Carbohydrate Research, 183 (1988) 227–240
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

PUMMERER REARRANGEMENTS AND SIMILAR REACTIONS OF SOME SIX-MEMBERED CYCLIC SULPHOXIDES: SYNTHESIS OF 3-DEOXY-5-THIOPENTOPYRANOSES BRANCHED AT C-3

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(Received March 31st, 1988; accepted for publication, May 26th, 1988)

ABSTRACT

Oxidation with 3-chloroperoxybenzoic acid of *meso*-3,5-diacetoxytetrahydrothiopyran derivatives 4,4-disubstituted variously with CO_2Et, CN, Boc, and $CONH_2$ and 4-substituted with NO_2 gave mixtures of the corresponding sulphoxides **2a–e** and **3a–e**. These sulphoxides were converted by Pummerer rearrangement into 1,2,4-tri-*O*-acetyl-3-deoxy-5-thio-DL-pentopyranoses (**4a–i**) branched at C-3. Treatment of the sulphoxides with thionyl chloride gave 2,4-di-*O*-acetyl-3-deoxy-5-thio-DL-pentopyranosyl chlorides (**4j–n**) branched at C-3.

INTRODUCTION

The synthesis of 5-thiopentopyranoses has been achieved by thiocarboxylate displacements on 5-sulphonates of the corresponding sugars[1–3]. We have devised a three-stage scheme for the synthesis of 1,2,4-tri-*O*-acetyl-3-deoxy-5-thio-DL-pentopyranoses (**4a–i**) branched at C-3, and 2,4-di-*O*-acetyl-3-deoxy-5-thio-DL-pentopyranosyl chlorides (**4j–n**) branched at C-3, from non-sugar starting materials.

First, the cyclic sulphides **1a–e** were prepared by reaction of thiodiglycolaldehyde with active methylene compounds (ethyl cyanoacetate[4], *tert*-butyl cyanoacetate[5], malononitrile[6], cyanoacetamide[7], and nitromethane[8]). Secondly, the tetrahydrothiopyrans **1a–e** were oxidised to the sulphoxide level **2a–e** and **3a–e**. Thirdly, the sulphoxides were converted by the Pummerer rearrangement into the α-acetoxysulphides **4a–i**, or by treatment with thionyl chloride into the α-chlorosulphides **4j–n**.

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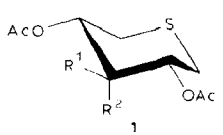
0008-6215/88/$ 03.50

RESULTS AND DISCUSSION

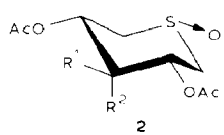
Oxidation of **1a–e** with 3-chloroperoxybenzoic acid[9], using a 1:1 molar ratio, gave mixtures of the corresponding sulphoxides **2a–e** and **3a–e** in high yields (82.0–95.5%). The mixtures of **2a,b,e** and **3a,b,e** were fractionated by column chromatography, but the components of the mixtures of **2c,d** and **3c,d** could not be resolved. Oxidation of cyclic sulphides by peroxy acids is subject to steric approach control[10–12]. Oxidation of the sulphides **1a–d** with 3-chloroperoxybenzoic acid yielded mainly the products (**3a–d**) of axial oxygenation whereas the sulphide **1e** yielded mainly the product (**2e**) of equatorial oxygenation. The preference for oxygen to be axial in six-membered cyclic sulphoxides is known[13–16].

The structures of **2a–e** and **3a–e** were established on the basis of elemental analyses and spectroscopic data. Thus, **2a–e** show characteristic i.r. bands[17,18] for sulphoxides, ester, amide, and nitro groups. The significant deshielding[19–22] of protons that are *syn*-axial to an axial sulphoxide group can be used to assign configuration at the S→O centre in **2a–e** and **3a–e**. For **2a–e**, the chemical shifts of the resonances of H-3,5 are essentially the same as those of the starting materials **1a–e**, whereas the corresponding signals for **3a–e** appear downfield ($\Delta\delta$ 0.77 ±0.04 p.p.m.) of those of **1a–e** (see Table I). In support[20,23] of this configurational assignment is the fact that the geminal coupling-constants (11.7–12.8 Hz) for the equatorial sulphoxides **2a–e** are smaller than those (13.2–14.1 Hz) for the respective axial sulphoxides **3a–e** (see Table II). The chemical shift difference for the resonances of the protons of the methylene groups that are vicinal to the sulphoxide centre is larger (0.87 p.p.m.) when the sulphoxide oxygen is axial than when it is equatorial[24] (0.48 p.p.m.). The difference in chemical shift of the resonances of the protons at C-2,6 in **2a–e** and **3a–e** are similar, which may be attributed to the 3,5-acetoxy groups[25]. Long-range ($J_{2e,6e}$) coupling[20,26,27] (accurate data could not be obtained) were observed for **2a–e** and **3a–e**. The ^{13}C-n.m.r. data accorded with the assigned structures. Introduction of an equatorial oxygen (isomers **2a–e**) induced a larger downfield shift (23.0 ±1.4 p.p.m.) in the signals for C-2,6 than when the oxygen was axial (16.7 ±0.8 p.p.m.) (isomers **3a–e**), as has been reported[25,28,29]. The resonances of C-3,5 in **2a–e** and **3a–e** showed about the same chemical shift with a



1

a R^1 = COOEt, R^2 = CN
b R^1 = Boc, R^2 = CN
c R^1 = R^2 = CN
d R^1 = $CONH_2$, R^2 = CN
e R^1 = NO_2, R^2 = H



