Carbohydrate Research, 164 (1987) 403–414
Elsevier Science Publishers B.V., Amsterdam - Printed in The Netherlands

REARRANGEMENT OF DERIVATIVES OF BIS(ETHYLSULPHONYL)-α-D-LYXOPYRANOSYLMETHANE*

J. GRANT BUCHANAN, ALAN R. EDGAR, AND RODERICK J. HUTCHISON
Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS (Great Britain)

Received September 4th, 1986; accepted for publication, November 7th, 1986)

ABSTRACT

Bis(ethylsulphonyl)(2,3-*O*-isopropylidene-α-D-lyxopyranosyl)methane (**3**) undergoes rearrangement in pyridine or methanolic sodium methoxide to give, at equilibrium, a mixture containing equal amounts of bis(ethylsulphonyl)-(2,3,*O*-isopropylidene-α-D-lyxofuranosyl)methane (**10**), the corresponding β-furanoid (**12**), and **3** itself. The rearrangement is completely suppressed by *C*-methylation of the bis(ethylsulphonyl) moiety. The mechanism of the MacDonald–Fischer degradation of bis(ethylsulphonyl) derivatives of sugars is discussed in the light of these observations.

INTRODUCTION

The degradation of aldohexose diethyl dithioacetal bis-sulphones by dilute ammonia, to give the corresponding pentoses, was described by MacDonald and Fischer[1] in 1953 as a modification of the procedure[2] involving acetylated derivatives. It was discovered[3,4] that the acyclic bis-sulphones readily underwent ring closure to form pyranoid derivatives which were themselves susceptible to alkaline cleavage, albeit at a slower rate. Thus, oxidation of D-galactose diethyl dithioacetal with aqueous peroxypropionic acid[3,4] gave bis(ethylsulphonyl)-α-D-lyxopyranosylmethane (**1**). The structure **1** was confirmed[3] by ^{1}H-n.m.r. spectroscopy[5] of the triacetate **2**. Isopropylidenation of **1** afforded the acetal[5,6] **3**, whose acetate[5,6] **4** and methanesulphonate[5,7] **5** have also been prepared.

The bis-sulphone **1** and its derivatives contain a *C*-glycosyl bond. They invite comparison with a number of compounds obtained by reaction of a sugar lactol with a stabilised Wittig reagent where the alkene, which is initially formed, readily undergoes intramolecular conjugate addition to give, for example, a glycosyl acetic ester[8]. An even closer analogy is to the D-mannofuranosyl malonates **6** and **8**, prepared[8–10] by reaction of a di-*O*-isopropylidene-D-mannofuranosyl halide with the sodium salt of diethyl malonate. Equilibration of **6** and **8** occurs in the presence of

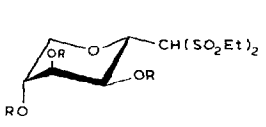
* Dedicated to the memory of Hermann O. L. Fischer on the centenary of his birth.

0008-6215/87/$ 03.50

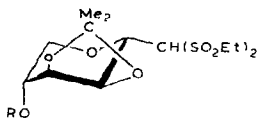
sodium ethoxide, presumably via the alkene **7** as intermediate; an interesting feature is that the all-*cis* isomer **8** is favoured at equilibrium. As part of a general study of *C*-nucleoside synthesis[11] we had experience of this kind of system[12,13] and wished to study the action of base on the 2,3-*O*-isopropylidene derivative **3** in the expectation that rearrangement would occur.

DISCUSSION

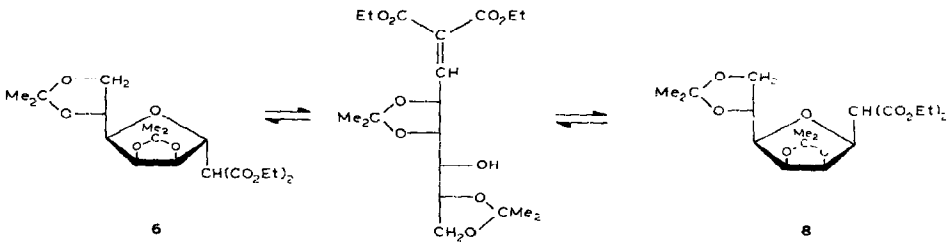
The bis-sulphone **1** and its triacetate **2** were readily prepared[3]. Their ^{1}H-n.m.r. spectra (Tables I and II) were fully consistent with the α-D-pyranoside structures, in the $^1C_4$ conformation, in agreement with the earlier work[5]. The triol **1** was converted into the 2,3-*O*-isopropylidene compound[6] **3** and its 4-acetate[6] **4**. The ^{1}H-n.m.r. spectra confirmed that both of these compounds existed in a slightly distorted $^1C_4$ conformation[5].



