Functionalised Carbocycles from Carbohydrates. Part 2.[1,2] The Synthesis of 3-Oxa-2-azabicyclo[3.3.0]octanes. *X*-Ray Crystal Structure of (1*R*,5*S*)-6-*exo*,7-*endo*,8-*exo*-Triacetoxy-*N*-methyl-4-*endo*-phenylthio-3-oxa-2-azabicyclo[3.3.0]octane

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Treatment of various 6-bromo-6-deoxy- and 6-deoxy-6-iodo-D-glucopyranosyl compounds with zinc in ethanol affords acyclic 5,6-dideoxy-D-*xylo*-hex-5-enoses which have been converted into 3-oxa-2-azabicyclo[3.3.0]octanes containing functional groups which permit specific reactions at C-4 and at C-8. One such compound (10a) was characterised by *X*-ray diffraction analysis. Aspects of the chemistry of 4-hydroxy derivatives are described including their conversion into novel functionalised cyclopentanes.

Our interest in the synthesis of specifically functionalised and optically pure carbocyclic compounds from carbohydrate derivatives [1] has led us to consider available methods for the preparation of cyclohexanes and cyclopentanes; whereas the former are well developed,[1] few efficient procedures for preparing cyclopentanes have been reported. Most successful conversions have used intramolecular aldol procedures,[3] but interesting alternatives have involved the construction of five-membered rings by employing the double bonds of unsaturated sugar derivatives as dienophiles in applications of the Diels–Alder reaction.[4,†]

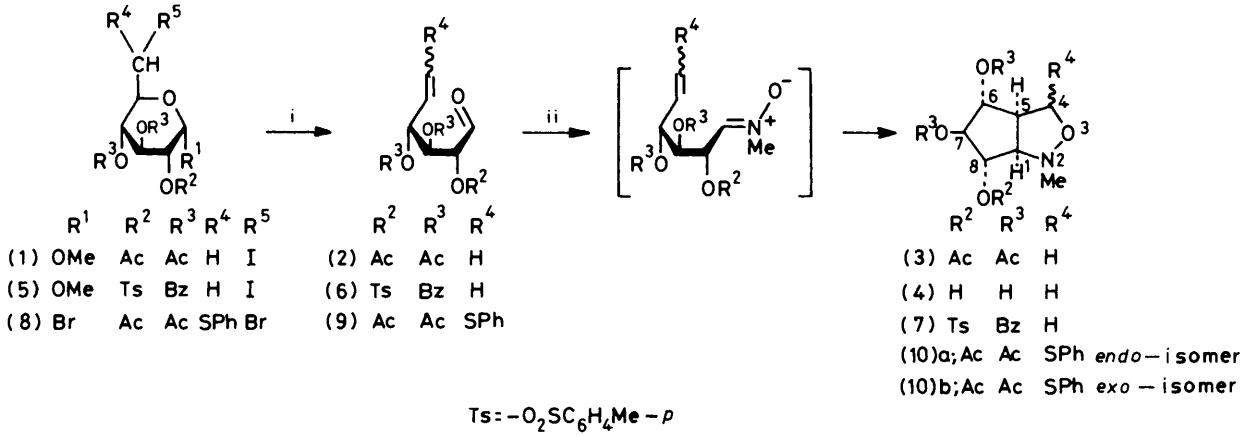
An alternative method which utilised an intramolecular 1,3-dipolar cycloaddition reaction of nitrones derived from 5-enals [5] which seemed suitably adaptable was first applied with carbohydrates by Bernet and Vasella.[6] These authors also introduced a simple method of preparing the required 5,6-dideoxyhex-5-enose derivatives by treating 6-bromo-6-deoxyhexopyranose compounds with zinc in aqueous alcohols but, apart from demonstrating that this reaction and subsequent treatment with *N*-methylhydroxylamine to give 3-oxa-2-azabicyclo[3.3.0]octanes (Scheme 1), could be effected in the presence of benzyl ether and acetal protecting groups, they did not explore widely the adaptability of the reactions. We now show that the elimination reaction can be applied readily with 6-deoxy-6-iodohexopyranose derivatives containing acetyl, benzoyl, and toluene-*p*-sulphonyl ester groups, and also with 6-bromo-6-phenylthio compounds, and that the products can be converted into the corresponding bicyclic isoxazolidines. Compounds of this type have been obtained which allow subsequent specific reactions at C-4 and C-8, and these have led to new cyclopentane derivatives and to a new route to prostanoids. These developments are described in this and the following paper.

Treatment of methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranoside (1) with zinc in boiling ethanol gave the enal (2) as a chromatographically less mobile and indiscrete product which was converted into the crystalline isoxazolidine (3) (50% isolated) by heating with *N*-methylhydroxylamine hydrochloride in ethanol containing pyridine. Deacetylation of the product gave the triol (4) analogous to a compound described by Bernet and Vasella [6] which was derived by a debenzylation step. The 2-tosylate (5) was then converted into the bicyclic product (7) by way of the enal (6). In this case the yield of crystalline product was 73% and it has been used in the development of a new route to a prostaglandin intermediate.[7,8] These observations indicate, therefore, that both steps of the conversions can be effected in the presence of acyl and sulphonyl ester groups and that 6-deoxy-6-iodohexopyranose derivatives, which are readily accessible,[9] can be used as starting materials. Indeed they may offer advantages over the corresponding bromides since they react with zinc which is not specifically activated, and this seemingly avoids competing deoxygenation reactions. Whereas Bernet and Vasella found contaminating products which had undergone such reaction at C-8,[6] no such compounds were encountered in the present study. In the case of the conversion (1) ⟶ (3), however, a second (unidentified) product was observed to be formed.

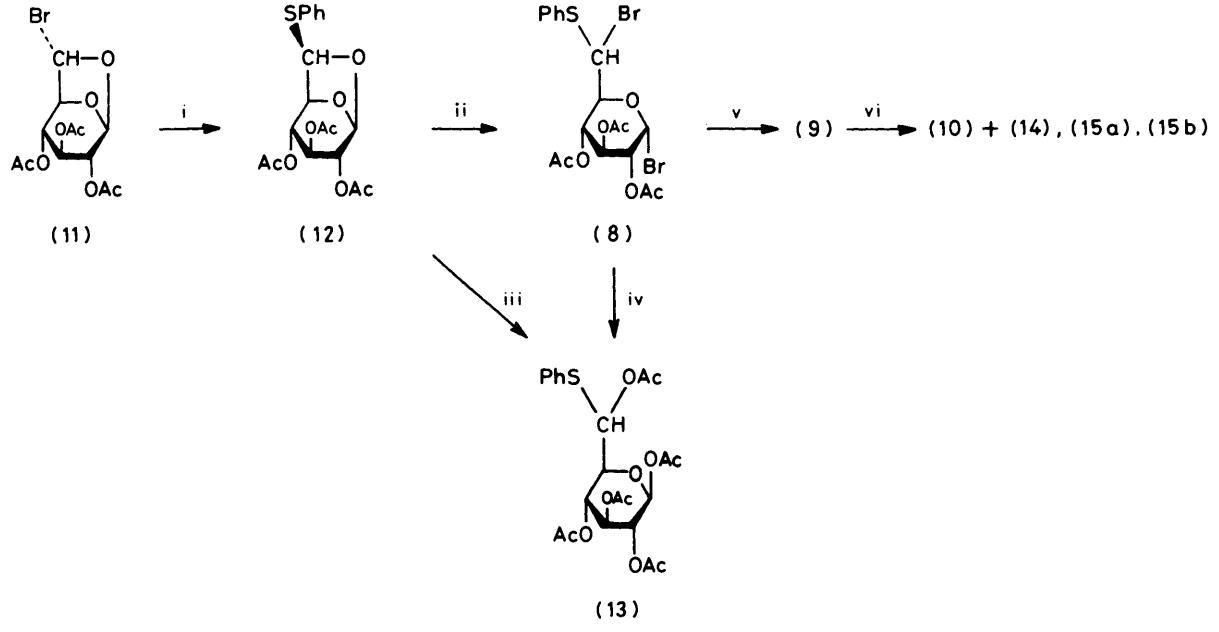
Following the finding of a good method of synthesis of compound (7) which enabled specific reactions to be effected at C-8 of the 3-oxa-2-azabicyclo[3.3.0]octanes,[7,8] methods were sought to effect specific changes at C-4, and to this end a hexopyranose compound was required which had both a halogen atom and a further electronegative substituent at C-6, and such a derivative became available from the 6-phenylthio compound (12) which is obtainable in high yield from the product (11) of photobromination of 2,3,4-tri-*O*-acetyl-1,6-anhydro-β-D-glucopyranose.[10] When treated with hydrogen bromide in acetic acid, the phenylthio compound gave, firstly, chromatographically slow products (presumably hydroxy derivatives) which were slowly converted into more mobile substances (presumably by acetylation or acid-catalysed bromine exchange), and the isolated syrup was a dibromide which, from its ^{1}H n.m.r. spectrum and optical rotation, was concluded to comprise the 6-epimeric glycosyl bromides (8) (Scheme 2). With mercury(II) acetate in acetic acid the same epimeric acetates (13) were produced from these bromides as were obtained as main products by direct acid-catalysed acetolysis of the phenylthio compound (12).

