3170	1765, 1720	1640	1220, 1032
2c	[illegible]	1726, 1704	1634	1242, 1100, 1070
2d	3470, 3230, 32[illegible]	1796, 1780, 1740, 1710	1636	1238, 1212, 1070
2e	[illegible]40, 32[illegible]	1785, 1755, 1722, 1695	1625	1235, 1200, 1055
2f	[illegible]20, 32[illegible]	1770, 1758, 1720, 1692	1640	1237, 1207, 1065
2g	[illegible]	[illegible]	1510	1230, 1060
2h	[illegible]	[illegible]	[illegible]	1220, 1025
2i	3330, [illegible]	1782, 1730, [illegible]	[illegible]	[illegible], 1215, 1075
2j	3360, [illegible]	[illegible], 1782, 1730	[illegible]	[illegible]220, 1200, 1070
2k	3270, [illegible]	[illegible], 1755, 1695	1500	1216, 1070

[a]Recorded for KBr discs. [b]Broad band at 3550–3200 cm^{-1} for ν_{N-H} and ν_{O-H}.

TABLE IV

VICINAL PROTON–PROTON COUPLING CONSTANTS (Hz) FOR COMPOUNDS **2a–k**

Compound	$J_{1,2}$	$J_{4,5a}$	$J_{4,5e}$	$J_{5a,5e}$
2a		10.5	4.9	11.5
2b		9.3	5.6	
2c	10.0	10.0	5.0	11.0
2d	10.0	11.0	5.0	10.0
2e	9.0	10.5	4.9	11.3
2f	[illegible]	[illegible].7	5.[illegible]	11.5
2g		[illegible]	5.[illegible]	[illegible]
2h		9.6	6.0	
2i	10.0	10.5	5.0	11.5
2j	10.0	10.5	4.7	11.7
2k	10.0	10.5	4.9	11.8

Compounds **3a** and **3b** had i.r. bands for $CONH_2$, OH, and COOR. Also, **3a** had λ_{max}^{MeOH} 263 nm (ε 20,000), and **3b** had λ_{max}^{MeOH} 261 nm (ε 15,300). The half-chair form is the lowest-energy conformation of 2,3-dihydropyran[11,12]. The conformation **5** is the most probable for **3a**. The configuration at C-4 is tentatively assigned as for C-3 in the precursor **2a**. The values of $J_{5,6}$ 8.0 and $J_{5,6'}$ 3.0 Hz for **3a** indicate a quasi-antiperiplanar disposition of H-5,6 as in **5**.

When **2a,b,d–f** were treated with boiling acetic anhydride, dehydration did not occur. The corresponding imides **2g–k** were isolated and their structures were assigned on the basis of elemental analyses and spectroscopic data (see Tables II, III, and IV). The $J_{1,2}$ and $J_{4,5a}$ values indicated the $^4C_1$(D) conformation. The dehydration products **2l–p** could be prepared by reaction of **2a,b,d–f** with $SOCl_2$ in pyridine at 0°. Their structures were established by comparison with authentic samples obtained by the reaction of **1a–e** with malononitrile[5].

