Novel Observations on Thiophosphoryl-group Transfer in Sugar β-Hydroxy Phosphorodithioate Systems. Synthesis and X-Ray Molecular Structure of 1,6-Anhydro-3,4-dideoxy-3,4-epithio-2-*O*-(*p*-tolylsulfonyl)-β-D-allopyranose

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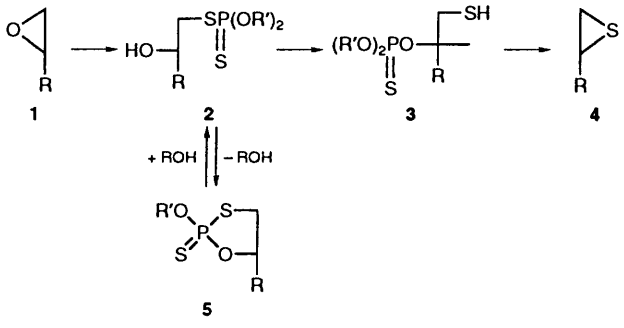
The reaction of 1,6;3,4-dianhydro-2-*O*-(*p*-tolylsulfonyl)-β-D-galactopyranose **6** with the triethylammonium salt of 2-mercapto-5,5-dimethyl-1,3,2-dioxaphosphorinane 2-sulfide **7'** gives the hitherto unknown 1,6-anhydro-3,4-dideoxy-3,4-epithio-2-*O*-(*p*-tolylsulfonyl)-β-D-allopyranose **8** in high yield. The intermediates in this reaction are: 1,6-anhydro-4-*S*-(5',5'-dimethyl-2'-thioxo-1',3',2'-dioxaphosphorinan-2'-yl)-4-thio-2-*O*-(*p*-tolylsulfonyl)-β-D-glucopyranose **9** and 1,6-anhydro-3-*O*-(5',5'-dimethyl-2'-thioxo-1',3',2'-dioxaphosphorinan-2'-yl)-4-thio-2-*O*-(*p*-tolylsulfonyl)-β-D-glucopyranose **10**. The former can be obtained by addition of 2-mercapto-5,5-dimethyl-1,3,2-dioxaphosphorinane 2-sulfide **7** to the dianhydro sugar **6**. Formation of the latter was confirmed by ^{31}P NMR spectroscopy. Comparative conformational studies of dianhydro compound **6** and of episulfide **8** were undertaken. They revealed that, despite the opposite orientation of the epoxy and epithio groups, the overall conformation of 5- and 6-membered rings remains the same. The absolute configuration of compound **6** has been determined as 1*R*,2*R*,3*S*,4*S*,5*R*, and of compound **8** as 1*R*,2*S*,3*S*,4*R*,5*R*.

Our investigations of sulfur and selenium analogues of sugar phosphates led to the elaboration of several efficient methods for the synthesis of functionalized monosaccharides.[1] The reactions of sugar oxiranes with mono- and di-thioacids of phosphorus are of particular interest from synthetic and mechanistic points of view.[2] One of their synthetic applications is the preparation of sugar episulfides.[3] This synthesis proceeds in three steps: opening of the oxirane ring **1** by phosphorodithioic acid gives dithiophosphate **2**; base-catalysed transphosphorylation leads to the intermediate mercapto phosphate **3**; transformation of compound **3** into the episulfide **4** by internal nucleophilic attack of the thiolate anion on the carbon atom bound to the thiophosphate group (which serves as a good leaving group). Oxathiaphospholanes **5** can also be formed

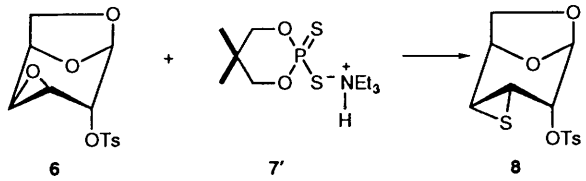


when cyclization is facilitated by the presence of a good leaving group (*e.g.*, R' = Ar) at phosphorus.