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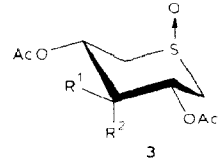


3

a R^1 = COOEt, R^2 = CN
b R^1 = Boc, R^2 = CN
c R^1 = R^2 = CN
d R^1 = $CONH_2$, R^2 = CN
e R^1 = NO_2, R^2 = H

TABLE I

^{1}H-N.M.R. CHEMICAL SHIFT DATA FOR **1a–e, 2a–e**, AND **3a–e**

Compound	*H-3,5*	*H-2e,6e*	*H-2a,6a*	*Others*
1a[a]	5.36dd	2.80 m		4.30 (q, 2 H, *J* 7.3 Hz, CH_3CH_2O), 2.08 (s, 6 H, 2 Ac), and 1.30 (t, 3 H, *J* 7.3 Hz, CH_3CH_2O)
2a[a]	5.26dd	3.74m	3.10ps-t[c]	4.25 (q, 2 H, *J* 7.2 Hz, CH_3CH_2O), 2.11 (s, 6 H, 2 Ac), and 1.27 (t, 3 H, *J* 7.2 Hz, CH_3CH_2O)
3a[a]	6.06dd	3.53m	2.75dd	4.27 (q, 2 H, *J* 7.1 Hz, CH_3CH_2O), 2.09 (s, 6 H, 2 Ac), and 1.28 (t, 3 H, *J* 7.1 Hz, CH_3CH_2O)
1b[a]	5.32dd	2.80 m		2.10 (s, 6 H, 2 Ac) and 1.47 (s, 9 H, Me_3C)
2b[a]	5.24dd	3.73m	3.10ps-t	2.12 (s, 6 H, 2 Ac) and 1.45 (s, 9 H, Me_3C)
3b[a]	6.05dd	3.50m	2.74dd	2.10 (s, 6 H, 2 Ac) and 1.46 (s, 9 H, Me_3C)
1c[a]	5.35dd	2.85 m		2.20 (s, 6 H, 2 Ac)
2c[a]	5.33dd	3.80m	3.08ps-t	2.26 and 2.23 (2 s, 6 H, 2 Ac)
3c[a]	6.12dd	3.57m	2.70dd	
1d[a]	5.30dd	2.85 m		6.30, 5.75 (2 bs, 2 H, $CONH_2$), and 2.10 (s, 6 H, 2 Ac)
2d[b]	5.50dd	3.92m	2.71ps-t	7.9 (m, 2 H, $CONH_2$) and 2.05 (s, 6 H, 2 Ac)
3d[b]	5.82dd	3.46m	2.86ps-t	
1e[a]	5.35dt	2.94ddd	2.54dd	4.54 (t, 1 H, *J* 10.8 Hz, H-4) and 2.02 (s, 6 H, 2 Ac)
2e[a]	5.37ddd	3.82m	2.83t	4.92 (t, 1 H, *J* 10.5 Hz, H-4) and 2.08 (s, 6 H, 2 Ac)
3e[a]	3.06dt	3.68m	2.54dd	4.95 (t, 1 H, *J* 10.7 Hz, H-4) and 2.06 (s, 6 H, 2 Ac)

[a]For a solution in $CDCl_3$ (internal Me_4Si). [b]For a solution in $(CD_3)_2SO$. [c]Pseudo triplet.

TABLE II

$^3J_{H,H}$ VALUES (Hz)[a] FOR **2a–e** AND **3a–e**

Compound	$J_{2a,3}$	$J_{2e,3}$	$J_{2a,2e}$
1a	8.8	6.3	
2a	12.6	2.8	12.4
3a	11.2	3.3	14.1
1b	9.0	6.0	
2b	12.6	3.1	12.5
3b	12.0	3.3	13.8
1c	8.0	6.7	
2c	12.5	2.7	12.8
3c	11.6	3.0	13.8
1d	9.3	5.6	
2d	12.2	2.8	11.7
3d	12.0	3.0	14.1
1e	10.8	4.4	12.7
2e	12.1	3.8	12.1
3e	12.2	3.9	13.2

[a]First order.

shielding effect of ~7.0 p.pm. when compared with **1a–e** (see Table III), so that there is no marked shielding of C-3,5 in isomers **3a–e** which would be subject to a γ-axial effect from an axial sulphoxide function[25,28,29].

The Pummerer reaction of sulphoxides, which provides a useful method for the synthesis of α-substituted and/or α,β-unsaturated sulphides, has been applied widely in the synthesis of organosulphur compounds[30–40] and of 4-thiofuranoses[12,41]. The Pummerer rearrangement was investigated under different conditions: *A*, in boiling dichloromethane containing acetic anhydride and toluene-*p*-sulphonic acid[10,34–39]; *B*, at ~55° in acetic anhydride containing toluene-*p*-sulphonic acid; and *C*, in boiling acetic anhydride containing sodium acetate[40]. The best yields (63–93%) were obtained under conditions *A*, and the mixtures of isomers **2a–e** and **3a–e** were used directly for the Pummerer reaction (see Experimental). Under conditions *A* and *C*, the reactions were stereospecific and β isomers (**4a,c,d,f,i**) were obtained; however, under conditions *C*, a dark-coloured product was formed quickly and the Pummerer product (**4c,f,i**) could not be isolated. Nevertheless, the isolation of **4a,d** shows that, under these conditions, the reaction was stereospecific. When **2a** + **3a**, **2c** + **3c**, and **2d** + **3d** were treated under conditions *B*, two products (**4a,b**, **4d,e**, and **4g,h**, respectively) were formed in each reaction. The α anomers **4b,e,g** were obtained by anomerisation[20,42] of the β anomers **4a,d,f** with perchloric acid in acetic acid–acetic anhydride (1:2) at room temperature. These results suggest that the anomeric effect is appreciable in these compounds.