1 R = H
2 R = Ac



3 R = H
4 R = Ac
5 R = MeSO2



6 7 8

During the acetylation of **3**, to give **4**, using acetic anhydride in pyridine, it was observed that two other compounds were formed, of slightly greater polarity on thin-layer chromatography in 1:5 benzene–ether. The three compounds appeared as spots of different colour under the conditions of the anisaldehyde–sulphuric acid spray[14]. Chromatography of the mixture on silica gel gave, besides the acetate **4**, two isomeric acetates **9** and **11**, in order of elution. The isomer ratio for **4**, **9**, and **11** was ~7:1:1.

The assignment of furanoid structures to **9** and **11** followed most clearly from their ^{13}C-n.m.r. spectra[8,15] (Table III). The position of the signal due to the acetal

TABLE I

^{1}H CHEMICAL SHIFTS FOR BIS (ETHYLSULPHONYL)-D-LYXOSYLMETHANES AND RELATED COMPOUNDS

Compound	*Chemical shifts*[a,b]											
	H_x[c]	*H-1*	*H-2*	*H-3*	*H-4*	*H-5a*	*H-5b*	CH_3CH_2	CH_3CH_2	$(CH_3)_2C$	CH_3CO	*Others*
1[d]	5.75(bs)	5.60(d)	5.44(dd)	4.70(m)	4.3(m)	4.15(d) (ax)	4.44(d) (eq)	1.32(t) 1.34(t)	3.73–4.15(m)	—	—	—
2	4.22(d)	4.89(dd)	5.69(dd)	5.54(m)	4.86(m)	3.95(dd) (ax)	4.04(dd) (eq)	1.34(t) 1.45(t)	3.58(m)	—	2.02(s) 2.16(s)(2 ×)	—
3	4.39(bs)	4.34(d)	4.84(dd)	4.40(m)	4.0(m)	3.84(dd) (ax)	3.98(dd) (eq)	1.43(t) (2 ×)	3.29–3.76(m)	1.37(s) 1.52(s)	—	2.97(bs)
4	4.37(bs)	4.40(dd)	4.90(dd)	4.27(m)	5.14(m)	3.85(dd) (ax)	4.04(m) (eq)	1.43(t) (2 ×)	3.46(m) 3.67(m)	1.38(s) 1.53(s)	2.10(s)	—
9	4.35(d)	5.01(dd)	5.19(dd)	4.89(dd)	4.60(m)	4.26(dd)	4.35(dd)	1.43(t) 1.44(t)	3.37–3.77(m)	1.34(s) 1.50(s)	2.05(s)	—
11	4.95(d)	4.25(dd)	5.04(dd)	4.78(dd)	3.85(ddd)	4.35(d)		1.41(t) (2 ×)	3.43–3.58(m)	1.34(s) 1.50(s)	2.07(s)	—
17	—	4.24(d)	4.90(dd)	4.30(m)	3.50(m)	3.60(dd) (ax)	4.06(m) (eq)	1.42(t) (2 ×)	3.08–3.92(m)	1.34(s) 1.50(s)	—	1.82(s) 3.39(s)
18	—	4.28(d)	4.97(dd)	4.26(m)	5.12(m)	3.79(dd) (ax)	3.98(dd) (eq)	1.45(t) (2 ×)	3.27–3.73(m)	1.36(s) 1.55(s)	2.11(s)	1.86(s)
19	—	4.20(d)	4.91(dd)	4.36(ddd)	3.95(m)	3.78(dd) (ax)	3.93(dd) (eq)	1.43(t) 1.45(t)	3.38–3.73(m)	1.34(s) 1.52(s)	—	3.02(bs)

[a]In chloroform-*d*. [b]At 220 MHz. [c]$CH_x(SO_2Et)_2$. [d]In pyridine-d_5, OH exchanged with D_2O.