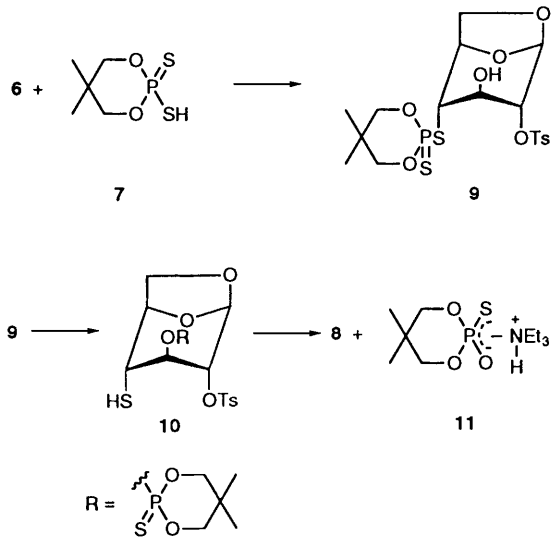
We have recently demonstrated that the relative rate of the thiophosphorylation step **2**→**3**[4] depends on the spatial arrangement of the substituents involved in phosphoryl-group transfer. The most favourable arrangement for phosphoryl-group transfer within the sugar ring is diequatorial. Axial–equatorial migration is slower and *trans*-diaxial migration in a rigid system (without the possibility of conformational changes) does not occur. In our previous studies the sugar ring in the epoxides employed was of conformation type $^4C_1$. The model epoxide **6**[5] used in the present investigations has a $^1C_4$ conformation imposed by its bicyclic system. The reacting centres are arranged *trans*-diaxially; the question is whether, in such a rigid system, transfer of the thiophosphoryl group from sulfur to oxygen and formation of the episulfide are still possible.

Results and Discussion

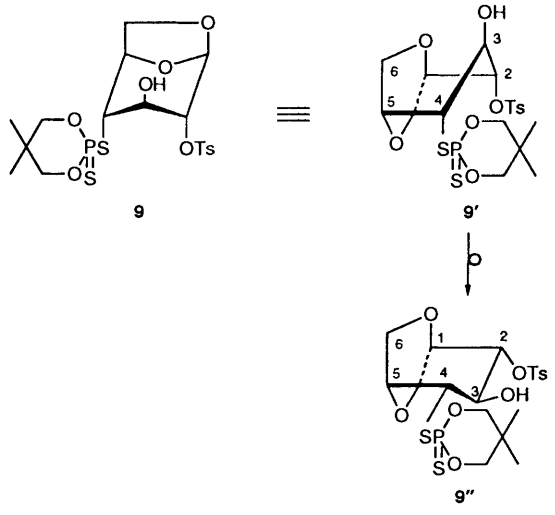
When equimolar amounts of the epoxide **6** and the triethylammonium salt **7'** were allowed to react in boiling benzene, the episulfide **8** was formed in high yield.

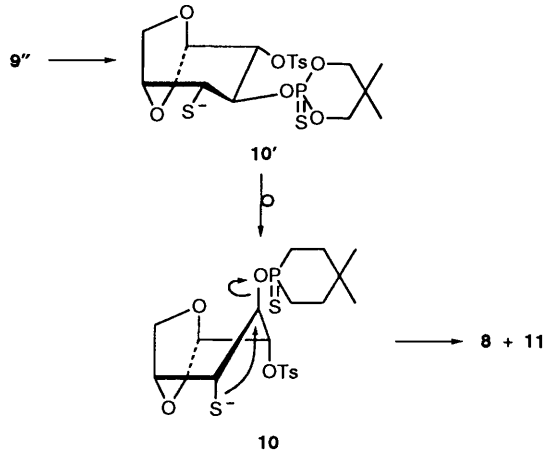


To gain insight into the mechanistic aspects of the reaction, the transient adduct **9** was independently prepared from the epoxide **6** and free acid **7**. The opening of the 3,4-epoxide ring of compound **6** is fully regio- and stereo-selective; it gives the *trans*-diaxial adduct **9** as the only phosphorus-containing product, in quantitative yield. The adduct **9** undergoes transphosphorylation into the mercapto thionophosphate **10** in pyridine solution at ambient temperature. However, the concentration of compound **10** in the reaction mixture is very low (as observed by ^{31}P NMR spectroscopy) because it is rapidly converted into the episulfide **8**. It can therefore be assumed that the transphosphorylation step **9**→**10** determines the rate of reaction.