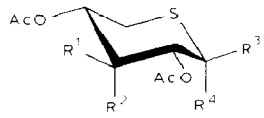
When the mixtures of the sulphoxides **2a,e** and **3a,e** were treated[43,44] with thionyl chloride in a heated solution of dichloromethane, **4j–n** were formed in good yields (70–94%). As in the above-mentioned Pummerer reaction, the reactions were stereospecific, yielding only the β anomers **4j–n**.

TABLE III

^{13}C-N.M.R. CHEMICAL SHIFT DATA FOR **1a–e**, **2a–e**, AND **3a–e**

Compound	*C-2,6*	*C-3,5*	*C-4*	*Others*
1a[a]	27.5	72.7	58.2	168.6 (2 MeCOO), 164.2 (COOEt), 113.6 (CN), 63.5 (CH_3CH_2O), 20.3 (2 *Me*COO), and 13.9 (CH_3CH_2O)
2a[a]	51.3	65.5	56.9	168.4 (2 MeCOO), 163.7 (COOEt), 113.1 (CN), 64.4 (CH_3CH_2O), 20.4 (2 *Me*COO), and 14.0 (CH_3CH_2O)
3a[a]	45.8	66.1	58.6	168.2 (2 MeCOO), 163.5 (COOEt), 113.7 (CN), 64.2 (CH_3CH_2O), 20.5 (2 *Me*COO), and 14.0 (CH_3CH_2O)
1b[a]	27.7	72.9	59.2	168.7 (2 MeCOO), 162.9 (COOBu^t), 114.0 (CN), 85.4 (CMe_3), 27.5 and 20.5 (2 *Me*COO)
2b[a]	51.4	65.6	57.9	168.4 (2 MeCOO), 162.2 (COOBu^t), 113.4 (CN). 86.6 (CMe_3), 27.6 (Me_3C), and 20.4 (2 *Me*COO)
3b[a]	46.1	66.2	59.7	168.1 (2 MeCOO), 162.0 (COOBu^t), 114.0 (CN), 86.3 (CMe_3), 27.6 (Me_3C), and 20.5 (2 *Me*COO)
1c[a]	27.5	72.0	45.8	168.5 (2 MeCOO), 111.8, 110.1 (2 CN), and 20.3 (2 *Me*COO)
2c[a]	50.5	64.1	[c]	167.6, 167.4 (2 MeCOO), 110.8 (CN), and 19.7 (*Me*COO)
3c[a]	44.5	64.9	44.5	
2d[b]	51.4	64.6	[c]	168.0 (MeCOO), 163.5 ($CONH_2$), 115.3 (CN), 20.3 and 20.2 (*Me*COO)
3d[b]	44.5	65.8	57.0	
1e[a]	30.1	72.1	90.6	169.0 (2 MeCOO), and 20.6 (2 *Me*COO)
2e[a]	52.7	64.6	88.8	168.7 (2 MeCOO), and 20.5 (2 *Me*COO)
3e[a]	46.8	65.8	89.0	168.7 (COO), and 20.1 (2 *Me*COO)

[a]For a solution in $CDCl_3$. [b]For a solution in $(CD_3)_2SO$. [c]Not observed.



4

a $R^1 = COOEt, R^2 = CN, R^3 = OAc, R^4 = H$
b $R^1 = COOEt, R^2 = CN, R^3 = H, R^4 = OAc$
c $R^1 = Boc, R^2 = CN, R^3 = OAc, R^4 = H$
d $R^1 = R^2 = CN, R^3 = OAc, R^4 = H$
e $R^1 = R^2 = CN, R^3 = H, R^4 = OAc$
f $R^1 = CONH_2, R^2 = CN, R^3 = OAc, R^4 = H$
g $R^1 = CONH_2, R^2 = CN, R^3 = H, R^4 = OAc$
h $R^1 = CONHAc, R^2 = CN, R^3 = H, R^4 = OAc$
i $R^1 = NO_2, R^2 = R^4 = H, R^3 = OAc$
j $R^1 = COOEt, R^2 = CN, R^3 = Cl, R^4 = H$
k $R^1 = Boc, R^2 = CN, R^3 = Cl, R^4 = H$
l $R^1 = R^2 = CN, R^3 = Cl, R^4 = H$
m $R^1 = CONH_2, R^2 = CN, R^3 = Cl, R^4 = H$
n $R^1 = NO_2, R^2 = R^4 = H, R^3 = Cl$

The structures of **4a–n** were established* on the basis of elemental analyses and spectroscopic data (see Tables IV–VI). The configuration at C-1 in **4a–n** and the $^4C_1$ conformation were deduced from the $J_{1,2}$ and $J_{4,5}$ values in the ^{1}H-n.m.r. spectra. Compounds **4a,c,d,f,i–k** showed $J_{1,2}$ values of 8.8–10.0 Hz, indicating H-1,2 to be *trans*-diaxial in a $^4C_1$ conformation. The same can be said for the configuration at C-4 in **4a–n**, based on the $J_{4,5a}$ values of 9.0–11.3 Hz. On the other hand, **4b,e,g,h** had $J_{1,2}$ values of 2.9–3.2 Hz, in accordance with the *e,a* disposition of H-1,2. Table VI includes the ^{13}C-n.m.r. data for **4a–n**. Each of the thio derivatives was characterised by upfield shifts of the signals for C-1,5[45–47]. For the β anomers, **4a,d,f**, C-1,3,5 resonate upfield of the corresponding carbon atoms in the α anomers **4b,e,g** (see Table VI), whereas the chemical shifts of the resonances C-2,4 were essentially the same. Substitution of a chlorine substituent for an acetoxyl group affects the resonances of H-1 and C-1. Thus, H-1 and C-1 of **4j–n** resonate ~1.1 and ~15 p.p.m., respectively, to higher field than H-1 and C-1 of the acetoxy analogues **4a,c,d,f,i**.