TABLE II

FIRST ORDER ^1H–^1H COUPLING CONSTANTS FOR BIS (ETHYLSULPHONYL)-D-LYXOSYLMETHANES AND RELATED COMPOUNDS

Compound	*Coupling constants*[a,b]						
	$J^c_{x,1}$	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5a}$	$J_{4,5b}$	$J_{5a,5b}$
1[d]	1	10.5	3	3	1	1	12
2[e]	2	11	3	3	1	1	13
3	<1	10	5	[f]	2	1	13
4[e]	1.5	10	5	2	2	1	14
6[g]	9.5	0	[f]	3.5	6		—
8[g]	10	3.5	6	3	7		—
9	2.5	2.5	6	4.5	4.5	7.5	12
11	10	3.5	6	3.5	6	6	0
17	—	9.5	5	~2	1	1.5	12.5
18	—	10	5	<1	1	1	12.5
19	—	9.5	5.5	~2	~1	~1	12

[a]In chloroform-*d*. [b]At 220 MHz. [c]$CH_x(SO_2Et)_2$. [d]In pyridine-d_5. [e]*Cf.* ref. 5. [f]Not resolved. [g]Ref. 8, at 100 MHz.

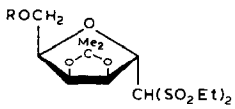
TABLE III

^{13}C CHEMICAL SHIFTS FOR ISOPROPYLIDENE COMPOUNDS

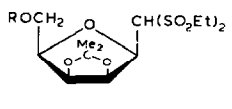
Compound	*Chemical shifts (δ)*[a]							
	Acetal carbon	*Acetal methyl carbons*	CH_2OAc	CH_3CO	CH_3CO	$CH_3CH_2SO_2$	$CH_3CH_2SO_2$	*Others*
4[b]	110.53	26.40 28.30	—	20.90	169.71	5.46 6.05	49.35 51.11	67.23, 67.77, 69.58 73.52, 74.17, 77.86
6[c]	113.20							
8[c]	112.91							
9[b]	113.93	24.99 26.61	62.78	20.77	170.57	5.14 5.71	48.58 50.01	80.46, 81.33 (×2), 82.32, 85.73
11[d]	113.28	24.82 25.96	61.65	20.74	170.55	5.99 6.29	50.62 51.07	74.64, 75.25, 79.83, 80.03, 81.96

[a]In chloroform-*d*. [b]At 20 MHz. [c]Ref. 8, at 22.62 MHz. [d]At 50 MHz.

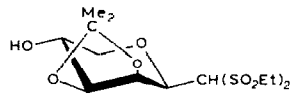
carbon in dioxolanes depends critically on whether the dioxolane is fused to a five- or a six-membered ring[15]. The signal at δ 110.53 in the spectrum of **4** is characteristic of a dioxolane attached to a pyranoid ring (range δ 108.1–111.4). The corresponding signals in **9** and **11** are at δ 113.93 and 113.28, well within the range (δ 111.3–115.7) for a dioxolane fused to a furanoid ring. Furthermore, in the spectra of **6** and **8** (Table III) the acetal carbon signal in **8**, the isomer in which the epimerisable substituent is *cis* to the isopropylidene group, is at higher field, in keeping with a number of other examples[8]. This has enabled us to assign individual structures to **9** and **11** and is confirmed by the chemical shifts of the acetal methyl groups, which are at higher field in the all-*cis* isomer **11**. The coupling constants in the ^{1}H-n.m.r. spectrum of **11** show a marked similarity to those of **8** (Table II). In the comparison of the spectra of **9** and **6** the difference in the coupling constant $J_{x,1}$ implies a difference in the rotameric population in the two cases.



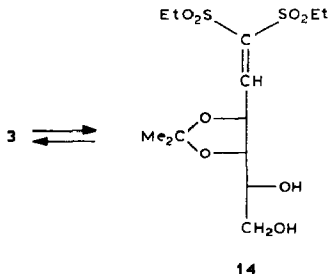
9 R = Ac
10 R = H



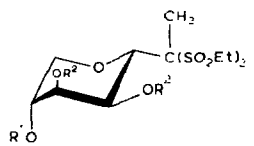
11 R = Ac
12 R = H



13



14



15 $R^1 = R^2 = H$
16 $R^1 = Me, R^2 = H$
17 $R^1 = Me, R^2 = Me_2C$
18 $R^1 = Ac, R^2 = Me_2C$
19 $R^1 = H, R^2 = Me_2C$

The pyranoid → furanoid conversion clearly occurred very readily, presumably due to the presence of pyridine, and it was important to establish the stage at which rearrangement took place. The acetate **4** was completely stable to anhydrous pyridine at room temperature for up to 3 months. Treatment of **9** or **11** under the same conditions, however, led to their equilibration over a period of several days, giving approximately equal quantities of the two isomers and no other product.