When the dibromides (8) in acetic acid were treated at room temperature with a suspension of zinc in aqueous acetic acid containing sodium acetate and copper(II) sulphate, a chromatographically slow and indiscrete product (9) was formed. This was isolated and then treated with *N*-methylhydroxylamine hydrochloride in warm ethanol–pyridine to give, as main products, the C-4 epimeric *endo*- and *exo*-(phenylthio)-isoxazolidines (10a and b) which were isolated crystalline in

† See B. M. Trost and T. A. Runge, *J. Am. Chem. Soc.*, 1981, **103**, 7559 for a new approach based on the palladium-catalysed isomerisation of 2-alkylidene-5-vinyltetrahydrofurans.



Scheme 1. *Reagents:* i, Zn, EtOH; ii, MeNHOH



Scheme 2. *Reagents:* i, PhS^-; ii, HBr, HOAc; iii, BF_3, Ac_2O; iv, $Hg(OAc)_2$, HOAc; v, Zn, HOAc; vi, MeNHOH

38 and 16% yield [from compound (12)], respectively. By-products of the reactions (8) ⟶ (9) ⟶ (10) were separated and characterised by ^1H n.m.r. spectroscopy as the unsaturated pyranose derivatives (14), (15a), and (15b) which are discussed below.

The ^1H and ^{13}C n.m.r. data given in Tables 1 and 2 for the new isoxazolidines are consistent with those recorded by Bernet and Vasella [6] for closely related compounds to which they assigned the *cis*-configuration at the ring junction and a *trans*-relationship between the cyclopentyl substituents at C-1 and C-8 and at C-5 and C-6. This is in accord with expectations based on steric considerations, and these configurational points have been confirmed unambiguously by a chemical method applied to the tosylate (7),[8] and by *X*-ray crystallographic analyses of the *endo*-isomer (10a) (see below) and of a compound derived from compound (7).[8] The configurations at C-4 of the phenylthio epimers (10a and b) were also obtained from the crystallographic analysis of the former, and it is noteworthy that their specific optical rotations (+211, −174°, respectively) are consistent with Hudson's Isorotation Rule if the C-4 positions on the isoxazolidine rings are considered as analogues of the anomeric centres of phenyl 1-thiofuranosides.

The *X*-ray crystal structure of the *S*-phenyl compound (10a) (Figure) shows that it is the *endo*-epimer, and that in the crystal the heterocyclic ring is a distorted envelope with C-4 exoplanar and the sulphur atom projecting outwards from the *endo*-space and the phenyl group orientated away from the remainder of the molecule. At the nitrogen atom the substituent methyl group occupies the *exo*-site. The cyclopentane ring is distorted unsymmetrically with each of the substituent oxygen atoms being displaced ' outwards ' by the interaction between the sulphur atom and O-14, and C-6 being exoplanar in a distorted envelope conformation.

The unsaturated pyranose derivatives (15a) and (15b) were apparently formed from the dibromides (8) by the zinc-based reaction which is normally used to prepare similar derivatives from glycosyl halides and by concurrent nucleophilic displacement at C-6. Compound (14) arose from the operation of the same elimination process and reductive

Table 1. ^{1}H N.m.r. data for 3-oxa-2-azabicyclo[3.3.0]octanes

	δ-values							
Compound	1-H	4-H	4′-H′	5-H	6-H	7-H	8-H	Me
(3)	3.47	4.05	4.06	3.05	4.91	5.37	5.12	2.62
(7)	3.62	4.20	4.18	3.25	5.15	5.87	5.01	2.60
(10a)	3.25	5.53		3.55	5.69	5.42	5.19	2.77
(10b)	3.56		5.38	3.07	5.15	5.38	5.15	2.85

	J-values (Hz)						
	$J_{1,5}$	$J_{1,8}$	$J_{4,5}$	$J_{4',5}$	$J_{5,6}$	$J_{6,7}$	$J_{7,8}$
(3)	9.7	5.8	6.6	4.2	6.5	8.1	8.1
(7)	9.7	5.2	5.9	4.4	6.3	8.3	8.3
(10a)	9.1	3.8	6.9		7.4	7.4	7.1
(10b)	9.2	4.3		3.4	5.5	7.0	7.0

Table 2. ^{13}C N.m.r. data for 3-oxa-2-azabicyclo[3.3.0]octanes

	δ-values (p.p.m.)							
Compound	C-1	C-4	C-5	C-6	C-7	C-8	Me	CO*Me*
(3)	73.1	71.0	50.6	77.2 [a]	79.0 [a]	79.9 [a]	43.9	21.7
(7)	72.9	69.6	50.4	77.5 [a]	79.0 [a]	83.9	43.3	21.5
(10a)	73.4	86.9	53.3	74.2 [a]	75.7 [a]	80.6 [a]	43.7	20.8
(10b)	71.8	89.6	57.6	74.8 [a]	77.9 [a]	79.2 [a]	43.4	20.7

[a] Not specifically assigned.

debromination at C-6. Such reduction of labile carbon–bromine bonds is known to occur in the presence of zinc powder.[11]

The epimers (15a) and (15b) were tested as possible alternative sources of functionalised cyclopentanes because, on treatment with mercury(II) ions, they should generate resonance-stabilised carbonium ions at C-6, and also nucleophilic character at C-2 following mercuriation of the vinyl ether groups. A related reaction has provided an efficient route to inosose derivatives from 6-deoxyhex-5-enopyranosyl compounds.[1] The crystalline 6-epimer (15b), which was assigned the (6*R*)-configuration on the basis of its more negative optical rotation and the relative polarisabilities of the substituent groups at this position,[12] on treatment with mercury(II) chloride in aqueous acetone did not react in this manner. Instead, it afforded mainly the (*E*)-enal (16) and smaller proportions of the (*Z*)-isomer (17) (Scheme 3), such a reaction being consistent with that previously encountered on similar treatment of other 3-*O*-acyl-1-enopyranoses.[13] In principle, the main product (16) could react further under the reaction conditions to lead to bonding between C-2 and C-6, but no further products were observed when the reaction was carried out under forcing conditions. This appears to be a further example of the failure of mercury(II) salts to generate carbonium ions from reactive phenylthio compounds which contain ester groups elsewhere in their structures.[14]