The i.r. band at ~2250 cm^{-1} for the cyano group[48] was not observed for **2a–e, 3a–c**, and **4a–d,j–k**, and was weak for **2d, 3d, 4f,** and **4m** as found[5,7,49] for cyano groups near to oxygenated functions.

The stereospecificity of the Pummerer rearrangement and the reaction with thionyl chloride suggest that the processes must be intermolecular, since the same products are obtained independently of the sulphoxide isomers used. This inference is not in agreement with the result reported[10] for compounds containing five-membered rings, but accords with the results reported[39] for acyclic sulphoxides. It is unlikely that the reactions were intramolecular followed by anomerisation because the same anomers were obtained in the presence of acid (conditions *A*) or base (conditions *C*), and these products were also the less thermodynamically stable. As mentioned above, the anomerisation was in the opposite direction when the β anomers were treated with perchloric acid in acetic acid–acetic anhydride.

*Only D forms are depicted in the formulae.

TABLE IV

^{1}H-N.M.R. CHEMICAL SHIFT DATA FOR **4a–n**[a]

Compound	*H-1*	*H-2*	*H-4*	*H-5*e	*H-5*a	*Others*
4a[b]	6.03d	5.63d	5.46dd	2.94dd	3.15dd	4.25 (q, 2 H, *J* 7.1 Hz, CH_3CH_2O), 2.05, 2.03 (2 s, 9 H, 3 Ac), and 1.27 (t, 3 H, *J* 7.1 Hz, CH_3CH_2O)
4b[b]	6.06d	5.47d	5.38dd	2.76dd	3.20dd	4.23 (q, 2 H, *J* 7.1 Hz, CH_3CH_2O), 2.15, 2.05, and 1.98 (3 s, 9 H, 3 Ac), and 1.23 (t, 3 H, *J* 7.1 Hz, CH_3CH_2O)
4c[b]	6.00d	5.63d	5.40dd	2.90dd	3.12dd	2.05, 2.03 (2 s, 9 H, 3 Ac), and 1.42 (s, 9 H, Me_3C)
4d[c]	6.00d	5.65d	5.45dd	←3.25–3.00m→		2.25 and 2.15 (2 s, 9 H, 3 Ac)
4e[b]	6.12d	5.44d	5.40dd	2.86dd	3.20dd	2.23, 2.20, and 2.16 (3 s, 9 H, 3 Ac)
4f[b]	6.00d	5.70d	5.40dd	2.80dd	3.10dd	6.46, 6.25 (2 bs, 2 H, $CONH_2$), 2.10, 2.08, and 2.05 (3 s, 9 H, 3 Ac)
4g[b]	6.15d	5.50d	5.38dd	2.86dd	3.17dd	6.53, 6.10 (2 bs, 2 H, $CONH_2$), 2.20, 2.09, and 2.03 (3 s, 9 H, 3 Ac)
4h[b]	6.16d	5.50d	5.40dd	2.90dd	3.20dd	8.62 (bs, 1 H, NH), 2.44 (s, 3 H, MeCONH), 2.20, 2.10, and 2.04 (3 s, 9 H, 3 Ac)
4i[b]	5.84d	5.73t	5.48dt	3.08dd	2.73dd	4.67 (t, 1 H, *J* 8.8 Hz, H-3), 2.05, 2.03, and 2.01 (3 s, 9 H, 3 Ac)
4j[c]	4.89d	5.57d	5.40dd	←3.3–2.75m→		4.28 (t, 2 H, *J* 7.1 Hz, CH_3CH_2O), 2.10 (s, 6 H, 2 Ac), and 1.27 (t, 3 H, *J* 7.1 Hz, CH_3CH_2O)
4k[b]	4.90d	5.54d	5.40dd	2.80dd	3.07dd	2.10, 2.03 (2 s, 6 H, 2 Ac), and 1.40 (s, 9 H, Me_3C)
4l[b]	4.90d	5.64d	5.43dd	2.95dd	3.08dd	2.28 and 2.22 (2 s, 6 H, 2 Ac)
4m[b]	4.82d	5.50d	5.33dd	2.88dd	2.94dd	6.72, 6.43 (2 bs, 2 H, $CONH_2$), 2.03 and 1.98 (2 s, 6 H, 2 Ac)
4n[b]	4.75d	5.64dt	5.50dt	3.06dd	2.73dd	4.63 (sex, 1 H, $J_{2,3} + J_{3,4}$ 20.8 Hz, H-3), 2.09 and 2.03 (2 s, 6 H, 2 Ac)

[a]For a solution in $CDCl_3$ (internal Me_4Si). [b]300 MHz. [c]80 MHz.