When the alcohol **3** was dissolved in pyridine, rearrangement was detectable by t.l.c. after a few minutes. Three components, with similar polarities, were present, including **3** itself, but column chromatography did not achieve a separation. Acetylation of the mixture afforded the acetates **4**, **9**, and **11** in the ratio ~1:1:1.

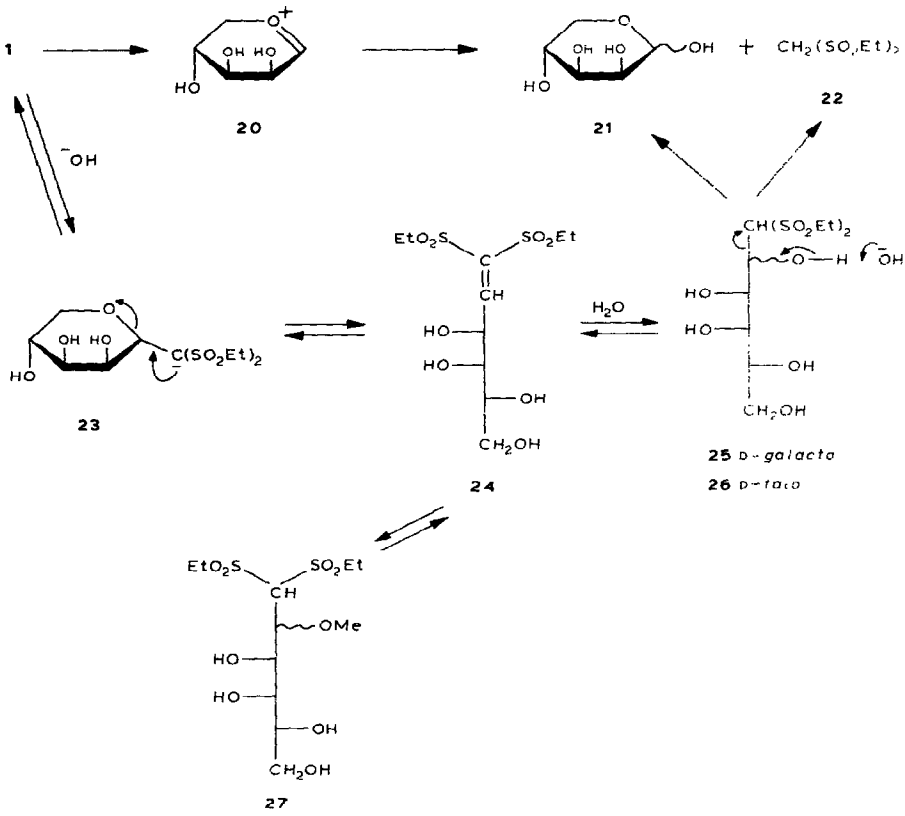
The same result, and the same ratio, was obtained when each individual acetate was subjected to Zemplén deacetylation followed by reacetylation. Assuming that acetylation with an excess of acetic anhydride is a relatively rapid process, this ratio corresponds to the equilibrium composition of the alcohols **3**, **10**, and **12**.

We had expected to find that the alcohol **3** would rearrange under basic conditions, via the alkene **14**, but were surprised that it should occur so readily, *e.g.* with pyridine as base. Because of the known stability of a 5-membered acetal ring fused to a furanose ring[8,16,17] we were interested to discover that an appreciable amount of the pyranoid **3** remained in the equilibrium mixture. Clearly in the D-mannose derivatives **6** and **8** no pyranoid ring is possible; although Hanessian[10] has degraded a mixture of **6** and **8** to the corresponding D-*lyxo* compounds there was no report of the formation of any product containing a six-membered ring. The bulk of the bis(ethylsulphonyl)methyl group is greater than that of malonate or any of the other groups studied by Moffatt[8], and it would appear that increased steric interactions may be present in the furanoid forms. In contrast to the malonates **6** and **8** there is no strong preference for the all-*cis* furanoid isomer **12** at equilibrium. We have noted above that the bis(ethylsulphonyl)methyl group in **9** is in a different rotameric form compared to **6**. There is no evidence for the presence of the second pyranoid isomer in the equilibrium; in the $^4C_1$ conformation **13** there would be appreciable crowding at C-1 (ref. 18). Hough and Richardson[19] recovered the triol **1** in 76% yield after treatment with methanolic sodium methoxide for 8 days at room temperature. In this case furanose forms would not be stabilised, and the β-pyranoid would be unstable, as in **13**.