We offer the following explanation of the experimental results. If transphosphorylation occurs in spite of the initial *trans*-diaxial arrangement of the reacting centres in compound **9**, the molecule must undergo changes which bring together the OH and SP(S)(OR)$_2$ groups. The six-membered ring of the adduct **9** has some freedom to undergo the conformational change **9′**→**9″**. The C(2)–C(3)–C(4) end of the hexopyranose ring in **9′** flips from chair to boat conformation, placing the reacting centres at C-3 and C-4 in favourable equatorial positions. This helps transphosphorylation, leading to the thiono compound **10′**. The latter returns to the primary chair conformation **10** in which the SH and OP(S)(OR)$_2$ groups are arranged *trans*-diaxially. Thiirane-ring closure ensues.





Structural Assignments.—The molecular structures of the oxirane **6** and the episulfide **8** have been determined by single-crystal X-ray analysis. The chiral centres of the 1,6;3,4-dianhydro-β-D-galactopyranose skeleton were found to have the 1*R*,2*R*,3*S*,4*S*,5*R* configuration while those of the 1,6-anhydro-3,4-dideoxy-3,4-epithio-β-D-allopyranose system were 1*R*,2*S*,3*S*,4*R*,5*R* (Fig. 1). As the result of configurational changes, differences in conformation about the C(2)–C(3) and C(4)–C(5) bonds are observed (Table 1, see below), so that only the C(1)···C(4) γ-*syn* interaction is similar in both compounds. Despite opposite orientations of the epoxy and epithio groups, the overall conformation of the 5- and 6-membered rings remains the same (Table 1, Fig. 2). The pyranose ring adopts a sofa conformation and the oxafuranose ring is half-chair. The bond distances (Table 2, see below) are equal within 3σ except for C(3)–C(4), which is significantly shorter in the oxirane than in the thiirane ring. The *p*-tolylsulfonyl substituent, in the crystal, is nearly anti-periplanar in 1,6;3,4-dianhydro-β-D-galactopyranose derivative **6** and synclinal in 1,6-anhydro-3,4-dideoxy-3,4-epithio-β-D-allopyranose system **8**.

The structure of adduct **9** was established by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. The undecoupled ^{31}P signal centred at δ_P 87.78 ($CDCl_3$) is a double triplet of triplets due to the coupling with two axial ($^3J_{P,a}$ 5.6 Hz) and two equatorial protons ($^3J_{P,e}$ 23.7 Hz) of the phosphorinane ring and with the equatorial 4-H proton ($^3J_{P,4}$ 16 Hz) (Fig. 3). A similar coupling

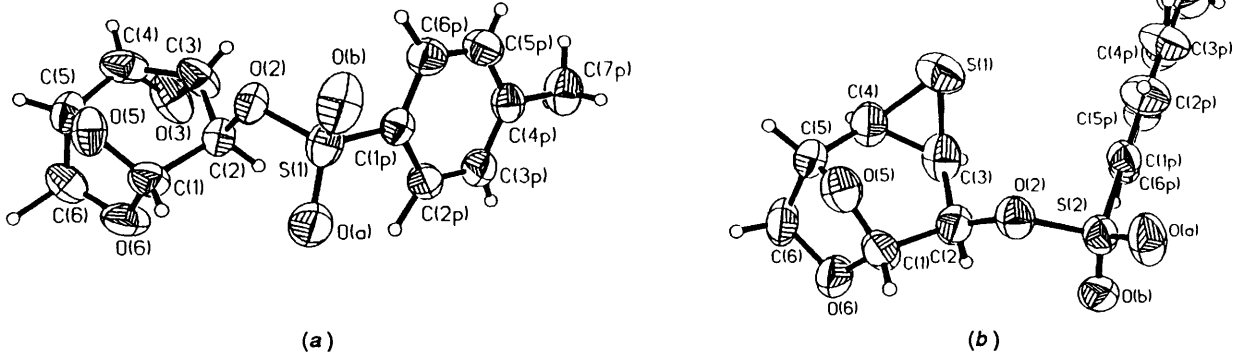


Fig. 1 Perspective views of the oxirane **6** (*a*) and the episulfide **8** (*b*) molecules with atomic labelling