TABLE V

$^3J_{H,H}$ VALUES (Hz)[a] FOR **4a–n**

Compound	$J_{1,2}$	$J_{4,5e}$	$J_{4,5a}$	$J_{5a,5e}$
4a	9.5	4.0	10.8	14.0
4b	3.1	3.8	11.3	13.5
4c	9.5	4.0	10.9	13.8
4d	9.0	6.0	9.0	
4e	3.2	3.7	11.1	13.9
4f	9.6	4.9	10.0	13.6
4g	2.9	3.8	11.3	13.5
4h	3.0	3.9	11.3	13.6
4i	8.8	4.5	10.2	13.8
4j	9.9	4.8	10.3	
4k	9.9	4.0	11.0	13.8
4l	9.8	4.1	10.7	14.3
4m	10.0	4.5	10.7	14.0
4n	9.7	4.5	10.8	13.7

[a]First order.

EXPERIMENTAL

Organic solutions were dried over anhydrous Na_2SO_4. Solvents were evaporated under reduced pressure at <40°. Column chromatography was carried out on silica gel (Merck, 70–230 mesh, ASTM). Melting points (uncorrected) were obtained with an Electrothermal apparatus. I.r. spectra were recorded with a Perkin–Elmer 983G spectrophotometer, using KBr discs for solids. N.m.r. spectra were obtained with Bruker WP-80-SY and AM-300 spectrometers.

Oxidation of **1a–e** *with 3-chloroperoxybenzoic acid.* — A solution of **1a–e** in dichloromethane (30 mL) at ~ −10° was treated dropwise with a solution of 3-chloroperoxybenzoic acid (85%) in dichloromethane (30 mL). After 30 min at 0° and 15 min at room temperature, the solution was shaken with aqueous $NaHCO_3$, dried, and concentrated.

The following amounts and conditions were used.

Starting materials (g)	*Peroxy acid (g)*	*Products (g, %)*
1a (1.00)[4]	0.65	**2a** (0.32, 30.4) **3a** (0.64, 60.8)
1b (0.93)[5]	0.55	**2b** (0.35, 36.0) **3b** (0.51, 54.8)
1c (0.83)[6]	0.63	**2c** + **3c** (0.84, 95.5) (**2c**:**3c** ratio ~1:4)[a]
1d (0.7)[7]	0.49	**2d** + **3d** (0.65, 88.0) (**2d**:**3d** ratio ~1:3.5)[a]
1e (0.69)[8]	0.53	**2e** + **3e** (0.6, 82.0) (**2e**:**3e** ratio ~4:1)[a]

[a]Based on the ^{1}H-n.m.r. data.

TABLE VI

^{13}C-N.M.R. CHEMICAL SHIFT DATA FOR **4a–n**[a]

Compound	*C-1*[b]	*C-2*[b]	*C-4*[b]	*C-3*	*C-5*	*Others*
4a	70.4	72.3	72.0	58.0	28.3	168.9, 168.4 (3 COO), 163.4 (4 COOEt), 113.4 (CN), 64.2 (CH_3CH_2O), 20.5, 20.2 (3 *Me*COO), and 13.9 (CH_3CH_2O)
4b	67.9	73.0	72.4	54.3	24.2	169.2, 168.8, 168.5 (3 COO), 164.4 (COOEt), 113.9 (CN), 64.1 (CH_3CH_2O), 20.48, 20.16 (3 *Me*COO), and 13.90 (CH_3CH_2O)
4c	70.6	72.4	72.2	59.2	28.5	168.8, 168.4, 168.2 (3 COO), 161.8 (COOBu^t), 113.6 (CN), 86.1 (CMe_3), 27.4 (CMe_3), 20.5 and 20.3 (3 *Me*COO)
4d	69.7	71.2		45.5	27.9	168.6, 168.2, 168.0 (3 COO), 113.1, 109.9 (2 CN), 20.0, 20.5, and 20.2 (3 *Me*COO)
4e	67.6	72.5	72.1	42.5	24.1	168.8, 168.7, 168.5 (3 COO), 112.1, 110.5 (2 CN), 20.5, 20.4, and 20.2 (3 *Me*COO)
4f	70.9	73.0	72.4	57.5	27.9	168.7, 167.9 (3 COO), 163.9 ($CONH_2$), 115.6 (CN), 20.7, 20.6, and 20.3 (3 *Me*COO)
4g	68.3	73.2	72.6	53.9	24.3	169.1, 168.7, 168.4 (3 COO), 164.9 ($CONH_2$), 116.5 (CN), 20.7 and 20.3 (3 *Me*COO)
4h	68.1	73.2	72.7	55.1	24.3	170.9 (Me*C*ONH), 169.0, 168.6, 168.3 (3 COO), 162.8 (*C*ONHAc), 115.3 (CN), 25.3 (*Me*CONH), 20.6, 20.5, and 20.3 (3 *Me*COO)
4i	71.1	72.0	71.6	88.8	28.0	169.1, 168.7, 168.4 (3 *C*OO), 20.6, 20.5, and 20.3 (3 CH_3COO)
4j	55.4	74.5	72.2	58.9	30.2	168.7, 168.3 (2 COO), 163.1 (COOEt), 113.3 (CN), 64.3 (CH_3CH_2O), 20.5, 20.2 (2 CH_3COO), and 13.9 (CH_3CH_2O)
4k	55.5	74.3	72.2	59.9	30.3	168.6, 168.1 (2 COO), 161.5 (COOBu^t), 113.5 (CN), 86.3 (CMe_3), 27.5 (Me_3C), 20.4 and 20.2 (2 *Me*COO)
4l	54.4	73.6	71.7	46.5	30.1	168.6, 168.0 (2 COO), 110.9, 109.9 (2 CN), 20.5, and 20.2 (2 *Me*COO)
4m	55.7	74.1	72.0	58.0	30.0	168.4, 167.6 (2 COO), 163.2 ($CONH_2$), 115.0 (CN), 20.2, and 19.9 (2 *Me*COO)
4n	56.5	74.7	71.5	89.7	30.7	169.0, 168.5 (2 COO), 20.6, 20.4 (2 *Me*COO)