The most likely mechanism for the rearrangement of the alcohols is *via* the alkene **14**, formation of which requires an acidic hydrogen atom in the cyclic bis-sulphones **3**, **10**, and **12**. It has been shown[6] that the *C*-methyl derivative **15** and the *C*,*O*-dimethyl derivative **16**, derived from the acetonide **17**, are stable to sodium hydroxide and aqueous ammonia, respectively. We prepared the *C*-methyl derivative **18** by methylation of **4** using methyl iodide and silver oxide in acetone solution[6]. A single product was obtained (99%) whose ^{1}H-n.m.r. spectrum (Tables I,II) shows that no rearrangement had taken place. Deacetylation of **18** using sodium methoxide gave the alcohol **19** (92%), again without rearrangement, providing further strong evidence for the rôle of **14** as an intermediate in the interconversion of **3**, **10**, and **12**. A similar mechanism can be proposed for the slower interconversion of **9** and **11**, where the acetyl group prevents expansion to a pyranoid ring.

The rapid rearrangement of **3** under basic conditions has a bearing on the mechanism of the MacDonald–Fischer degradation[1,2,6,19,20] of sugar bis-sulphones. The pentahydroxy bis-sulphone **25**, the initially-formed product from the peracid oxidation of D-galactose diethyl dithioacetal, undergoes rapid degradation by dilute, aqueous ammonia to give D-lyxose (**21**) and bis(ethylsulphonyl)methane (**22**). The reaction is probably a retroaldol fission, described for simpler systems by Rothstein[21].

The cyclic bis-sulphones, *e.g.* **1**, also undergo degradation but at a much slow-



er rate[1,2]. This led Hough and Taylor[3] to suggest that in the case of the cyclic sulphones a nucleophilic mechanism was involved, to yield the free sugar (D-lyxose in the case of **1**) directly in the pyranose form. Later, an SN1 mechanism was proposed[6,19], *via* the oxonium ion **20**, on the basis of kinetic studies[19] and the behaviour of the *C*-methyl derivatives **15** and **16** and the acetonide **3** towards dilute aqueous ammonia[6]. We believe that the evidence can be more easily accommodated by a mechanism involving ring-opening of the carbanion **23** to give the alkene **24** followed by hydration to the pentol **25** or **26** and retroaldol cleavage. The reaction exhibits a marked pH-dependence[19], which is not a feature of a normal SN1 reaction. The stability of **15** and **16** towards alkaline cleavage is most likely due to their inability to form an alkene. The triol **1** is stable in methanolic sodium methoxide[19] because **27**, the product of methanol addition to **24**, is incapable of retroaldol fission, and **24** and **27** do not exist to significant extents in the equilibrium with **1**; none of the methyl lyxoside, to be expected from an SN1 mechanism, was observed.

The isopropylidene compound **3** is stable to dilute aqueous ammonia but is cleaved by sodium hydroxide or concentrated aqueous ammonia. This slow rate can

be accounted for by increased steric hindrance by the isopropylidene group to the addition of hydroxyl ion to the alkene **14**, rather than a conformational effect on the formation of the isopropylidene derivative of the oxonium ion **20** (ref. 19). Models show that intramolecular return to give the alcohols **3**, **10**, or **12** from **14** is a favourable process.

EXPERIMENTAL

^{1}H-N.m.r. spectra were recorded at 220 MHz with a Varian HR-220 spectrometer (at P.C.M.U., Harwell) and at 200 MHz with a Bruker WP-200SY spectrometer. ^{13}C-N.m.r. spectra were recorded at 20 MHz with a Varian CFT-20 spectrometer (University of Edinburgh) and at 50 MHz (Bruker WP-200SY) (internal Me_4Si). T.l.c. was carried out on Kieselgel 60 HF-254 (Merck), with detection by anisaldehyde–sulphuric acid in ethanol[14]. Adsorption chromatography was done on silica gel (Merck Kieselgel H, type 60). Columns were run under positive pressure. Light petroleum refers to the fraction having b.p. 40–60°. Specific rotations were measured at room temperature (20–25°) with a Bendix-NPL 143D automatic polarimeter (path-length 1 cm).