Compounds (10a) and (10b), which can be considered as formylcyclopentane derivatives, were then examined as potential sources of prostaglandin-like substances. The epimers, on separate heating in aqueous media in the presence of mercury(II) acetate, underwent ready hydrolysis to give the same mixture of epimeric hemiacetals from which the crystalline *exo*-isomer (18) was isolated in high yield. A singlet in the ^{1}H n.m.r. spectrum arising from 4-H and a negative optical rotation [see comment above regarding compounds (10a) and (10b)] are consistent with the configurational assignment. Acetylation with acetic anhydride in cold pyridine gave the corresponding (4-*exo*)-tetra-acetate (19a) which also showed no observable coupling between

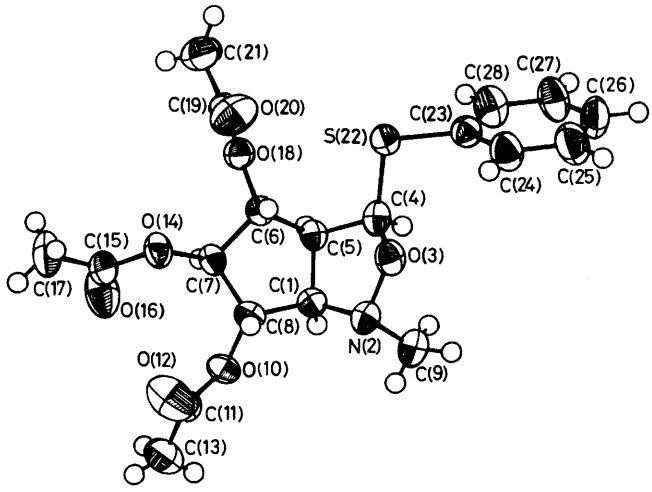


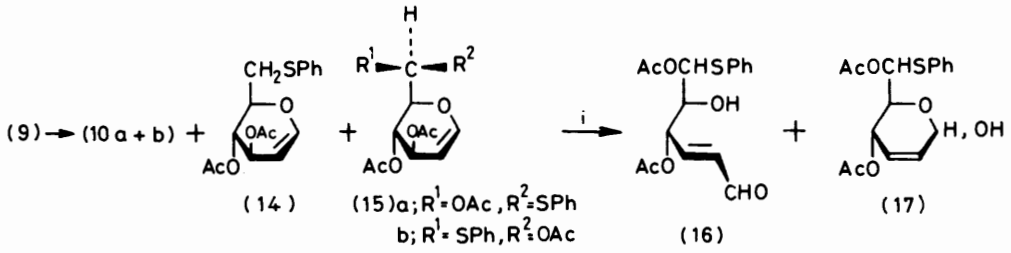
Figure. *X*-Ray crystal structure of (1*R*,5*S*)-6-*exo*,7-*endo*,8-*exo*-triacetoxy-*N*-methyl-4-*endo*-phenylthio-3-oxa-2-azabicyclo[3.3.0]-octane (10a).

4-H and 5-H and also showed a strong laevorotation. Otherwise, this acetate was obtained by boron trifluoride-catalysed acetolysis of the *endo*-phenylthio compound (10a) but, in this case, 25% of the *endo*-acetate (19b) was also produced. The latter had a $J_{4,5}$-value of 6.2 Hz and was dextrorotatory, adding support to the conclusion that Hudson's Isorotation Rule is obeyed by epimeric 4-substituted isoxazolidines if they are treated as analogues of anomeric furanosyl derivatives.

The *endo*-isoxazolidine (10a), on deacetylation, gave the crystalline triol (20a) which, on mercury(II) ion-catalysed hydrolysis, afforded a syrupy product, and ^{1}H and ^{13}C n.m.r. spectra of which indicated that it was a 1 : 1 mixture of the epimeric hemiacetals from which the previous tetra-acetate (19a) was produced after acetylation with acetic anhydride in pyridine (Scheme 4). The tetraols (21), however, did not react with methanolic hydrogen chloride which indicates that the nitrogen atom modifies the hemiacetal function—presumably by protonating and then inhibiting the ability of the unshared electrons at O-3 to stabilise a carbonium ion at C-4. Consistent with this, the hemiacetals (21) did not react to form an anhydro derivative on heating in solution in the presence of toluene-*p*-sulphonic acid. On the grounds that 3-*endo*-hydroxybicyclo-[3.2.0]heptan-6-one derivatives can readily form intramolecular hemiacetals,[15] and that free sugars form anhydrides under acidic conditions,[16] it was anticipated that the 4,7-anhydro derivative (23) would have been obtainable. Reaction of the triol (20b) in acetonitrile with mercury(II) acetate did, however, give a product believed to be the anhydro derivative (23). It had lower chromatographic mobility than the starting material, and on heating in aqueous acetonitrile gave a slower product with the mobility of the tetraol (21). The hydrolysis of compounds (10a) and (10b) with mercury(II) chloride was inhibited by the hydrogen chloride produced in the reaction, the rates being initially rapid but being slow towards the end of the process. This also shows that the behaviour of such compounds in acid differs from that of normal thioacetals. To produce the methyl acetal (22), compound (20a) was methanolysed in the presence of mercury(II) acetate.

To test the potential value of C-4 hemiacetals of this series as precursors of functionalised cyclopentanes bearing a carbon-bonded side-chain, compound (18) was treated with the ylide derived from triphenyl(phenylthiomethyl)phosphonium chloride [17] (by use of dimsyl sodium *,[18]) which has been

* Dimsyl sodium is $CH_3S(O)CH_2^-Na^+$.



Scheme 3. *Reagents:* i, $HgCl_2$, H_2O

employed successfully with carbohydrates,[19] and the dienes (24a) and (24b) were obtained. These were readily characterised from their ^1H n.m.r. spectra and were formed presumably by base-catalysed elimination of acetic acid either from the first derived products or from the aldehydo form of the starting material (18). Although these dienes were obtained pure by chromatographic methods they underwent interconversion with time.

Compounds (24a) and (24b) both failed to give specific aldehydes when treated with mercury(II) chloride in aqueous acetone despite the fact that several examples have been reported of such hydrolysis of other vinyl sulphides—particularly of compounds which contain appropriate hydroxy groups for intramolecular hemiacetal formation.[20,21] Alternatively, other workers have encountered difficulties with the hydrolysis of vinyl sulphides,[20,22] especially those with conjugated double bonds.[23]

Experimental

^1H and ^{13}C N.m.r. spectra were measured in deuteriochloroform solutions with Perkin-Elmer R20 and Varian FT 80A instruments, respectively. Optical rotations were measured in chloroform (unless otherwise noted) and within the concentration range 0.5—1.5%. Organic solutions were dried with sodium sulphate or magnesium sulphate, light petroleum refers to that fraction boiling in the range 60—80 °C.