[a]For a solution in $CDCl_3$. [b]Assignments for C-1, C-2, and C-4 were made by 2D-^{13}C–^{1}H shift-correlation spectroscopy, using the assignments for H-1, H-2, and H-4.

t-*3*,t-*5*-*Diacetoxy*-*4*-*cyano*-r-*4*-*ethoxycarbonyltetrahydrothiopyran* t-*1*- (**2a**) *and* c-*1*-*oxide* (**3a**). — Column chromatography (ether) of the crude product gave, first, **2a**, m.p. 153–154° (from ethanol); ν_{max}^{KBr} 1763, 1735, 1293, 1266, 1204, 1044, 975, 925, and 898 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables I–III (Found: C, 47.04; H, 5.00; N, 4.08. $C_{13}H_{17}NO_7S$ calc.: C, 47.12; H, 5.17; N, 4.22%).

Eluted second was **3a**, m.p. 149–150° (from ethanol); ν_{max}^{KBr} 1757, 1222, 1088, and 1040 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables I–III (Found: C, 47.30; H, 4.96; N, 4.10%).

t-*3*,t-*5*-*Diacetoxy*-r-*4*-tert-*butoxycarbonyl*-*4*-*cyanotetrahydrothiopyran* t-*1*- (**2b**) *and* c-*1*-*oxide* (**3b**). — Column chromatography (1:5 hexane–ether) of the crude product gave, first, **2b**, m.p. 146–147°; ν_{max}^{KBr} 1761, 1730, 1299, 1213, 1159, 1042, and 927 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables I–III (Found: C, 50.19; H, 5.76; N, 3.81. $C_{15}H_{21}NO_7S$ calc.: C, 50.12; H, 5.90; N, 3.89%).

Eluted second was **3b**, m.p. 164–165° (from chloroform–hexane); ν_{max}^{KBr} 1759, 1736, 1291, 1210, 1157, and 1042 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables I–III (Found: C, 50.20; H, 6.00; N, 3.78%).

r-*3*,c-*5*-*Diacetoxy*-*4*,*4*-*dicyanotetrahydrothiopyran* c-*1*- (**2c**) *and* t-*1*-*oxide* (**3c**). — Crystallisation of the crude product from ethanol gave a mixture of **2c** and **3c**, m.p. 214–215°; ν_{max}^{KBr} 1752, 1209, 1042, 923, and 895 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables I–III (Found: C, 46.45; H, 3.85; N, 9.77. $C_{11}H_{12}N_2O_5S$ calc.: C, 46.47; H, 4.25; N, 9.85%).

t-*3*,t-*5*-*Diacetoxy*-r-*4*-*carbamoyl*-*4*-*cyanotetrahydrothiopyran* t-*1*- (**2d**) *and* c-*1*-*oxide* (**3d**). — The product was separated from 3-chlorobenzoic acid by extraction of the concentrated reaction mixture with ether (2 × 25 mL), giving **2d** + **3d**, m.p. >280°; ν_{max}^{KBr} 3391, 3167, 2266, 1755, 1712, 1632, 1372, 1212, 1075, 1040, 925, and 920 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables I–III (Found: C, 43.90; H, 4.54; N, 9.52. $C_{11}H_{14}N_2O_6S$ calc.: C, 43.68; H, 4.66; N, 9.30%).

t-*3*,t-*5*-*Diacetoxy*-r-*4*-*nitrotetrahydrothiopyran* t-*1* (**2e**) *and* c-*1*-*oxide* (**3e**). — The product was separated from 3-chlorobenzoic acid by extraction of the concentrated reaction mixture with ether (2 × 25 mL), giving **2e** + **3e**. Column chromatography (5:1 ether–acetone) of the mixture **2e** + **3e** (0.1 g) gave, first, **2e**, m.p. 190° (from 1:3 acetone–ether); ν_{max}^{KBr} 1752, 1563, 1428, 1380, 1234, 1211, and 1036 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables I–III (Found: C, 39.00; H, 4.52; N, 4.85. $C_9H_{13}NO_7S$ calc.: C, 38.71; H, 4.69; N, 5.01%).

Eluted second was **3e**, m.p. 210–212° (from ether); ν_{max}^{KBr} 1743, 1556, 1430, 1370, 1218, and 1019 cm^{-1} (Found: C, 38.54; H, 4.80; N, 4.68%).

Pummerer rearrangement. — The sulphoxide was treated with acetic anhydride under conditions *A*–*C*: *A*, the mixture of the sulphoxide (1.21 mmol) in dichloromethane (20 mL) containing acetic anhydride (20 mmol) and toluene-*p*-sulphonic acid (0.3 g) was boiled under reflux under nitrogen; *B*, the sulphoxide (1.21 mmol) in acetic anhydride (40 mmol) containing toluene-*p*-sulphonic (0.25 g) was stirred at ~55° under nitrogen; *C*, the sulphoxide (1.21 mmol), acetic anhydride (8 mL), and sodium acetate (5 mmol) were boiled under reflux under nitrogen.

After the reaction, the mixture was diluted with water (25 mL) and extracted with dichloromethane (40 mL). The extract was washed with saturated aqueous $NaHCO_3$ (3 × 50 mL) and then with water (25 mL), dried, filtered, and concentrated.