*Bis(ethylsulphonyl)(α-*D*-lyxopyranosyl)methane* (**1**). — A solution of D-galactose diethyl dithioacetal (5 g) in dioxane (125 mL) was stirred at 80° while peroxypropionic acid (21 mL, 15% excess over 4 equiv.) was added at such a rate that the temperature did not exceed 95°. The mixture was allowed to cool to room temperature and filtered. The solid was subjected to several additions and evaporations of methanol, and recrystallised from ethanol to give the bis-sulphone **1** (5.52 g, 90%), m.p. 203–205°, $[\alpha]_D$ +13.5° (*c* 2.97, water); lit.[3] m.p. 193–195°, $[\alpha]_D$ +3.1° (methanol); lit.[4] m.p. 202–202.5°, $[\alpha]_D$ +14.7° (water).

*Bis(ethylsulphonyl)(2,3,4-tri-*O*-acetyl-α-*D*-lyxopyranosyl)methane* (**2**). — Prepared by treatment of **1** with acetic anhydride and pyridine[3], m.p. 187–188°, $[\alpha]_D$ −20° (*c* 1.20, chloroform); lit.[3] m.p. 187–188°, $[\alpha]_D$ −21.9° (chloroform).

*Bis(ethylsulphonyl)(2,3-*O*-isopropylidene-α-*D*-lyxopyranosyl)methane* (**3**). — A suspension of **1** (4.0 g, 10.7 mmol) was stirred at room temperature in a mixture of acetone (100 mL), 2,2-dimethoxypropane (10 mL), and toluene-*p*-sulphonic acid (30 mg). When **1** had completely dissolved the mixture was neutralised (anhydrous Na_2CO_3), filtered, and concentrated to a syrup which rapidly crystallised. Recrystallised from ethanol, **3** (3.01 g, 67%) had m.p. 137–139°, $[\alpha]_D$ +22.1° (*c* 3.85, methanol); lit.[5] m.p. 138–139°, $[\alpha]_D$ +29.1° (methanol).

*Acetylation of bis(ethylsulphonyl)(2,3-*O*-isopropylidene-α-*D*-lyxopyranosyl) methane.* — A solution of **3** (ref. 6) (3.5 g, 9.4 mmol) in dry pyridine (35 mL) was treated with acetic anhydride (40.5 g) at room temperature overnight. Examination of the product by t.l.c. in 1:5 benzene–ether (anisaldehyde spray[14]) showed three products: R_F 0.76, purple (major); R_F 0.67, grey-blue (minor); and R_F 0.58, green (minor). The crude product was isolated, using chloroform, as a syrup (3.71 g) and subjected to chromatography on silica gel using 2:1 light petroleum–ether as eluant.

This gave the three acetates **4**, **9**, and **11** in the ratio 7:1:1 in a total yield of 3.64 g (94%). In order of elution were isolated:

Bis(ethylsulphonyl)(4-O-acetyl-2,3-O-isopropylidene-α-D-lyxopyranosyl)-methane (**4**). — Recrystallised from ethanol as needles, m.p. 116–117°, $[\alpha]_D$ +25.2° (*c* 1.62, chloroform); lit.[6] m.p. 99–101°, $[\alpha]_D$ +27° (methanol); ν_{max}^{KBr} 1750 cm^{-1} (carbonyl); mass spectrum: *m/z* 414 (0.2%, M^+), 399 (50%, $M^+ - Me$).

Bis(ethylsulphonyl)(5-O-acetyl-2,3-O-isopropylidene-α-D-lyxofuranosyl)-methane (**9**). — The syrup slowly crystallised, and was recrystallised from aqueous ethanol as fine needles, m.p. 96–98°, $[\alpha]_D$ +36.2° (*c* 0.94, chloroform); ν_{max}^{film} 1740 cm^{-1} (carbonyl); mass spectrum: *m/z* 399 (95%, $M^+ - Me$).

Anal. Calc. for $C_{15}H_{26}O_9S_2$: C, 43.5; H, 6.3; S, 15.5. Found: C, 43.5; H, 6.5; S, 15.6.