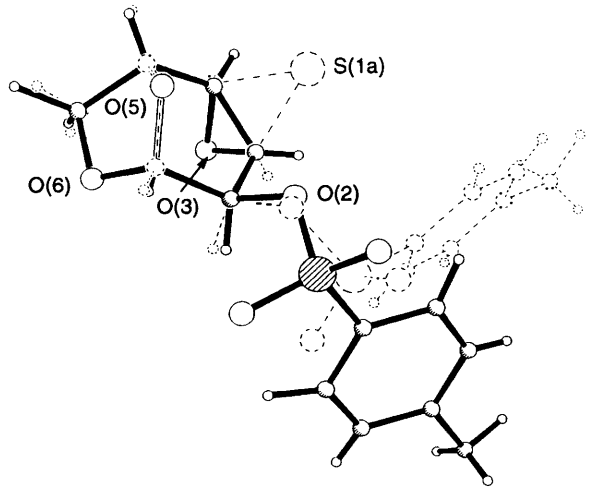


Fig. 2 Diagram of the superposition of the molecular structures of 1,6;3,4-dianhydro-2-*O*-(*p*-tolylsulfonyl)-β-D-galactopyranose **6** (solid lines) and 1,6-anhydro-3,4-dideoxy-3,4-epithio-2-*O*-(*p*-tolylsulfonyl)-β-D-allopyranose **8** (dashed lines)

constant is observed for the ^1H NMR signal at δ_H 3.6, corresponding to 4-H which is a double triplet with $^3J_{P,4}$ 16.8 Hz and $^3J_{3,4} = {}^3J_{4,5} = 1$ Hz.

Although β-mercapto thionophosphate **10** has not been isolated from the transphosphorylation process of compound **9** in pyridine solution, its presence in the reaction medium was confirmed by the appearance of a signal at $\delta(^{31}P)$ 59.98, characteristic of this type of structure.

Phosphoromonothioate **11**, the co-product of episulfide formation, was identified by comparison of its chemical-shift value with that of an authentic specimen [$\delta(^{31}P)$ 57.5]. The pattern of the proton-undecoupled ^{31}P signal (C_5D_5N), a triplet of triplets, characteristic of the $(RO)_2P(S)O^-$ anion, supported the structure of compound **11** (Fig. 4).