The following amounts and conditions were used:

Starting materials (g)	*Conditions*	*Time (h)*	*Products (%)*
2a + **3a**	*A*	7	**4a** (93.3)
	B	20	**4a** + **4b** (97.0)[a]
	C	6	**4a** (88.0)
2b + **3b**	*A*	10	**4c** (63.1)
2c + **3c**	*A*	7	**4d** (90.8)
	B	20	**4d** + **4e** (75.5)[b]
2d + **3d**	*A*[c]	10	**4f** (76.0)
	B[c]	20	**4g** (57.3), **4h** (20.2)
2e + **3e**	*A*	5	**4i** (71.0)

[a]In the ratio 1.5:1. [b]In the ratio 1:3. [c]Acetonitrile (10 mL) was added.

1,2,4-Tri-O-*acetyl-3*-C-*cyano-3-deoxy-3*-C-*ethoxycarbonyl-5-thio-β*-DL-xylo-*pentopyranose* (**4a**). — Column chromatography (1:1 hexane–ethyl acetate) of the crude product (condition *A*) gave **4a**, m.p. 121–122° (from ethanol); ν_{max}^{KBr} 1761, 1281, 1199, 1068, 1024, 901, 758, and 635 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables IV–VI (Found: C, 48.51; H, 4.85; N, 3.66. $C_{15}H_{19}NO_8S$ calc.: C, 48.25; H, 5.13; N, 3.75%).

1,2,4-Tri-O-*acetyl-3*-C-tert-*butoxycarbonyl-3*-C-*cyano-3-deoxy-5-thio-β*-DL-xylo-*pentopyranose* (**4c**). — Column chromatography (3:1 ether–hexane) of the crude product (condition *A*) gave **4c**, m.p. 135–136° (from hexane); ν_{max}^{KBr} 1759, 1281, 1210, 1148, 1022, and 971 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables IV–VI (Found: C, 50.65; H, 5.94; N, 3.20. $C_{17}H_{23}NO_8S$ calc.: C, 50.86; H, 5.77; N, 3.49%).

1,2,4-Tri-O-*acetyl-3,3-di*-C-*cyano-3-deoxy-5-thio-β*-DL-erythro-*pentopyranose* (**4d**). — Column chromatography (1:1 hexane–ether) of the crude product (condition *A*) gave **4d**, m.p. 137–138° (from hexane): ν_{max}^{KBr} 1765, 1209, 1066, 1031, 930, and 901 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables IV–VI (Found: C, 47.50; H, 4.64; N, 8.35. $C_{13}H_{14}N_2O_6S$ calc.: C, 47.84; H, 4.32; N, 8.58%).

1,2,4-Tri-O-*acetyl-3*-C-*carbamoyl-3*-C-*cyano-3-deoxy-5-thio-β*-DL-xylo-*pentopyranose* (**4f**). — Column chromatography (5:1 ether–hexane) of the crude product (condition *A*) gave **4f**, m.p. 194–195° (from ether–hexane); ν_{max}^{KBr} 3354, 3211, 2219, 1760, 1710, 1625, and 1211 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables IV–VI (Found: C, 45.24; H, 4.83; N, 8.00. $C_{13}H_{16}N_2O_7S$ calc.: C, 45.34; H, 4.68; N, 8.13%).

1,2,4-Tri-O-*acetyl-3*-C-*carbamoyl-3*-C-*cyano-3-deoxy-5-thio-α*-DL-xylo-*pentopyranose* (**4g**), *and 1,2,4-tri*-O-*acetyl-3*-C-*acetylcarbamoyl-3*-C-*cyano-3-deoxy-5-*

thio-α-DL-xylo-*pentopyranose* (**4h**). — Column chromatography (3:1 ether–hexane) of the crude product (condition *B*) gave **4h**, m.p. 160–162° (from ether–hexane); ν_{max}^{KBr} 3341, 1775, 1750, 1730, 1449, 1381, 1236, 1217, 1194, and 1049 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables IV–VI (Found: C, 46.70; H, 4.85; N, 7.32. $C_{15}H_{18}N_2O_8S$ calc.: C, 46.63; H, 4.70; N, 7.25%).

Eluted second was **4g**, m.p. 208–209° (from ether–hexane); ν_{max}^{KBr} 3430, 3190, 1760, 1744, 1700, 1617, 1482, 1222, 1024, 954, and 909 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables IV–VI (Found: C, 45.30; H, 4.45; N, 8.24. $C_{13}H_{16}N_2O_7S$ calc.: C, 45.34; H, 4.68; N, 8.13%).

*1,2,4-Tri-*O*-acetyl-3-deoxy-3-*C*-nitro-5-thio-β*-DL-xylo-*pentopyranose* (**4i**). — Crystallisation of the crude product from ethanol gave **4i**, m.p. 149–150°; ν_{max}^{KBr} 1759, 1559, 1377, 1234, 1213, 1055, 1029, 982, and 901 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables IV–VI (Found: C, 41.30; H, 6.87; N, 4.24. $C_{11}H_{15}NO_8S$ calc.: C, 41.11; H, 7.06; N, 4.36%).

Anomerisation of **4a,d,f** *and synthesis of* **4b,e,g**. — A solution of **4a,d,** or **f** (0.3 g) in acetic anhydride (2.0 mL) and acetic acid (1.0 mL) containing aqueous 60% perchloric acid (0.07 g) was left for 1 day at room temperature. Chloroform (50 mL) was added, and the mixture was washed with saturated aqueous $NaHCO_3$ (2 × 50 mL) and water (25 mL), then dried, filtered, and concentrated.