(1R,5R)-6-exo,7-endo,8-exo-*Triacetoxy*-N-*methyl*-3-*oxa*-2-*azabicyclo*[3.3.0]*octane* (3).—To a solution of methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranoside (1) (2.0 g) in warm, wet ethanol (50 ml; 95%) was added zinc dust (2.0 g) and the mixture was heated under reflux for 45 min after which the iodide had been replaced by a t.l.c.-indiscrete but less mobile product. Removal of the solids by filtration and evaporation of the filtrate left a yellow oil which was dried under high vacuum and dissolved in a mixture of pyridine (5 ml) and ethanol (30 ml). *N*-Methylhydroxylamine hydrochloride (0.46 g, 1.2 mol equiv.) was added and the solution was heated at 65 °C for 3 h. The cooled reaction mixture was poured into ice–water and the mixture was extracted with chloroform (× 4). The combined extracts were washed in turn with aqueous potassium hydrogen sulphate and water and were then dried. Evaporation of the solvent gave an oil (1.14 g) which, on fractionation on a column of silica gel gave the crystalline *isoxazolidine* (3) (0.69 g, 49%). Recrystallisation from diethyl ether–light petroleum gave crystals, m.p. 84—85 °C, $[\alpha]_D$ +48° (Found: C, 51.6; H, 6.3; N, 4.7. $C_{13}H_{19}NO_7$ requires C, 51.8; H, 6.3; N, 4.6%).

(1R,5R)-6-exo,7-endo,8-exo-*Trihydroxy*-N-*methyl*-3-*oxa*-2-*azabicyclo*[3.3.0]*octane* (4).—Deacetylation of the triacetate (3) was effected with traces of sodium methoxide to give the *triol* (4) (100%), m.p. 145—146 °C (from ethanol–light petroleum); $[\alpha]_D$ +16° (*c* 0.4 in MeOH) (Found: C, 44.5; H, 8.2; N, 7.4. $C_7H_{13}NO_4 \cdot 0.75\ H_2O$ requires C, 44.6; H, 8.3; N, 7.4%). The compound proved very difficult to dehydrate, the analysed sample being initially found to contain 0.15 mol water. After further recrystallisation from the above solvent mixture and extensive drying *in vacuo* the recorded analytical figures were obtained (in duplicate).

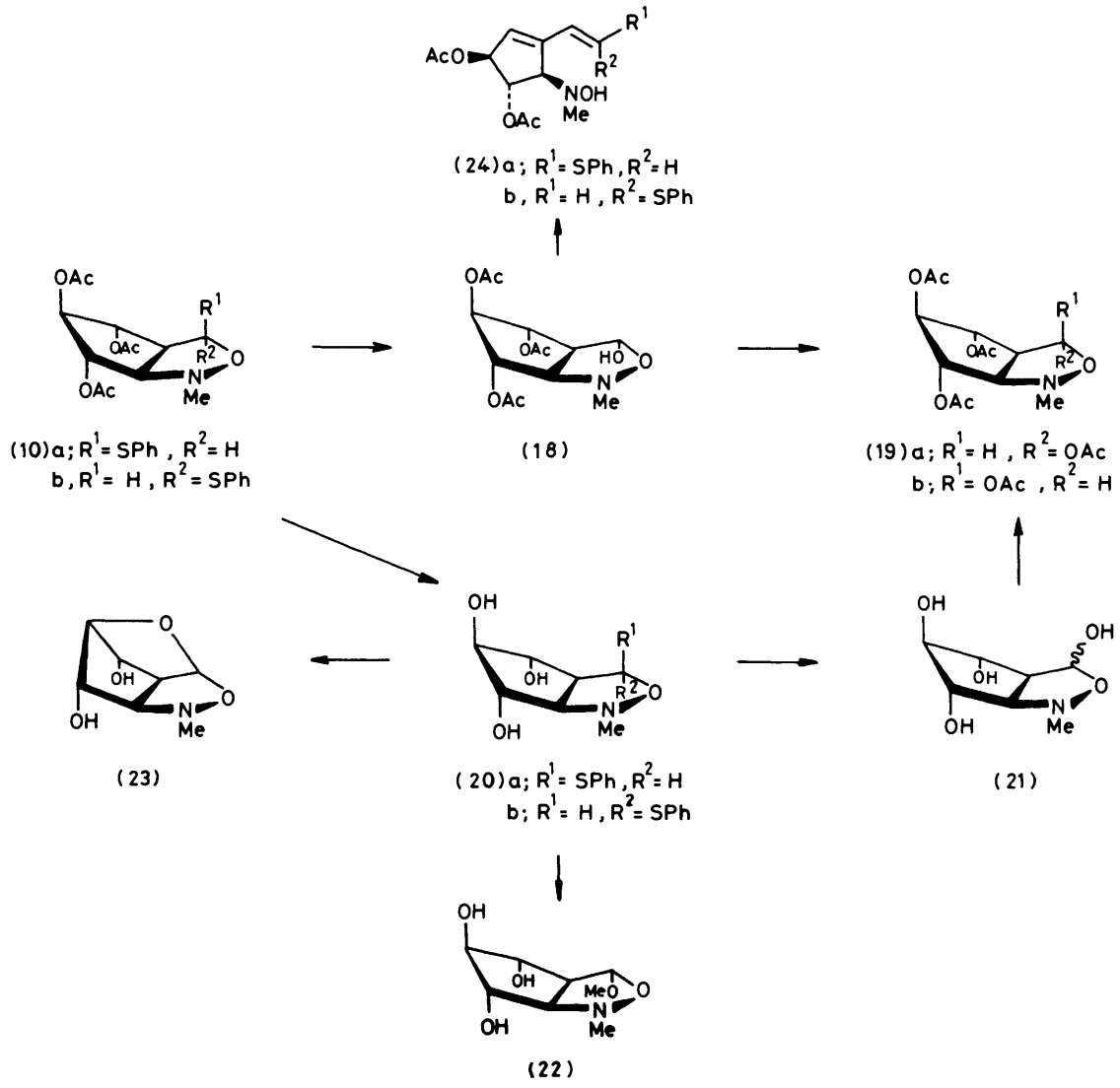
(1R,5R)-6-exo,7-endo-*Dibenzoyloxy*-N-*methyl*-8-exo-*tosyloxy*-3-*oxa*-2-*azabicyclo*[3.3.0]*octane* (7).—Methyl 3,4-di-*O*-benzoyl-6-deoxy-6-iodo-2-*O*-tosyl-α-D-glucopyranoside[1] (5) (20 g) was heated under reflux in wet ethanol (650 ml; 95%) for 1 h in the presence of zinc dust (20 g). Filtration, and evaporation of the filtrate, gave a light yellow oil (15.6 g) of which 12.5 g were dissolved in pyridine–ethanol (80%; 200 ml). *N*-Methylhydroxylamine hydrochloride (3.76 g, 1.2 mol equiv.) was added and the mixture was heated at 45 °C for 2 h. The solvents were removed and the residual oil was poured onto ice to give a crystalline product. Recrystallisation from methanol gave the *isoxazolidine* (7) (11.8 g, 73%), m.p. 129—131 °C; $[\alpha]_D$ −53° (Found: C, 62.4; H, 5.1; N, 2.7; S, 5.7. $C_{28}H_{27}NO_8S$ requires C, 62.6; H, 5.0; N, 2.6; S, 6.0%).

Acid-catalysed Reactions of the Phenylthio Compound (12).—(1) *Reaction with hydrogen bromide.* A solution of hydrogen bromide in acetic acid (10 ml; 60% w/v) was added to a solution of the phenylthio derivative (12) [10] (1 g) in chloroform (10 ml) and after 1.3 h (room temperature) the products were partitioned between water and chloroform. The organic phase was washed in turn with aqueous sodium hydrogen carbonate and water and, after being dried and evaporated, gave a syrup which afforded, after chromatography, a sample of (6*RS*)-2,3,4-tri-*O*-acetyl-6-bromo-6-*S*-phenyl-6-thio-α-D-glucopyranosyl bromide (8) (1.2 g, 88%), $[\alpha]_D$ +139° (Found: Br, 26.5. $C_{18}H_{20}Br_2O_7S$ requires Br, 29.6%); δ 6.68 (1 H, d, $J_{1,2}$ 4.1 Hz, 1-H).