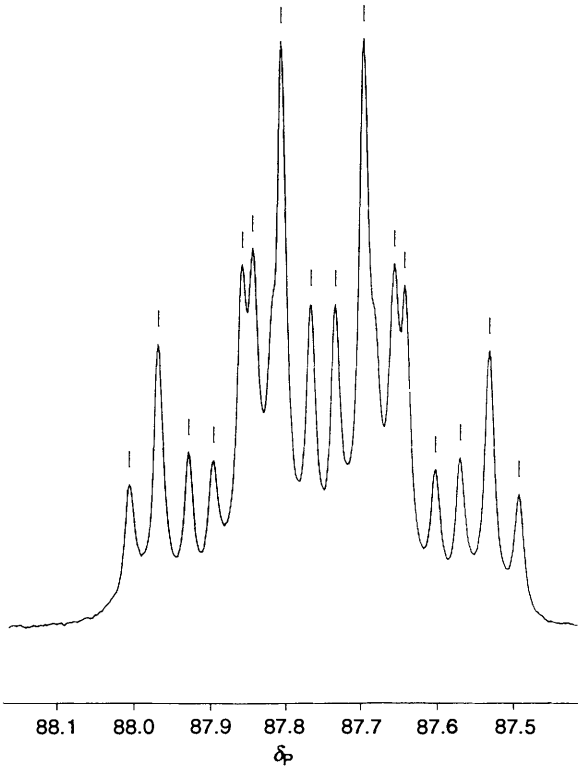


Fig. 3 Undecoupled ^{31}P NMR signal corresponding to compound **9**

Experimental

M.p.s were determined with a Boetius PHMK 05 apparatus and are uncorrected. Optical rotations were determined with a Polamat polarimeter, and are given in units of 10^{-1} deg cm^2 g^{-1}. IR spectra were obtained by using a Unicam SP-200G spectrophotometer. NMR spectra were recorded with Bruker 200 AC, Bruker 300 MSL and Bruker 400 AM spectrometers. ^{31}P NMR spectra were measured with H_3PO_4 as external standard (Bruker 200 AC operating at 81.01 MHz). ^1H NMR spectra were measured in $CDCl_3$ with Me_4Si as the internal standard (Bruker 300 MSL or Bruker 400 AM spectrometers). ^{13}C NMR spectra were determined on solutions in $CDCl_3$ with a Bruker 300 MSL spectrometer operating at 75.46 MHz. Chemical shifts are given in parts per million, the coupling constants are expressed as *J*-values in Hertz. Mass spectra were taken with LS/MS, Cs +13 KeV, matrix glycerol. Elemental analyses were performed by the Microanalytical Laboratory of the Centre of Molecular and Macromulecular Studies of the

Table 1 Selected torsion angles (°)

6		**8**	
5-membered ring			
C(1)–O(5)–C(5)–C(6)	46.4(4)		44.3(7)
O(5)–C(5)–C(6)–O(6)	−36.1(4)		−33.8(7)
C(1)–O(6)–C(6)–C(5)	12.4(5)		10.7(8)
O(5)–C(1)–O(6)–C(6)	16.8(5)		16.6(8)
O(6)–C(1)–O(5)–C(5)	−40.1(4)		−38.3(7)
6-membered ring			
O(5)–C(1)–C(2)–C(3)	−42.6(5)		−41.3(8)
C(1)–C(2)–C(3)–C(4)	1.1(6)		2.2(10)
C(2)–C(3)–C(4)–C(5)	2.6(7)		0.5(11)
O(5)–C(5)–C(4)–C(3)	33.2(6)		35.1(9)
C(1)–O(5)–C(5)–C(4)	−72.8(4)		−73.6(7)
C(2)–C(1)–O(5)–C(5)	78.9(4)		77.6(7)
external			
O(2)–C(2)–C(1)–O(5)	71.7(4)	O(2)–C(2)–C(1)–O(5)	81.4(7)
O(2)–C(2)–C(3)–O(3)	178.1(4)	O(2)–C(2)–C(3)–S(1)	−40.9(8)
O(3)–C(3)–C(2)–C(1)	−66.5(5)	S(1)–C(3)–C(2)–C(1)	78.4(8)
O(3)–C(3)–C(4)–C(5)	106.6(5)	S(1)–C(3)–C(4)–C(5)	−111.2(7)
O(3)–C(4)–C(5)–O(5)	101.0(5)	S(1)–C(4)–C(5)–O(5)	−40.0(8)
C(1)–C(2)–O(2)–S(1)	98.3(3)	C(1)–C(2)–O(2)–S(2)	147.1(5)
C(3)–C(2)–O(2)–S(1)	−143.4(3)	C(3)–C(2)–O(2)–S(2)	−90.5(6)