*1,2,4-Tri-*O*-acetyl-3-*C*-cyano-3-deoxy-3-*C*-ethoxycarbonyl-5-thio-α*-DL-xylo-*pentopyranose* (**4b**). — Column chromatography (1:2 hexane–ether) of the crude product gave **4b** (0.24 g, 80.0%), m.p. 116–117° (from ethanol); ν_{max}^{KBr} 1744, 1371, 1212, 1106, 1080, 1041, and 949 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables IV–VI (Found: C, 48.20; H, 5.40; N, 3.47. $C_{15}H_{19}NO_8S$ calc.: C, 48.25; H, 5.13; N, 3.75%).

*1,2,4-Tri-*O*-acetyl-3,3-di-*C*-cyano-3-deoxy-5-thio-α*-DL-erythro-*pentopyranose* (**4e**). — Column chromatography (1:1 hexane–ether) of the crude product gave **4e** (0.2 g, 66.6%), m.p. 135–136° (from ethanol); ν_{max}^{KBr} 1753, 1379, 1212, 1042, 956, and 900 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables IV–VI (Found: C, 47.70; H, 4.80; N, 8.70. $C_{13}H_{14}N_2O_6$ calc.: C, 47.84; H, 4.32; N, 8.58%).

*1,2,4-Tri-*O*-acetyl-3-*C*-carbamoyl-3-*C*-cyano-3-deoxy-5-thio-α*-DL-xylo-*pento-pyranose* (**4g**). — Column chromatography (5:1 ether–hexane) of the crude product gave **4g** (0.21 g, 70.0%).

Treatment of **2a–d** *and* **3a–d** *with* $SOCl_2$ *and synthesis of* **4j–n**. — The mixture of the sulphoxide in dichloromethane containing $SOCl_2$ was boiled under reflux under nitrogen. Dichloromethane (50 mL) was added, and the mixture was washed with saturated aqueous $NaHCO_3$ (2 × 100 mL) and water (25 mL), then dried, filtered, and concentrated.

*2,4-Di-*O*-acetyl-3-*C*-cyano-3-deoxy-3-*C*-ethoxycarbonyl-5-thio-β*-DL-xylo-*pentopyranosyl chloride* (**4j**). — Crystallisation of the crude product from hexane gave **4j**, m.p. 130–131°; ν_{max}^{KBr} 1768, 1745, 1370, 1206, 1021, 930, and 898 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables IV–VI (Found: C, 44.55; H, 4.74; N, 3.83. $C_{13}H_{16}ClNO_6S$ calc.: C, 44.63; H, 4.61; N, 4.00%).

The following amounts and conditions were used:

Starting materials (g)	*CH_2Cl_2–$SOCl_2$*	*Time (h)*	*Products (g, %)*
2a + **3a** (0.66)	20:4	6	**4j** (0.58, 83.2)
2b + **3b** (0.40)	15:3	7	**4k** (0.37, 88.0)
2c + **3c** (0.40)	15:3	6	**4l** (0.30, 70.5)
2d + **3d** (0.30)	20:3[a]	15	**4m** (0.29, 91.1)
2e + **3e** (0.27)	25:3	5	**4n** (0.27, 93.7)

[a]Acetonitrile (10 mL) was added.

*2,4-Di-*O*-acetyl-3-*C*-*tert*-butoxycarbonyl-3-*C*-cyano-3-deoxy-5-thio-β-*DL*-xylo-pentopyranosyl chloride* (**4k**). — Crystallisation of the crude product from hexane gave **4k**, m.p. 114–115°; ν_{max}^{KBr} 1766, 1740, 1293, 1204, 1148, 931, and 899 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables IV–VI (Found: C, 47.50; H, 5.50; N, 3.87. $C_{15}H_{20}ClNO_6S$ calc.: C, 47.68; H, 5.33; N, 3.70%).

*2,4-Di-*O*-acetyl-3,3-di-*C*-cyano-3-deoxy-β-*DL*-erythro-pentopyranosyl chloride* (**4l**). — Crystallisation of the crude product from hexane gave **4l**, m.p. 123–125°; ν_{max}^{KBr} 1763, 1205, 1035, 925, and 895 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables IV–VI (Found: C, 43.50; H, 3.14; N, 8.97. $C_{11}H_{10}ClN_2O_4S$ calc.: C, 43.78; H, 3.34; N, 9.28%).

*2,4-Di-*O*-acetyl-3-*C*-carbamoyl-3-*C*-cyano-3-deoxy-β-*DL*-xylo-pentopyranosyl chloride* (**4m**). — Column chromatography (ether) of the crude product gave **4m**, m.p. 204° (from ether); ν_{max}^{KBr} 3416, 3157, 2256, 1766, 1713, 1630, 1369, 1205, 1040, 1021, and 970 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables IV–VI (Found: C, 41.25; H, 4.23; N, 8.90. $C_{11}H_{13}ClN_2O_5S$ calc.: C, 41.18; H, 4.08; N, 8.73%).

*2,4-Di-*O*-acetyl-3-deoxy-3-*C*-nitro-5-thio-β-*DL*-xylo-pentopyranosyl chloride* (**4n**). — Crystallisation of the crude product from hexane gave **4n**, m.p. 145–147°; ν_{max}^{KBr} 1750, 1559, 1429, 1376, 1217, 1029, 977, and 898 cm^{-1}. For the ^1H- and ^{13}C-n.m.r. data, see Tables IV–VI (Found: C, 36.12; H, 4.18; N, 4.57. $C_9H_{12}ClNO_6S$ calc.: C, 36.30; H, 4.06; N, 4.70%).

ACKNOWLEDGMENT

This work was supported by the Comisión Asesora de Investigación Cientifica y Técnica, Grant No. PB85–0390.

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