A fraction (0.24 g) of this dibromide in acetic acid (3 ml) was treated with mercury(II) acetate (0.3 g) and the mixture was stirred for 1 h. The product was isolated as above and shown to be a mixture of the C-6 epimeric 1,2,3,4,6-penta-*O*-acetyl-6-phenylthio-β-D-glucopyranoses * (13); δ 6.33 (0.7 H, d, $J_{5,6}$ 2.4 Hz, 6-H) and 6.18 (0.3 H, d, *J* 2.2 Hz, 6-H').

(2) *Reaction with acetic anhydride and boron trifluoride–diethyl ether.* Repetition of this previously reported reaction [10] with the phenylthio compound (12) (2 g) in acetic anhydride (10 ml) and boron trifluoride–diethyl ether (4 drops) for 2.5 h at 20 °C gave a water-insoluble product which was fractionated by column chromatography to give a previously undetected, minor product (6S)-2,3,4-*tri*-O-*acetyl*-1,6-*anhydro*-6-*phenylthio*-β-D-*glucopyranose*, *i.e.* the 6-epimer of the starting material, in 6% yield. The product was recrystal-

* (6*RS*)-2,3,4,6-Tetra-*O*-acetyl-6-phenylthio-β-D-glucopyranosyl acetate.



Scheme 4.

lised from ethanol, m.p. 98—100 °C; $[\alpha]_D$ −124° (Found: C, 54.4; H, 5.0; S, 8.4. $C_{18}H_{20}O_8S$ requires C, 54.5; H, 5.1; S, 8.1%).

The main products, as before,[10] were the epimeric penta-*O*-acetyl-6-phenylthio-β-D-glucopyranoses (13), the major isomer was the previously reported crystalline compound (m.p. 182—183 °C, $[\alpha]_D$ −6°) and the *minor isomer*, isolated by preparative t.l.c., had $[\alpha]_D$ −5.4° (Found: C, 53.0; H, 5.4; S, 6.7. $C_{22}H_{26}O_{11}S$ requires C, 53.0; H, 5.3; S, 6.4%).

(1R,5S)-6-exo,7-endo,8-exo-*Triacetoxy*-N-*methyl*-4-endo- and -4-exo-*phenylthio*-3-*oxa*-2-*azabicyclo*[3.3.0]*octane* (10a) *and* (10b).—Hydrogen bromide (130 ml; 60% w/v in glacial acetic acid) was added to a solution of (6*R*)-2,3,4-tri-*O*-acetyl-1,6-anhydro-6-phenylthio-β-D-glucopyranose (12) (30 g) in chloroform–acetic anhydride (90 ml; 5 : 1) and after 5 h at 20 °C the majority of the volatile components were removed (<40 °C). The syrupy residue was redissolved in acetic acid (100 ml) and the solution was added gradually to a stirred suspension of zinc powder (50 g) in acetic acid–water (750 ml; 4 : 1) containing sodium acetate (68 g) and copper(II) sulphate (3 g). The mixture was stirred for a further 2 h, the solids were filtered off, and the filtrate was extracted with chloroform. The extracts were washed in turn with water, aqueous sodium hydrogen carbonate, and water, and were then dried and the solvent was removed under reduced pressure to leave a light yellow syrup which was dissolved in ethanol–pyridine (270 ml; 12.5 : 1). *N*-Methylhydroxylamine hydrochloride (10.1 g, 1.6 mol equiv.) was added and the solution was warmed at 50 °C for 0.5 h, the solvents were then removed under reduced pressure, and the residue was washed with water and taken up in chloroform. The extracts were again washed in turn with water, dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water, and were then dried and the solvent was removed under reduced pressure to leave a dark coloured, partially crystalline residue. Treatment of this in hot ethanol (200 ml) with decolourising charcoal, followed by filtration and cooling of the filtrate, gave the endo-*phenylthioisoxazolidine* (10a) as needles (11.7 g, 38%). The product was recrystallised from ethyl acetate–light petroleum, m.p. 153—154 °C; $[\alpha]_D$ +211° (Found: C, 55.7; H, 5.7; N, 3.6; S, 8.0. $C_{19}H_{23}NO_7S$ requires C, 55.7; H, 5.7; N, 3.4; S, 7.8%).

The filtrate was treated with light petroleum and cooled to 0 °C where it deposited the exo-*isomer* (10b) as fine needles (3.3 g, 11%). The product was recrystallised from diethyl ether–light petroleum, m.p. 109—110 °C; $[\alpha]_D$ −174° (Found: C, 55.6; H, 6.0; N, 3.5; S, 7.9%).

Evaporation of the mother liquors gave a red syrup (10.9 g) which was fractionated on a column of silica gel to give a compound identified from its ^{1}H n.m.r. spectrum as 3,4-di-*O*-acetyl-1,5-anhydro-2-deoxy-6-*S*-phenyl-6-thio-D-*arabino*-hex-1-enitol (14) [δ 7.0—7.8 (5 H, m, Ph), 6.42 (1 H, d, $J_{1,2}$ 6.2 Hz, 1-H), 5.10—5.45 (2 H, m, 3- and 4-H), 4.84 (1 H, m, virtual coupling displayed, 2-H), 4.20 (1 H, m, virtual coupling displayed, 5-H), 3.15—3.3 (2 H, m, 6-H_2), and 2.02 (6 H, s, 2 × Ac)]. A second fraction (1.4 g, 5%) contained the epimeric tri-*O*-acetyl-6-phenylthio-D-*arabino*-hex-1-enitols (15) discussed below, and a third fraction gave a second crop of the *exo*-isoxazolidine (10b) (1.5 g, 5%, total yield 16%).

(6S)- and (6R)-3,4,6-*Tri*-O-*acetyl*-1,5-*anhydro*-2-*deoxy*-6-*phenylthio*-D-arabino-*hex*-1-*enitol* * (15a) and (15b).—Repeated chromatographic separations of the second fraction (see above) gave a more mobile syrup ([α]$_D$ +2°), (6*S*)-isomer (15a), δ ([$^2H_6$]acetone) 7.2—7.7 (5 H, m, Ph), 6.55 (1 H, dd, $J_{1,2}$ 6.0, $J_{1,3}$ 1.1 Hz, 1-H), 6.53 (1 H, d, $J_{5,6}$ 5.3 Hz, 6-H), 5.2—5.6 (2 H, m, 3- and 4-H), 4.89 (1 H, dd, $J_{2,3}$ 3.6, 2-H), 4.41 (1 H, dd, $J_{4,5}$ 6.4 Hz, 5-H), and 1.93, 1.96, and 2.00 (9 H, 3 × s, 3 × Ac), and the crystalline (6R)-*isomer* (15b) m.p. 103—104 °C, [α]$_D$ −123° (Found: C, 57.1; H, 5.4; S, 8.4. $C_{18}H_{20}O_7S$ requires C, 56.9; H, 5.3; S, 8.4%); δ ([$^2H_6$]-acetone) 7.2—7.6 (5 H, m, Ph), 6.51 (1 H, dd, $J_{1,2}$ 6.1, $J_{1,3}$ 1.0 Hz, 1-H), 6.31 (1 H, d, $J_{5,6}$ 6.7 Hz, 6-H), 5.31 (1 H, br t, $J_{2,3}$ 3.7, $J_{3,4}$ 4 Hz, 3-H), 5.17 (1 H, br t, $J_{4,5}$ 5.4 Hz, 4-H), 4.92 (1 H, dd, 2-H), 4.21 (1 H, dd, 5-H), and 2.00, 2.02, and 2.11 (9 H, 3 × s, 3 × Ac).