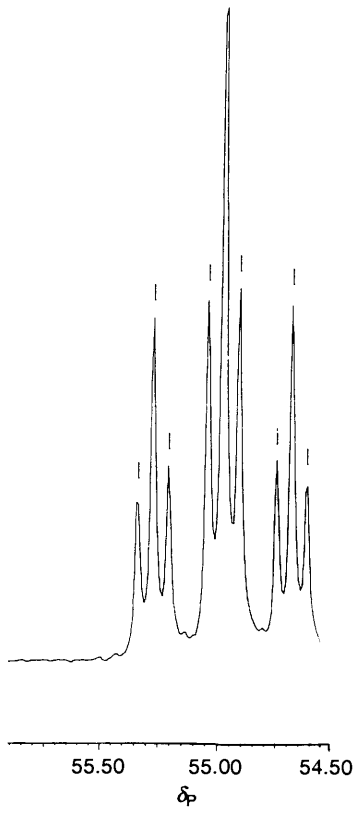


Fig. 4 Undecoupled ^{31}P NMR signal corresponding to compound **11**

Polish Academy of Sciences, Łódź. Light petroleum refers to the fraction boiling in the range 40–60 °C.

Materials.—1,6;3,4-Dianhydro-2-*O*-(*p*-tolylsulfonyl)-β-D-galactopyranose **6** was obtained by the procedure described in ref. 5. 2-Mercapto-5,5-dimethyl-1,3,2-dioxaphosphorinane 2-sulfide was prepared by the procedure described in ref. 6.

1,6-*Anhydro*-3,4-*dideoxy*-3,4-*epithio*-2-O-(p-*tolylsulfonyl*)-β-D-*allopyranose* **8**.—Equimolar amounts of the dianhydride **6** (1.5 g, 5 mmol), dithioacid **7** (1 g, 5 mmol) and triethylamine (0.51 g, 5 mmol) in benzene (100 cm^3) were refluxed for 40 h. The reaction mixture was washed several times with water and dried ($MgSO_4$). Evaporation of solvent under reduced pressure gave a semi-crystalline residue. Trituration with diethyl ether gave crystalline crude product **8**, m.p. 70–80 °C. Further purification by precipitation (benzene–light petroleum) afforded the *episulfide* **8** (1 g, 62.5%) as crystals, m.p. 103–104 °C (Found: C, 49.6; H, 5.1. $C_{13}H_{14}O_5S_2$ requires C, 49.67; H, 4.68%); $[\alpha]_D^{22}$ −154.05 (*c* 1.8, $CHCl_3$); δ_H(300 MHz) 5.24 (1 H, s, 1-H), 4.65 (1 H, d, $J_{2,3}$ 5.9, 2-H), 3.2–3.0 (2 H, m, 3- and 4-H), 4.8 (1 H, d, $J_{5,6exo}$ 4.3, 5-H), 4.0 (1 H, d, $J_{5,6}$ 4.5, 6*endo*-H), 3.82 (1 H, dd, J_{6exo} 4.3, $J_{6exo,6endo}$ 7.4 6*exo*-H), 2.45 (3 H, s, *Me*C_6H_4) and 7.9–7.2 (ArH); δ_C 100.47 (C-1), 71.77 (C-2), 29.57 (C-3), 34.54 (C-4), 71.13 (C-5), 67.73 (C-6), 145.23, 133.79, 129.98 and 127.88 (ArC) and 21.60 (Me).