TABLE III

^{1}H-N M.R CHEMICAL SHIFTS (δ, p.p.m.) FOR **2a–k**

Compound	*Furan H-4*	*H-2*	*H-4*	*H-1*	*H-5*e	*H-5*a	2R^1	*Furan Me-2*	*Others*
2a[d,f]		←5.25dd→			4.15dd	3.40dd	2.10s		4.0 (bs, 1 H, NH)[a], and 5.2 (bs, 1 H, NH)[a]
2b[d,f]		←5.30dd→			←2.85m→		2.10s		6.3 (bs, 1 H, NH)[a], and 5.75 (bs, 1 H, NH)[a]
2c[e,g]	6.70s	4.12m[b]	4.0m[c]	4.22d	3.83dd	3.41dd	6.1d[a], 6.0d[a]	2.54s	7.7 (s, 1 H, NH)[a], 7.53 (s, 1 H, NH)[a], 4.22 (q, 2 H, *J* 7.3 Hz), and 1.25 (t, 3 H, *J* 7.3 Hz)
2d[e,f]	6.67s	5.63d	5.44dd	4.53d	4.30m	3.67dd	2.14s, 1.97s	2.55s	6.45 (s, 2 H, NH_2)[a], 4.26 (q, 2 H, *J* 7.3 Hz), and 1.33 (t, 3 H, *J* 7.3 Hz)
2e[d,f]	6.67s	5.62d	5.45dd	4.50d	4.30dd	3.65dd	2.12s, 1.97s	2.56s	6.32 (bs, 2 H, NH_2)[a], and 3.82 (s, 3 H, $MeCO_2$)
2f[d,f]	6.72s	5.65d	5.47dd	4.57d	4.30dd	3.70dd	2.12s, 1.97s	2.55s	7.0–6.75 (m, 2 H, NH_2)[a], and 2.39 (s, 3 H, furan MeCO-3).
2g[d,f]		←5.25dd→			4.15dd	3.45dd	2.10s		8.45 (bs, 1 H, NH)[a], and 2.47 (s, 3 H, MeCONH)
2h[d,f]		←5.30dd→			←2.90m→		2.10s		8.50 (bs, 1 H, NH)[a], and 2.47 (s, 3 H, MeCONH)
2i[d,f]	6.70s	5.60d	5.50dd	4.54d	4.30dd	3.70dd	2.15s, 2.00s	2.55s	8.57 (bs, 1 H, NH)[a], 4.3 (q, 2 H, *J* 7.0 Hz), 2.47 (s, 3 H, MeCONH), and 1.3 (t, 3 H, *J* 7.0 Hz)
2j[d,f]	6.67s	5.60d	5.47dd	4.54d	4.30dd	3.70dd	2.12s, 1.67s	2.56s	8.47 (bs, 1 H, NH)[a], 3.80 (s, 3 H, $MeCO_2$), and 2.47 (s, 3 H, MeCONH)
2k[d,f]	6.67s	5.61d	5.46dd	4.56d	4.30dd	3.70dd	2.14s, 1.97s	2.57s	8.45 (bs, 1 H, NH)[a], 2.47 (s, 3 H, MeCONH), and 2.37 (s, 3 H, furan MeCO-3)

[a]Exchangeable with D_2O. [b]d, *J* 10.0 Hz, after isotopic change. [c]dd, *J* 11.0 and 5.0 Hz, after isotopic change. [d]80 MHz. [e]200 MHz. [f]For a solution in $CDCl_3$ (internal Me_4Si). [g]For a solution in $(CD_3)_2SO$.

EXPERIMENTAL

The general methods have been described[13]. ^{1}H-N.m.r. spectra (80 MHz) were obtained with a Bruker WP-80-SY spectrometer.

Diglycolaldehyde (**1a**) was prepared in the polymeric state from its bis(dimethyl acetal)[14] or bis(di-isopropyl acetal)[15]. Thiodiglycolaldehyde (**1b**) was used in the form of its hydrate *cis*-2,6-dihydroxy-1,4-oxathiane, and was obtained[16] from thiodiglycolaldehyde bis(dimethyl acetal) or thiodiglycolaldehyde bis(diethyl acetal).

Reaction of cyanoacetamide with **1a–e**. — Cyanoacetamide and piperidine (0.15 mL) were added to a solution of the aldehyde **1a–e** in aqueous 1,4-dioxane. The solvents were removed after 72–96 h at room temperature (see Table I). The crude product was purified by column chromatography (ether) or was acetylated.

(*a*) The crude product from diglycolaldehyde (**1a**) was acetylated conventionally at room temperature for 20 h with acetic acid–acetic anhydride–acetyl chloride (6:6:10 mL) or acetic anhydride–pyridine at −10°. Column chromatography (ether) of the products yielded *cis*-3,5-diacetoxy-4-carbamoyl-4-cyanotetrahydropyran (**2a**), m.p. 278–280° (from ethanol). For i.r. and ^{1}H-n.m.r. data, see Tables II–IV (Found: C, 48.60; H, 5.20; N, 10.50. $C_{11}H_{14}N_2O_6$ calc.: C, 48.88; H, 5.22; N, 10.36%).