Bis(ethylsulphonyl)(5-O-acetyl-2,3-O-isopropylidene-β-D-lyxofuranosyl)-methane (**11**). — Isolated as a syrup, $[\alpha]_D$ +5.7° (*c* 2.09 chloroform); ν_{max}^{film} 1740 (carbonyl), 1330, 1150, and 1130 cm^{-1} (SO_2); mass spectrum: *m/z* 414 (1%, M^+), 399 (70%, $M^+ - Me$).

Anal. Calc. for $C_{15}H_{26}O_9S_2$: C, 43.5; H, 6.3. Found: C, 43.6; H, 6.4.

1,1-Bis(ethylsulphonyl)-1-(2,3-O-isopropylidene-4-O-methyl-α-D-lyxopyranosyl)ethane (**17**). — To a solution of **3** (1.0 g, 3.0 mmol) in dry acetone was added freshly prepared silver oxide (4.8 g) and methyl iodide (2.9 mL, 46 mmol). The mixture was stirred under gentle reflux. After 2 h a further addition of acetone (10 mL) and methyl iodide (2.5 mL) was made. After 3 h the mixture was cooled, filtered, and the filtrate evaporated to a pale yellow syrup (0.98 g). Chromatography on silica gel (10 g), eluting with 2:1 light petroleum–ether, gave **17** as a syrup (0.93 g, 86%) which crystallised and was recrystallised from methanol. Compound **17** had m.p. 111–112°, $[\alpha]_D$ +14.9° (*c* 3.08, chloroform); lit.[6], m.p. 111–112°, $[\alpha]_D$ +22.4° (methanol).

1,1-Bis(ethylsulphonyl)-1-(4-O-acetyl-2,3,-O-isopropylidene-α-D-lyxopyranosyl)methane (**18**). — To a solution of **4** (1 g, 2.4 mmol) in dry acetone (10 mL) was added freshly prepared silver oxide (4.1 g) and methyl iodide (2.0 mL, 32 mmol). The mixture was stirred under gentle reflux for 2 h, when a further addition of acetone (10 mL) and methyl iodide (2.5 mL, 40 mmol) was made. After a further 3 h of heating the cooled mixture was filtered and concentrated to a pale yellow syrup which was shown by t.l.c. in 2:1 benzene–ether to be mainly one compound with a trace of polar impurities. Chromatography on silica gel, with 2:1 light petroleum–ether as eluant gave the pure *ethane* (1.03 g, 99%) as a syrup, $[\alpha]_D$ +12.0° (*c* 1.58, chloroform); ν_{max}^{film} 1740 cm^{-1} (carbonyl).

Anal. Calc. for $C_{16}H_{28}O_9S_2$: C, 44.8; H, 6.6; S, 15.0. Found: C, 45.1; H, 6.5; S, 14.8.

1,1-Bis(ethylsulphonyl)-1-(2,3-O-isopropylidene-α-D-lyxopyranosyl)ethane (**19**). — Sodium (20 mg) was added to a solution of **18** (0.21 g) in methanol (5 mL). Deacetylation was complete in 3 h at room temperature (t.l.c. in 2:1 benzene–ether). The reaction mixture was neutralised and the *ethane* **19** was isolated, using chloro-

form, as a homogeneous syrup (0.17 g, 92%), $[\alpha]_D$ +28.6° (*c* 3.77, chloroform); ν_{max}^{film} 3500 cm^{-1} (hydroxyl).

Anal. Calc. for $C_{14}H_{26}O_8S_2$: C, 43.5; H, 6.7; S, 16.6. Found: C, 42.6; H, 6.3; S, 15.5.

Base-catalysed rearrangement of some bis-sulphones. — (*a*) *Deacetylation reactions.* The α-pyranoid derivative **4** (1.0 g, 2.4 mmol) was dissolved in methanol (15 mL) containing sodium methoxide (20 mg of Na). After 6 h all starting material had disappeared and t.l.c. (ether) indicated the formation of a mixture of three hydroxy bis-sulphones. Several attempts to resolve the mixture by silica-gel chromatography failed. Reacetylation (acetic anhydride–pyridine) gave three components (t.l.c. 1:5 benzene–ether). Column chromatography gave **4**, **9**, and **11** in a 1:1:1 ratio, identified by t.l.c., m.p. (**4** and **9**), i.r., and ^{1}H-n.m.r..

In a separate experiment it was shown that following the same procedure from either **9** or **11** also led to **4**, **9**, and **11** in the same ratio (1:1:1) after chromatography, via the same mixture of three hydroxy bis-sulphones (t.l.c.).