Preparation of 1,6-*Anhydro*-4-S-(5′,5′-*dimethyl*-2′-*thioxo*-1′,-3′,2′-*dioxaphosphorinan*-2′-*yl*)-4-*thio*-2-O-(p-*tolylsulfonyl*)-β-D-*glucopyranose* **9**.—(*a*) A solution of dianhydride **6** (1.5 g, 5 mmol) and the dithioacid **7** (1 g, 5 mmol) in benzene (100 cm^3) was heated under reflux for 20 h. Removal of the solvent by evaporation under reduced pressure gave a crystalline residue [$\delta(^{31}P)$, 1 signal, 87.7, $CHCl_3$]. The residue was dissolved in benzene and the product **9** was obtained by precipitation with light petroleum (long needles, m.p. 117–118 °C) (4 mol of **9** to 1 mol of benzene of crystallization). The mother liquors were concentrated under reduced pressure, and additional amounts of compound **9** were obtained by repeated precipitation (benzene–light petroleum). Total yield of *product* **9** was 1.2 g (72%), m.p. 117–118 °C [Found: C, 45.2; H, 5.2; P, 5.9. $C_{18}H_{25}O_8PS_3 \cdot 1/4\,C_6H_6$ (496.56 + 19.528 = 516.088) requires C, 45.38; H, 5.17; P, 6.00%]; $[\alpha]_D^{22}$ −39.15 (*c* 1.8, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 690 (P=S) and 3450 (OH); δ_P($CDCl_3$) 87.7; δ_H(400 MHz) 0.95 [3 H, s, CMe(e)], 1.3 [3 H, s, CMe(a)], 2.5 (3 H, s, *Me*C_6H_4), 2.82 (1 H, d, $^3J_{3,OH}$ 5.8, OH), 3.61 (1 H, dt, $^3J_{4,P}$ 16.8, $^3J_{3,4}$ < 1, 4-H), 3.8 (1 H, dd, $^2J_{6exo,6endo}$ 8.4, $^3J_{5,6}$ 5.5, 6*exo*-H), 4.0 [2 H, q, $^2J_{a,e}$ 10.5, $^3J_{P,e}$ 25, 2 × OCH_2(e)], 4.15 (1 H, m, $^3J_{3,OH}$ 5.8, 3-H), 4.22 (1 H, s, $J_{1,2}$ < 1, $J_{2,3}$ < 1, 2-H), 4.28 (1 H, d, $J_{6exo,6endo}$ 8.4, 6*endo*-H), 4.33 [2 H, q, $^3J_{P,a}$ 6.3, $^2J_{a,e}$ 10.5, 2 × OCH_2(a)], 4.73 (1 H, d, $^3J_{5,6exo}$ 5.5, 5-H) and 5.32 (1 H, s, 1-H); δ_C 98.58 (C-1), 75.61 (C-2), 75.085 (d, $^3J_{P,C}$ 3.4, C-3), 49.28 (C-4), 70.39 (d, $^3J_{P,C}$ 4.7, C-5), 66.91 (C-6), 21.25, 20.85 and 19.89 (3 × Me), 131.86–127.04 and 144.7 (ArC) and 31.6 (d, *J* 6.8, *C*Me_2); *m*/*z* 497 (M^+ + H).

(*b*) Compound **9** can also be obtained, by allowing the dianhydride **6** to react with an equimolar amount of the acid **7** at 20 °C in benzene solution for 4 months, in quantitative yield.

Transphosphorylation of Compound **9** *in Deuteriated Pyridine Monitored by* ^{31}P *NMR Spectroscopy.*—A solution of β-hydroxy phosphorodithioate **9** (0.05 g) in [$^2H_5$]pyridine (0.5 cm^3) was placed in an NMR tube and the course of transphosphorylation, at room temperature, was monitored by ^{31}P NMR spectroscopy until complete disappearance of the signal at $\delta(^{31}P)$ 88.08 corresponding to compound **9**. The spectrum taken after 6.5 h showed two new signals, of very low intensity, at δ_P 60.00 and 57.5 which correspond to the β-mercapto thionophosphate **10** and phosphorothioate anion **11**, respectively. The signal at δ_P 60.00 showed maximum intensity after 9 h, the relative intensity being still very low. The intensity proportions of signals at δ_P 88.08, 60.00 and 57.5 after 9 h were 14:1:0.8, respectively. After 6 days the intensity proportions changed to 4.7:0.85:14.6. The low-intensity signal corresponding to compound **10** disappeared after 18 days along with the signal corresponding to compound **9**.

X-Ray Analysis.—The crystal data for compounds **6** and **8**, X-ray data collection, and structure determination and refinement parameters are summarized in Table 3. Diffraction data were collected on a KM4 diffractometer. All calculations were performed using the SHELX76 program.[8] Tables of atomic

Table 2 Selected bond lengths (Å)