Treatment of the D-altro-*Hexenitol Derivative* (15b) *with Mercury*(II) *Chloride*.—The crystalline epimer (15b) (0.2 g) was dissolved in acetone (5 ml), water (2 ml) and mercury(II) chloride (0.5 g, 3.4 mol equiv.) were added, and the solution was kept at room temperature for 24 h. Barium carbonate was then added and hydrogen sulphide was used to precipitate the mercury(II) ions, the solids and solvent were removed (filtration followed by evaporation) and the residue was partitioned between chloroform and water. Fractionation of the chloroform-soluble material on a column of silica gel gave a syrup (0.04 g, 22%), [α]$_D$ +35° with ^{1}H n.m.r. resonances indicating that it was 4,6-di-*O*-acetyl-2,3-dideoxy-6-phenylthio-D-*erythro*-hex-2-enopyranose (17), δ 7.2—7.6 (5 H, m, Ph), 6.31 (1 H, d, $J_{5,6}$ 2.5 Hz, 6-H), 5.88—5.94 (2 H, m, 2- and 3-H), 5.63 (1 H, d, $J_{4,5}$ 9.1 Hz, 4-H), 5.50 (1 H, d, $J_{1,2}$ 1.7 Hz, 1-H), 4.34 (1 H, dd, 5-H), 3.3 (1 H, br s, OH), and 2.05 and 2.08 (6 H, 2 × s, 2 × Ac).

A less mobile syrup (0.12 g, 66%), [α]$_D$ −86°, was similarly identified as the acyclic (*E*)-isomer (16), δ 9.56 (1 H, d, $J_{1,2}$ 7.5 Hz, 1-H), 7.1—7.6 (5 H, m, Ph), 6.87 (1 H, dd, $J_{2,3}$ 15.9, $J_{3,4}$ 4.8 Hz, 3-H), 6.17 (1 H, ddd, $J_{2,4}$ 1.4 Hz, 2-H), 6.08 (1 H, d, $J_{5,6}$ 5.9 Hz, 6-H), 5.67 (1 H, ddd, $J_{4,5}$ 5.5 Hz, 4-H), 4.01 (1 H, dd, 5-H), 3.05 (1 H, br s, OH), and 2.05 and 2.08 (6 H, 2 × s, 2 × Ac).

(1R,5S)-6-exo,7-endo,8-exo-*Triacetoxy*-4-exo-*hydroxy*-N-*methyl*-3-*oxa*-2-*azabicyclo*[3.3.0]*octane* (18).—Compounds (10a) and (10b) (0.2 g) were separately dissolved in acetone (7.5 ml), and a solution of mercury(II) acetate (0.17 g, 1.1 mol equiv.) in water (2.5 ml) was added. In each case the solution had [α]$_D$ −0.87° after 20 min (constant). The solutions were then combined and the components were partitioned between water and chloroform. The organic phase was dried, treated with hydrogen sulphide, filtered through Celite, and taken to dryness to give a residue which was crystallised from ethanol–acetone–light petroleum. The exo-*hydroxy compound* (0.26 g, 83%), recrystallised from this solvent, had m.p. 141—142 °C [α]$_D$ −75° (1 min) ⟶ −45° (2 d) (Found: C, 49.1; H, 6.0; N, 4.5. $C_{13}H_{19}NO_8$ requires C, 49.2; H, 6.0; N, 4.4%); δ 2.09, 2.06, and 2.04 (9 H, 3 × s, 3 × OAc), 2.87 (3 H, s, NMe), 3.05 (1 H, dd, $J_{1,5}$ 8.9, $J_{5,6}$ 6.6 Hz, 5-H), 3.72 (1 H, dd, $J_{1,8}$ 5.4 Hz, 1-H), 4.1 (1 H, br s, OH), 4.85—5.50 (3 H, m, 6-, 7-, and 8-H), and 5.69 (1 H, s, 4-H).

(1R,5S)-4-exo,6-exo,7-endo,8-exo-*Tetra-acetoxy*-N-*methyl*-3-*oxa*-2-*azabicyclo*[3.3.0]*octane* (19a).—(a) *By acetylation of the alcohol* (18). The hydroxy compound (0.1 g) was acetylated with acetic anhydride (0.5 ml) and pyridine (0.5 ml) for 0.5 h at −15 °C and 2 h at 20 °C. Recrystallisation from light petroleum–ethanol gave the (4-exo)-*tetra-acetate* (0.1 g, 89%), m.p. 134—135 °C; [α]$_D$ −111° (Found: C, 49.9; H, 6.0; N, 3.9. $C_{15}H_{21}NO_9$ requires C, 50.1; H, 5.9; N, 3.9%); δ 2.04, 2.06, 2.06, and 2.08 (12 H, 3 × s, 4 × OAc), 2.85 (3 H, s, NMe), 3.17 (1 H, dd, $J_{1,5}$ 8.7, $J_{5,6}$ 6.2 Hz, 5-H), 3.69 (1 H, dd, $J_{1,8}$ 5.0 Hz, 1-H), 5.08 (1 H, dd, $J_{6,7}$ 7.2 Hz, 6-H), 5.17 (1 H, dd, $J_{7,8}$ 7.2 Hz, 8-H), 5.38 (1 H, t, 7-H), and 6.42 (1 H, s, 4-H).

(b) *By acetolysis of the phenylthio compound* (10a). Boron trifluoride–diethyl ether (0.08 g) was added to a solution of the phenylthio compound (0.24 g) in acetic anhydride (3 ml) and the mixture was heated at 85 °C for 1.5 h. The solution was diluted with chloroform, washed in turn with aqueous sodium hydrogen carbonate and water, and dried to give a syrup containing the epimeric acetals (19a) and (19b) in the ratio 3 : 1 (^{1}H n.m.r. analysis). Fractionation on a column of silica gel gave the 4-*exo*-compound (0.12 g, 59%), m.p. 134—135 °C; [α]$_D$ −113°; ^{1}H n.m.r. spectrum identical to that of sample prepared by method (a). This was preceded off the column by the 4-endo-*isomer* (19b) (0.05 g, 24%), [α]$_D$ +85° (Found: C, 50.2; H, 6.1; N, 3.7%); δ 2.04, 2.06, 2.09, and 2.15 (12 H, 4 × s, 4 × OAc), 2.77 (3 H, s, NMe), 3.09 (1 H, dd, $J_{1,5}$ 10, $J_{1,8}$ 3.7 Hz, 1-H), 3.43 (1 H, m, 5-H), 4.9—5.8 (3 H, m, 6-, 7-, and 8-H), and 6.33 (1 H, d, $J_{4,5}$ 6.2 Hz, 4-H).

(c) *By acetylation of the tetraol* (21). Acetylation of the tetraol (see below) was effected as in (a) above with acetic anhydride in pyridine to give the (4-*exo*)-tetra-acetate, m.p. 133—134 °C; ^{1}H n.m.r. spectrum identical to that of the previous samples.

(1R,5S)-6-exo,7-endo,8-exo-*Trihydroxy*-N-*methyl*-4-endo-*phenylthio*-3-*oxa*-2-*azabicyclo*[3.3.0]*octane* (20a).—The triacetate (10a) (0.5 g) was deacetylated with catalytic sodium methoxide in methanol. The solvent was removed and the residue was dissolved in chloroform, washed onto a column of silica gel, and eluted with ethyl acetate. Evaporation of the solvent gave a residue which was crystallised from ethanol–acetone–light petroleum to afford the *triol* (20a) (0.285 g, 82%). Recrystallised from this solvent it had m.p. 147—148 °C, [α]$_D$ +150° (*c* 2 in water) (Found: C, 54.7; H, 6.6; N, 4.9; S, 11.1. $C_{13}H_{17}NO_4S$ requires C, 55.1; H, 6.1; N, 4.9; S, 11.3%).