(*b*) *Rearrangements involving hydroxy bis-sulphones.* The 4-hydroxy compound **3** (20 mg) was dissolved in pyridine. After 2–3 min t.l.c. (ether) indicated the presence of the same mixture of compounds as formed in the deacetylation of **4**, **9**, or **11** in (a), above. The same behaviour was observed when methanolic sodium methoxide was used in place of pyridine.

(*c*) *Rearrangements involving the acetates* **4**, **9**, *and* **11**. Samples of **4**, **9**, and **11** (5 mg of each) were severally dissolved in pyridine (0.5 mL) and examined by t.l.c. 1:5 (benzene–ether). Each compound appeared as a differently coloured spot when sprayed with anisaldehyde–sulphuric acid[14], **4** being purple, **9** grey-blue, and **11** bright green. The acetate **4** was unchanged after 3 months, but **9** and **11** were interconverted over a period of several days. From t.l.c. there appeared to be equal amounts of **9** and **11** at equilibrium; neither **9** nor **11** gave any trace of **4** under these conditions.

ACKNOWLEDGMENTS

We thank Dr. Neil A. Hughes, University of Newcastle upon Tyne, for discussions on the mechanism of the MacDonald–Fischer degradation, Dr. I. H. Sadler and his colleagues at Edinburgh University for ^{13}C-n.m.r. spectra, and the S.E.R.C. for a research studentship (to R.J.H.) and for n.m.r. spectra measured at the P.C.M.U. (Harwell).

REFERENCES

1 D. L. MacDonald and H. O. L. Fischer, *Biochim. Biophys. Acta*, 12 (1953) 203–206.
2 D. L. MacDonald and H. O. L. Fischer, *J. Am. Chem. Soc.*, 74 (1952) 2087–2090.
3 L. Hough and T. J. Taylor, *J. Chem. Soc.*, (1956) 970–980.
4 R. Barker and D. L. MacDonald, *J. Am. Chem. Soc.*, 82 (1960) 2297–2301.
5 L. D. Hall, L. Hough, K. A. McLauchlan, and K. Pachler, *Chem. Ind. (London)*, (1962) 1465–1466.
6 L. Hough and A. C. Richardson, *J. Chem. Soc.*, (1962) 1024–1032.

7 A. FARRINGTON AND L. HOUGH, *Chem. Commun.*, (1965) 219–220; *Carbohydr. Res.*, 38 (1974) 107–115.
8 H. OHRUI, G. H. JONES, J. G. MOFFATT, M. L. MADDOX, A. T. CHRISTENSEN, AND S. K. BYRAM, *J. Am. Chem. Soc.*, 97 (1975) 4602–4613.
9 H. OHRUI AND J. J. FOX, *Tetrahedron Lett.*, (1973) 1951–1954.
10 S. HANESSIAN AND A. G. PERNET, *Can. J. Chem.*, 52 (1974) 1266–1279.
11 J. G. BUCHANAN, *Prog. Chem. Org. Nat. Prod.*, 44 (1983) 243–299; *Nucleosides, Nucleotides*, 4 (1985) 13–19.
12 J. G. BUCHANAN, A. R. EDGAR, M. J. POWER, AND P. D. THEAKER, *Carbohydr. Res.*, 38 (1974) C22–C24.
13 P. D. THEAKER, Ph. D. Thesis, Heriot-Watt University, 1973.
14 E. STAHL AND U. KALTENBACH, *J. Chromatogr.*, 5 (1961) 351–355.
15 J. G. BUCHANAN, A. R. EDGAR, D. I. RAWSON, P. SHAHIDI, AND R. H. WIGHTMAN, *Carbohydr. Res.*, 100 (1982) 75–86.
16 J. F. STODDART, *Stereochemistry of Carbohydrates*, Wiley-Interscience, New York, 1971, pp. 202–208.
17 S. J. ANGYAL, *Adv. Carbohydr. Chem. Biochem.*, 42 (1984) 15–68, esp. pp. 58–60.
18 Ref. 16, pp. 70–72.
19 L. HOUGH AND A. C. RICHARDSON, *J. Chem. Soc.*, (1962) 1019–1023.
20 J. D. WANDER AND D. HORTON, *Adv. Carbohydr. Chem. Biochem.*, 32 (1976) 15–123.
21 E. ROTHSTEIN, *J. Chem. Soc.*, (1940) 1560–1565.