(*b*) The crude product from thiodiglycolaldehyde (**1b**) was acetylated as in (*a*). Column chromatography (ether) of the product gave *cis*-3,5-diacetoxy-4-carbamoyl-4-cyanotetrahydrothiopyran (**2b**), m.p. 276–278° (from ethanol). For i.r. and ^{1}H-n.m.r. data, see Tables II–IV (Found: C, 45.97; H, 4.65; N, 10.02. $C_{11}H_{14}N_2O_5S$ calc.: C, 46.11; H, 4.93; N, 9.78%).

(*c*) The crude product from (2*S*)-2-(3-ethoxycarbonyl-2-methyl-5-furyl)-3,5-dihydroxy-1,4-dioxane[17] (**1c**) was purified by column chromatography (ether) to give, first, (4*S*,5*S*)-4-carbamoyl-4-cyano-2-(3-ethoxycarbonyl-2-methyl-5-furyl)-5-hydroxy-5,6-dihydropyran (**3a**), m.p. 194–195° (from ether), $[\alpha]_D^{20}$ −8° (*c* 1, methyl sulfoxide); λ_{max}^{MeOH} 263 nm (ε 20,200); ν_{max}^{KBr} 3490, 3240, 2240, 1734, 1703, 1625, 1601, 1566, 1285, 1267, 1243, 1172, 1124, 1095, 840, 805, and 775 cm^{-1}. ^{1}H-n.m.r. data [$(CD_3)_2SO$]: δ 7.75 (bs, 2 H, exchangeable with D_2O, NH_2), 6.75 (s, 1 H, furan H-4), 6.35 (d, 1 H, *J* 5.5 Hz, exchangeable with D_2O, OH), 5.42 (s, 1 H, H-3), 4.3 (m, 1 H, H-5), 4.23 (q, 2 H, *J* 7.3 Hz, CO_2-CH_2), 4.1 (dd, 1 H, *J* 11.5 and 3.0 Hz, H-6), 3.92 (dd, 1 H, *J* 11.5 and 8.0 Hz, H-6′), 2.57 (s, 3 H, furan Me-2), and 1.28 (t, 3 H, *J* 7.3 Hz, CH_3CH_2) (Found: C, 56.29; H, 4.60; N, 8.88. $C_{15}H_{16}N_2O_6$ calc.: C, 56.25; H, 5.03; N, 8.74%).

Eluted second was 5-(3-carbamoyl-3-cyano-3-deoxy-β-D-*xylo*-pentopyranosyl)-3-ethoxycarbonyl-2-methylfuran (**2c**), m.p. 203–204° (from ether), $[\alpha]_{4360}^{25}$ −53° (*c* 1, methyl sulfoxide). For i.r. and ^{1}H-n.m.r. data, see Tables II–IV (Found: C, 53.22; H, 5.14; N, 8.02. $C_{15}H_{18}N_2O_7$ calc.: C, 53.25; H, 5.36; N, 8.27%). Compound **2c** (0.13 g, 0.38 mmol) was acetylated as in (*a*). Column chromatography (ether) of the product and recrystallisation from ether gave 5-(2,4-di-*O*-acetyl-3-carbamoyl-3-cyano-3-deoxy-β-D-*xylo*-pentopyranosyl)-3-ethoxycarbonyl-2-methyl-

furan (**2d**; 0.13 g, 80%), m.p. 158–159°, $[\alpha]_D^{25}$ −31° (*c* 1, chloroform). For i.r. and ^{1}H-n.m.r. data, see Tables II–IV (Found: C, 54.06; H, 5.40; N, 6.64. $C_{19}H_{22}N_2O_9$ calc.: C, 54.02; H, 5.25; N, 6.63%).

To a solution of **2d** (0.5 g, 1.48 mmol) in 1,4-dioxane–water (2:1, 12 mL) was added piperidine (0.12 mL). The mixture was left at room temperature for 4 days and then concentrated. Column chromatography (20:1 ether–hexane) of the crude material gave, first, **3a** (0.16 g, 33.8%) and then **2c** (0.1 g, 20.0%).