6		8	
O(3)–C(3)	1.431(6)	S(1)–C(3)	1.789(9)
O(3)–C(4)	1.429(7)	S(1)–C(4)	1.791(9)
O(5)–C(1)	1.396(6)	O(5)–C(1)	1.404(9)
O(5)–C(5)	1.434(6)	O(5)–C(5)	1.416(10)
O(6)–C(1)	1.414(6)	O(6)–C(1)	1.410(10)
O(6)–C(6)	1.427(6)	O(6)–C(6)	1.440(10)
C(1)–C(2)	1.533(6)	C(1)–C(2)	1.537(11)
C(2)–C(3)	1.496(6)	C(2)–C(3)	1.524(11)
C(3)–C(4)	1.446(8)	C(3)–C(4)	1.481(12)
C(4)–C(5)	1.502(8)	C(4)–C(5)	1.501(9)
C(5)–C(6)	1.508(7)	C(5)–C(6)	1.488(12)
S(1)–O(A)	1.434(3)	S(2)–O(A)	1.443(5)
S(1)–O(B)	1.413(4)	S(2)–O(B)	1.425(5)
S(1)–C(1P)	1.747(4)	S(2)–C(1P)	1.764(6)
O(2)–C(2)	1.448(6)	O(2)–C(2)	1.454(9)
O(2)–S(1)	1.592(3)	O(2)–S(2)	1.585(4)

Table 3 Crystal data and experimental details for 1,6;3,4-dianhydro-2-*O*-(*p*-tolylsulfonyl)-β-D-galactopyranose **6** and 1,6-anhydro-3,4-dideoxy-3,4-epithio-2-*O*-(*p*-tolylsulfonyl)-β-D-allopyranose **8**

	6	**8**
Formula	$C_{13}H_{14}O_6S$	$C_{13}H_{14}O_5S_2$
M_r	298.31	314.37
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a (Å)	6.226(1)	5.731(1)
b (Å)	13.476(2)	9.848(2)
c (Å)	15.796(2)	25.259(4)
V (Å^3)	1325.3(8)	1425.6(6)
Z	4	4
D_x (g cm^{-3})	1.495	1.465
$F(000)$	624	656
μ(Cu-Kα) (cm^{-1})	23.5	34.85
Crystal size (mm)	0.6, 0.2, 0.2	0.6, 0.1, 0.2
Orientation matrix		
Number of reflections	25	25
2θ range (deg)	23–30	23–32
Scan technique	$\omega/2\theta$-scan	$\omega/2\theta$-scan
2θ range (deg)	4–164	4–164
hkl range	$-7\rightarrow7, 0\rightarrow17, 0\rightarrow20$	$0\rightarrow6, 0\rightarrow12, 0\rightarrow30$
Absorption corrections	none	none
Extinction parameter, x $F_{corr} = F(1 - xF^2/\sin\theta)$	1.66(9) × 10^{-8}	0.51(5) × 10^{-8}
Number of reflections		
Collected	2772	1787
Unique	2032	1643
Observed ($F_o \geqslant 3\sigma$)	1913	1379
Number of parameters	238	236
Final R (R_w)	0.045 (0.0432)	0.049 (0.0417)
w	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$
Max shift/esds: for non-H	0.019	0.007
and H-atom parameters	0.058	0.015
Min; max ($\Delta\rho$) [e Å^{-3}]	−0.32; 0.27	−0.32; 0.33
Determination of the absolute configuration:[7]		
R_w after refinement of atomic coordinates x, y, z using atomic scattering factors with $\Delta f'' = 0$	0.0634	0.0489
$R_w(+)$ for positive $\Delta f''$	0.0679	0.0484
$R_w(-)$ for negative $\Delta f''$	0.0615	0.0519
Number of parameters (variables)	1918 (181)	1379 (181)
Hamilton's test	$R = R_w(+)/R_w(-) = 1.104$	$R = R_w(-)/R_w(+) = 1.072$
theoretical R	$R_{1,\,1737,\,0.005} = 1.0023$	$R_{1,\,1198,\,0.005} = 1.003\,26$
Correct enantiomer	$-x, -y, -z$	x, y, z

positional and thermal parameters for correct enantiomers, and full lists of bond distances and angles, have been deposited with the CCDC.*

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* For full details of the Cambridge Crystallographic Data Centre deposition scheme see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1994, Issue 1.

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