Hydrolysis of Compound (20a).—A solution of mercury(II) chloride (0.16 g, 1 mol equiv.) in water (3 ml) was added to the triol (0.165 g) in water. A white solid which immediately precipitated was filtered off and the filtrate was evaporated to give the syrupy tetraols (21) (0.11 g, 100%), δ_H (D_2O) 5.90 (0.5 H, s, 4-H *exo*-isomer) and 6.02 (0.5 H, d, $J_{4,5}$ 5.9 Hz, 4-H *endo*-isomer); δ_C (D_2O) 38.2 and 44.2 (NMe), 53.2 and 55.2 (C-5), and 99.5 and 103.4 p.p.m. (C-4).

(1R,5S)-6-exo,7-endo,8-exo-*Trihydroxy*-4-exo-*methoxy*-N-*methyl*-3-*oxa*-2-*azabicyclo*[3.3.0]*octane* (22).—A solution of the

* 3,4,6-*Tri*-O-*acetyl*-1,5-*anhydro*-2-*deoxy*-6-*phenylthio*-L-galacto- and -D-altro-*hex*-1-*enitol*.

Table 3. Atomic co-ordinates for compound (10a) with e.s.d.s in parentheses

	10^4x	10^4y	10^4z		10^4x	10^4y	10^4z
C(1)	7 008(5)	1 959(4)	1 914(9)	C(15)	8 506(5)	525(5)	−2 106(10)
N(2)	6 765(4)	2 810(3)	2 074(8)	O(16)	8 004(4)	−1(3)	−1 743(8)
O(3)	7 520(3)	3 184(2)	2 878(6)	C(17)	9 090(7)	541(6)	−3 574(13)
C(4)	7 892(5)	2 596(4)	3 967(9)	O(18)	9 340(3)	1 363(3)	2 170(6)
C(5)	7 851(4)	1 831(4)	2 943(9)	C(19)	10 111(5)	1 696(5)	1 689(11)
C(6)	8 553(5)	1 747(4)	1 601(8)	O(20)	10 153(4)	2 305(4)	909(8)
C(7)	8 076(4)	1 250(4)	300(9)	C(21)	10 879(7)	1 235(6)	2 236(16)
C(8)	7 234(5)	1 716(4)	124(9)	S(22)	8 973(1)	2 881(1)	4 592(3)
C(9)	6 002(7)	2 913(6)	3 173(12)	C(23)	8 731(3)	3 588(2)	6 158(6)
O(10)	6 525(3)	1 245(3)	−555(6)	C(24)	8 795(3)	3 368(2)	7 832(6)
C(11)	6 396(5)	1 302(5)	−2 213(11)	C(25)	8 620(3)	3 928(2)	9 077(6)
O(12)	6 805(4)	1 713(4)	−3 118(7)	C(26)	8 382(3)	4 708(2)	8 650(6)
C(13)	5 653(8)	774(6)	−2 726(12)	C(27)	8 318(3)	4 927(2)	6 977(6)
O(14)	8 592(3)	1 194(3)	−1 188(6)	C(28)	8 492(3)	4 367(2)	5 731(6)

endo-phenylthio compound (20a) (0.44 g) in methanol (30 ml) was stirred and treated with mercury(II) acetate (0.5 g, 1.0 mol equiv.). Reaction was complete within 2 min, the solvent was removed, and the residue was extracted with water. Removal of the water gave the *methoxy product* (22) (0.21 g, 70%) after crystallisation from ethyl acetate–ethanol–light petroleum, m.p. 147—148 °C; $[\alpha]_D$ −99° (*c* 1 in EtOH) (Found: C, 47.0; H, 7.8; N, 7.0. $C_8H_{15}NO_5$ requires C, 46.8; H, 7.4; N, 6.8%).

E- and Z-(3S,4S,5R)-3,4-*Diacetoxy*-5-(N-*hydroxy*-N-*methylamino*)-1-[2-(*phenylthio*)*vinyl*]*cyclopent*-1-*ene* (24a) *and* (24b).—The crystalline hemiacetal (18) (0.5 g) was added to a deep red solution of the ylide prepared by treatment of triphenyl(phenylthiomethyl)phosphonium chloride (0.66 g, 1.0 mol equiv.) in dimethyl sulphoxide (3 ml) with 1.25M-dimsyl sodium in dimethyl sulphoxide (1.26 ml, 1.0 mol equiv.). When the mixture was heated under nitrogen at 80 °C two chromatographically less mobile products were formed, but the starting material was not removed completely until two further aliquot portions of ylide, similar to the first, had been added (1 h and 3 h) and the mixture has been heated for a further 6 h. The dark mixture was then partitioned between chloroform and water and the aqueous phase was extracted (× 6) with chloroform. The combined organic extracts were washed with water, dried, and concentrated to leave a red syrup which was fractionated on a column of silica gel.

Fraction 1 gave the *E*-isomer (24a) (0.105 g, 19%), $[\alpha]_D$ +114°; $\lambda_{max.}$ (95% EtOH) 296 nm (ε 16 600) (Found: C, 59.8; H, 6.0; N, 3.9; S, 8.9. $C_{18}H_{21}NO_5S$ requires C, 59.5; H, 5.8; N, 3.9; S, 8.8%); δ ([$^2H_6$]acetone) 1.99 and 2.02 (6 H, 2 × s, 2 × OAc), 2.59 (3 H, s, NMe), 2.85 (1 H, br s, OH), 4.14 (1 H, d, $J_{4,5}$ 3.2 Hz, 5-H), 5.51, 5.67, and 5.84 (3 H, m, m, t, 2-, 3-, and 4-H), 6.37 (1 H, d, $J_{1',2'}$ 15.5 Hz, 1'-H), 7.33 (1 H, d, 2'-H), and 7.1—7.5 (5 H, Ph).

Fraction 2 gave the *Z*-isomer (24b) (0.13 g, 24%), $[\alpha]_D$ +74°; $\lambda_{max.}$ (95% EtOH) 295 nm (ε 13 800) (Found: C, 59.4; H, 6.1; N, 3.7; S, 9.3%); δ ([$^2H_6$]acetone) 2.02 and 2.04 (6 H, 2 × s, 2 × OAc), 2.63 (3 H, s, NMe), 2.85 (1 H, br s, OH), 3.95 (1 H, d, $J_{4,5}$ 4.3 Hz, 5-H), 5.67, 5.84, and 5.96 (3 H, 3 × m, 2-, 3-, and 4-H), 6.25 (1 H, d, $J_{1',2'}$ 10.7 Hz, 1'-H), 6.72 (1 H, d, 2'-H), and 7.1—7.5 (5 H, Ph).

When the preparation was repeated with *N*,*N*-dimethylformamide as solvent and 1,5-diazabicyclo[5.4.0]undec-5-ene as base the *Z*-isomer was isolated as the main product in 42% yield.

X-*Ray Crystal Analysis of Compound* (10a).—*Crystal data.* $C_{19}H_{23}NO_7S$, orthorhombic, a = 15.231(2), b = 16.713(2), c = 8.023(1) Å, U = 2 042.3 Å^3, Z = 4, D_c = 1.33, D_o = 1.34(1) g cm^{-3}. Space group $P2_12_12_1$, μ(Mo-K_α) = 2.01 cm^{-1}. Intensities were collected on a Hilger and Watts Y290 diffractometer using a crystal *ca.* 0.17 × 0.23 × 0.54 mm in size and zirconium-filtered, Mo-K_α radiation.