(*d*) Column chromatography (ether) of the crude product from (2*S*)-3,5-dihydroxy-2-(3-methoxycarbonyl-2-methyl-5-furyl)-1,4-dioxane[5,18] (**1d**) gave, first, (4*S*,5*S*)-4-carbamoyl-4-cyano-5-hydroxy-2-(3-methoxycarbonyl-2-methyl-5-furyl)-5,6-dihydropyran (**3b**), m.p. 173–175° (from ether), $[\alpha]_D^{20}$ −10° (*c* 0.6, methyl sulfoxide); λ_{max}^{MeOH} 261 nm (ε 15,300); ν_{max}^{KBr} 3480, 3345, 1745, 1705, 1610, 1565, 1263, 1238, 1095, 965, 805, and 775 cm^{-1}. ^{1}H-N.m.r. data [$(CD_3)_2SO$]: δ 7.72 (bs, 2 H, exchangeable with D_2O, NH_2), 6.77 (s, 1 H, furan H-4), 6.29 (d, 1 H, *J* 5.5 Hz, exchangeable with D_2O, OH), 5.42 (s, 1 H, H-3), 4.25–3.9 (m, 3 H, H-5,6,6′), 3.75 (s, 3 H, COOMe), and 2.57 (s, 3 H, furan Me-2) (Found: C, 54.62; H, 4.81; N, 9.06. $C_{14}H_{14}N_2O_6$ calc.: C, 54.90; H, 4.60; N, 9.14%).

Eluted second was a mixture (0.85 g) of 5-(3-carbamoyl-3-cyano-3-deoxy-β-D-*xylo*-pentopyranosyl)-3-methoxycarbonyl-2-methylfuran and cyanoacetamide, which was acetylated as in (*a*). Column chromatography (acetone–hexane, 1:1) of the product, with recrystallisation from ether, gave 5-(2,4-di-*O*-acetyl-3-carbamoyl-3-cyano-3-deoxy-β-D-*xylo*-pentopyranosyl)-3-methoxycarbonyl-2-methylfuran (**2e**), m.p. 223–224°, $[\alpha]_D^{20}$ −33° (*c* 1, chloroform). For i.r. and ^{1}H-n.m.r. data, see Tables II–IV (Found: C, 52.97; H, 4.87; N, 7.36. $C_{18}H_{20}N_2O_9$ calc.: C, 52.94; H, 4.93; N, 6.86%).

(*e*) The crude product from (2*S*,3*R*,5*S*)-2-(3-acetyl-2-methyl-5-furyl)-3,5-dihydroxy-1,4-dioxane[19] was acetylated as in (*a*). Column chromatography (ether) of the product gave 3-acetyl-5-(2,4-di-*O*-acetyl-3-carbamoyl-3-cyano-3-deoxy-β-D-*xylo*-pentopyranosyl)-2-methylfuran (**2f**), m.p. 161–162° (from ethanol–water), $[\alpha]_D^{20}$ −18° (*c* 1, chloroform). For i.r. and ^{1}H-n.m.r. data, see Tables II–IV (Found: C, 52.53; H, 5.30; N, 6.70. $C_{18}H_{20}N_2O_8 \cdot H_2O$ calc.: C, 52.68; H, 5.40; N, 6.82%).

Reaction of **2a,b,d,f** *with acetic anhydride.* — A mixture of **2a,b,d** or **f** and acetic anhydride was stirred and boiled under reflux. Chloroform (50 mL) was added, and the mixture was washed with saturated aqueous $NaHCO_3$ (4 × 50 mL) and then with water (25 mL), dried, filtered, and concentrated.