A total of 1 112 reflections, within the limit θ ≤ 27°, were measured with intensities greater than 3.0 times their standard deviation (from counting statistics). Intensities were corrected for Lorentz and polarisation effects; no absorption corrections were deemed necessary (transmission factor range 1.035—1.049). The structure was solved by direct methods.[24] Refinement by full-matrix least-squares, minimizing $\Sigma\omega\Delta^2$, [$\Delta = |F_o| - |F_c|$, $\omega = \sigma(F_o)^{-2}$], was carried out using standard scattering factors [25] and the SHELX-78 program suite.[26]

The phenyl carbon and hydrogen atoms were constrained to benzene geometry; hydrogen atoms were constrained to one of three isotropic thermal parameters. All non-hydrogen

Table 4. Intramolecular bond distances and angles for compound (10a) [a] with e.s.d.s in parentheses

Atoms	Distance (Å)	Atoms	Distance (Å)
C(1)–N(2)	1.475(9)	C(7)–O(14)	1.433(8)
C(1)–C(8)	1.532(10)	C(8)–O(10)	1.443(8)
C(1)–C(5)	1.541(9)	O(10)–C(11)	1.348(9)
N(2)–O(3)	1.459(7)	C(11)–O(12)	1.178(9)
N(2)–C(9)	1.469(10)	C(11)–C(13)	1.494(13)
O(3)–C(4)	1.432(8)	O(14)–C(15)	1.345(8)
C(4)–C(5)	1.521(9)	C(15)–O(16)	1.201(8)
C(4)–S(22)	1.786(8)	C(15)–C(17)	1.476(12)
C(5)–C(6)	1.523(9)	O(18)–C(19)	1.355(9)
C(6)–C(7)	1.519(9)	C(19)–O(20)	1.197(9)
C(6)–O(18)	1.435(8)	C(19)–C(21)	1.469(13)
C(7)–C(8)	1.506(9)	S(22)–C(23)	1.764(5)

Atoms	Angle (°)	Atoms	Angle (°)
C(5)–C(1)–N(2)	107.2(6)	C(4)–C(5)–C(6)	115.5(6)
C(1)–N(2)–O(3)	104.7(5)	C(1)–N(2)–C(9)	111.3(7)
N(2)–O(3)–C(4)	106.7(4)	O(3)–N(2)–C(9)	107.9(6)
O(3)–C(4)–C(5)	103.4(5)	C(5)–C(4)–S(22)	114.5(5)
C(4)–C(5)–C(1)	101.9(6)	O(3)–C(4)–S(22)	110.7(5)
C(1)–C(5)–C(6)	102.6(6)	C(5)–C(6)–O(18)	113.8(5)
C(5)–C(6)–C(7)	101.6(5)	C(7)–C(6)–O(18)	111.9(5)
C(6)–C(7)–C(8)	100.8(5)	C(6)–C(7)–O(14)	110.2(5)
C(7)–C(8)–C(1)	103.9(5)	C(8)–C(7)–O(14)	115.0(6)
C(8)–C(1)–C(5)	106.1(5)	C(7)–C(8)–O(10)	112.9(5)
N(2)–C(1)–C(8)	113.2(6)	C(1)–C(8)–O(10)	109.3(6)

[a] Phenyl ring geometry constrained: C–C, 1.395 Å; C–H, 0.95 Å; H–C–C, C–C–C, 120°.

Table 5. Torsion angles for compound (10a). The torsion angle of the bonded atoms A–X–Y–B is the angle between the planes A–X–Y and X–Y–B and is positive when clockwise [a]

Atoms	Angle (°)
C(5)–C(1)–N(2)–O(3)	10.3
C(5)–C(1)–N(2)–C(9)	−106.1
C(8)–C(1)–N(2)–O(3)	−106.4
C(8)–C(1)–N(2)–C(9)	137.2
C(1)–N(2)–O(3)–C(4)	−32.6
C(9)–N(2)–O(3)–C(4)	86.2
N(2)–O(3)–C(4)–C(5)	41.5
N(2)–O(3)–C(4)–S(22)	164.5
O(3)–C(4)–C(5)–C(1)	−32.9
O(3)–C(4)–C(5)–C(6)	77.5
S(22)–C(4)–C(5)–C(1)	−153.3
S(22)–C(4)–C(5)–C(6)	−42.9
C(4)–C(5)–C(1)–N(2)	13.6
C(4)–C(5)–C(1)–C(8)	134.8
C(6)–C(5)–C(1)–N(2)	−106.3
C(6)–C(5)–C(1)–C(8)	14.9
C(4)–C(5)–C(6)–C(7)	−149.8
C(4)–C(5)–C(6)–O(18)	89.7
C(1)–C(5)–C(6)–C(7)	−39.8
C(1)–C(5)–C(6)–O(18)	−160.3
C(5)–C(6)–C(7)–C(8)	50.2
C(5)–C(6)–C(7)–O(14)	172.1
O(18)–C(6)–C(7)–C(8)	171.9
O(18)–C(6)–C(7)–O(14)	−66.1
C(6)–C(7)–C(8)–C(1)	−40.3
C(6)–C(7)–C(8)–O(10)	−158.6
O(14)–C(7)–C(8)–C(1)	−158.8
O(14)–C(7)–C(8)–O(10)	82.8
C(7)–C(8)–C(1)–C(5)	15.7
C(7)–C(8)–C(1)–N(2)	133.1
O(10)–C(8)–C(1)–C(5)	136.5
O(10)–C(8)–C(1)–N(2)	−106.1
C(1)–C(8)–O(10)–C(11)	149.3
C(7)–C(8)–O(10)–C(11)	−95.6
C(8)–O(10)–C(11)–O(12)	−1.4
C(8)–O(10)–C(11)–C(13)	179.2
C(8)–C(7)–O(14)–C(15)	−97.4
C(6)–C(7)–O(14)–C(15)	149.5
C(7)–O(14)–C(15)–O(16)	2.1
C(7)–O(14)–C(15)–C(17)	−178.6
C(7)–C(6)–O(18)–C(19)	109.4
C(5)–C(6)–O(18)–C(19)	−136.1
C(6)–O(18)–C(19)–O(20)	4.1
C(6)–O(18)–C(19)–C(21)	−176.3
C(5)–C(4)–S(22)–C(23)	−164.6
O(3)–C(4)–S(22)–C(23)	79.1
C(4)–S(22)–C(23)–C(24)	101.7
C(4)–S(22)–C(23)–C(28)	−79.5
C(25)–C(24)–C(23)–S(22)	178.8

[a] W. Klyne and V. Prelog, *Experientia*, 1960, **16**, 521.

atoms were refined with anisotropic thermal parameters to give converged *R*-values of 0.040 ($R_w = 0.045$). Observed and calculated structure factors and thermal parameters and weighted mean-plane data are listed in Supplementary Publication No. SUP 23631 (11 pages).*

Atomic co-ordinates are listed in Table 3. Bond lengths and angles, and torsion angles, are given in Tables 4 and 5 respectively; they are both self-consistent and similar to other observed values.[27,28] Only van der Waals intermolecular contacts are observed, with closest contact O(12) · · · H(4), 2.42 Å.

* For details of the Supplementary Publications Scheme, see Instructions for Authors (1983), *J. Chem. Soc., Perkin Trans. 1*, 1983, Issue 1.

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1 Part 1 is considered to be R. J. Ferrier, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1455.
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