The following amounts and conditions were used:

Starting products (g)	*Ac_2O (mL)*	*Time (h)*	*Products (g, %)*
2a (0.11)	5	4	**2g** (0.10, 78.7)
2b (0.11)	5	2	**2h** (0.09, 71.3)
2d (0.20)	8	3	**2i** (0.18, 81.8)
2e (0.10)	6	5	**2j** (0.09, 81.6)
2f (0.10)	6	4	**2k** (0.10, 94.3)

cis-3,5-Diacetoxy-4-acetylcarbamoyl-4-cyanotetrahydropyran (**2g**) had m.p. 158° (from ethanol). For i.r. and ^{1}H-n.m.r. data, see Tables II–IV (Found: C, 49.87; H, 4.92; N, 8.71. $C_{13}H_{16}N_2O_7$ calc.: C, 50.00; H, 5.16; N, 8.96%).

cis-3,5-Diacetoxy-4-acetylcarbamoyl-4-cyanotetrahydrothiopyran (**2h**). The crude product yielded **2h**, m.p. 215–216° (from ethanol). For i.r. and ^{1}H-n.m.r. data, see Tables II–IV (Found: C, 47.39; H, 4.56; N, 8.24. $C_{13}H_{16}N_2O_6S$ calc.: C, 47.55; H, 4.91; N, 8.53%).

5-(2,4-Di-*O*-acetyl-3-acetylcarbamoyl-3-cyano-3-deoxy-β-D-*xylo*-pentopyranosyl)-3-ethoxycarbonyl-2-methylfuran (**2i**), after column chromatography (hexane–ether, 1:3), had m.p. 103–105° (from ether–hexane), $[\alpha]_D^{20}$ −12° (*c* 1, chloroform). For i.r. and ^{1}H-n.m.r. data, see Tables II–IV (Found: C, 54.58; H, 4.87; N, 5.73. $C_{21}H_{24}N_2O_{10}$ calc.: C, 54.31; H, 5.21; N, 6.03%).

5-(2,4-Di-*O*-acetyl-3-acetylcarbamoyl-3-cyano-3-deoxy-β-D-*xylo*-pentopyranosyl)-3-methoxycarbonyl-2-methylfuran (**2j**), after column chromatography (hexane–ether, 1:5), had m.p. 135–136° (from hexane), $[\alpha]_D^{20}$ −29° (*c* 1, chloroform). For i.r. and ^{1}H-n.m.r. data, see Tables II–IV (Found: C, 53.17; H, 4.88; N, 6.00. $C_{20}H_{22}N_2O_{10}$ calc.: C, 53.33; H, 4.92; N, 6.21%).

3-Acetyl-5-(2,4-di-*O*-acetyl-3-acetylcarbamoyl-3-cyano-3-deoxy-β-D-*xylo*-pentopyranosyl)-2-methylfuran (**2k**), after column chromatography (hexane–ethyl acetate, 1:1), had m.p. 62–64° (from ether–hexane), $[\alpha]_D^{20}$ −29° (*c* 1, chloroform). For i.r. and ^{1}H-n.m.r. data, see Tables II–IV (Found: C, 54.85; H, 5.00; N, 6.10. $C_{20}H_{22}N_2O_9$ calc.: C, 55.35; H, 5.10; N, 6.44%).

Dehydration of **2a,b,d–f**. — To a cooled (ice-bath) solution of **2a,b,d,e** or **f** in pyridine was added $SOCl_2$, and then the mixture was kept at 0°. Chloroform (50 mL) was added, and the mixture was washed with saturated aqueous $NaHCO_3$ (50 mL), aqueous 5% HCl (4 × 50 mL), saturated, aqueous $NaHCO_3$ (50 mL), and water (25 mL), then dried, filtered, and concentrated. The residue was subjected to column chromatography (hexane–ether, 1:1). The following amounts and conditions were used:

Starting products (g)	*Pyridine–$SOCl_2$ (mL)*	*Time (h)*	*Products[a] (g, %)*
2a (0.16)	8:1.5	16	**2l** (0.06, 40.2)
2b (0.11)	5:0.7	2	**2m** (0.09, 87.3)
2d (0.14)	7:1.0	7	**2n** (0.05, 37.3)
2e (0.20)	8:2.0	18	**2o** (0.05, 26.1)
2f (0.20)	8:2.0	8	**2p** (0.05, 27.4)[b]

[a]Indentified by comparison with authentic specimens[5]. [b]17.0% of **2f** was recovered.

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