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O,O-DIALKYLPHOSPHOROSELENOIC ACIDS AS FUNCTIONALISING REAGENTS OF MONOSACCHARIDES—III

A NOVEL SYNTHESIS OF UNSATURATED SUGARS BY DEOXYGENATION OF SUGAR EPOXIDES WITH DIALKYLPHOSPHOROSELENOIC ACIDS

WIESŁAWA KUDELSKA and MARIA MICHALSKA*
Department of Organic Chemistry, Faculty of Pharmacy, Medical Academy, 90-145 Lodz, Narutowicza 120A, Poland

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Abstract—Sugar epoxides are transformed in almost quantitative yields, under mild reaction conditions, into their corresponding unsaturated monosaccharides by reaction with O,O-dialkylphosphoroselenoic acids salts. A mechanism involving the formation of a penta-coordinate phosphorus intermediate is proposed.

The deoxygenation was performed with the following sugar epoxides: 5,6 - anhydro - 1,2 - O - isopropylidene - α - D - glucofuranose (1), 5,6 - anhydro - 1,2 - O - cyclohexylidene - α - D - glucofuranose (2), methyl - 2,3 - anhydro - 4,6 - O - benzylidene - α - D - allopyranoside (3), methyl - 2,3 - anhydro - 4,6 - O - benzylidene - α - D - mannopyranoside (4) and 3,4,6 - tri - O - acetyl - 1,2 - anhydro - α - D - glucopyranose (Brigl's anhydride) (5).

In our previous papers the reaction of monosaccharide epoxides with dialkylphosphorothioic and dithioic acids and with their alkyl ammonium salts were described.[1,2] These investigations led to elaboration of a new synthetic method of sugar episulphides and enabled the introduction of S-phosphoryl residues into different positions of the hexopyranosyl and hexofuranosyl ring of monosaccharides.

The present paper is concerned with the extension of our systematic studies on functionalisation of monosaccharides by organophosphorus reagents and describes the reaction of sugar epoxides with the alkylammonium salts of dialkylphosphoroselenoic acids. These salts were used by us previously[3] for introducing selenophosphoryl groups into the glycosylic position of hexo- and pentopyranoses by reaction with glycosyl halides. The application of the above reagents in the field of sugar epoxides provided a new method of deoxygenation of epoxides leading to unsaturated sugars.

The recognition of the biological role of unsaturated monosaccharides and of their nucleosidic derivatives, e.g. the participation in metabolic processes,[4] as well as the discovery of their antibiotic,[5] antitumour[6] and antibacterial[7] properties created a need for new effective ways of synthesis of this important class of sugar derivatives. In addition, unsaturated monosaccharides can serve as valuable starting materials in the synthesis of modified carbohydrates and as a source of a very important class of deoxysugars.

Among the known methods of synthesis of unsaturated sugars the most important role play various methods based on the deoxygenation of sugar epoxides.[8] Our work presents a new deoxygenation procedure of sugar anhydrides by using easily accessible alkylammonium salts of O,O-dialkylphosphoroselenoic acids. As models of sugar epoxides for our investigations, exocyclic and endocyclic anhydrides were used, e.g. 1,2 - O - isopropylidene - 5,6 - anhydro - α - D - glucofuranose (1), 1,2 - O - cyclohexylidene - 5,6 - anhydro - α - D - glucofuranose (2)[9] methyl - 2,3 - anhydro - 4,6 - O - benzylidene - α - D - allo-pyranoside (3), methyl - 2,3 - anhydro - 4,6 - O - benzylidene - α - D - mannopyranoside (4), and 3,4,6 - tri - O - acetyl - 1,2 - anhydro - α - D - glucopyranose (Brigl's anhydride; 5).

The alkylammonium O,O-dialkylphosphoroselenoates used by us as deoxygenating reagents were: O,O-diethylphosphoroselenoate (**6a**),[10] 5,5 - dimethyl - 1,3,2 - dioxophosphorinanylselenoate[11] (**6d**) and O,O-di-neopentylphosphoroselenoate (**6c**).[11]

RESULTS AND DISCUSSION

The reaction of 1,2 - O - isopropylidene - 5,6 - anhydro - α - D - glucofuranose **1** with the dicyclohexylammonium salt of the O,O-diethylphosphoroselenoic acid **6a** proceeds smoothly in boiling benzene or methylene chloride yielding 5,6 - dideoxy - 1,2 - O - isopropylidene - α - D - xylo - hex - 5 - enofuranose with quantitative yield. The reaction is completed in *ca* 2 hr when performed in benzene and in *ca* 5 hr, in methylene chloride (Scheme 1).

Other products of this reaction, namely ammonium salt of O,O-diethylphosphate and elemental Se, can be readily removed from the crude mixture. The former by extraction with water, the latter by filtration. It is of interest to note, that the reaction proceeds also at room temperature but the reaction time is under these conditions much longer, and takes *ca* 48 hr. The deoxygenation reaction was followed by ^{31}P NMR. The crude mixture was purified by column chromatography to give 80% yield of the analytically pure 5,6-dideoxy-5,6-eno sugar (**12**). The structure of the product obtained by deoxygenation was confirmed by comparison of ^{1}H NMR spectrum and physical data of **12** with the data given by Horton and Turner[6a] for 5,6 - dideoxy - 1,2 - O - isopropylidene - α - D - xylo - hex - 5 - enofuranose.

When the epoxide **1** was reacted with the O,O-dialkylphosphoroselenoic acids salts containing more bulky alkyl groups derived from the neopentyl glycol (**6b**) or

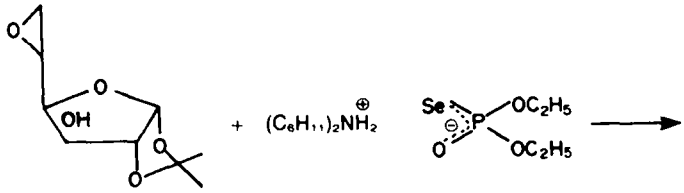
neopentyl alcohol (**6c**) the formation of a substantial amount of the side products **13**[12] was observed, thus diminishing the yield of the unsaturated sugar **12**. The amounts of the side-products **13** were dependent on the reaction conditions: at room temperature the proportions of the unsaturated sugar **12** and of the side-product **13** were 60:40, respectively. These proportions were inversed in favour of **13**, when the reaction was performed under oxygen. This is not surprising, taking under consideration the diselenide structure of the side-products **13** (Scheme 4). When the reaction was performed in boiling benzene, quantitative yields of the 5,6-eno-sugar **12** were obtained and the reaction was completed in 2–3 hr. Under such conditions the formation of **13** is suppressed. 1,2 - O - cyclohexylidene - 5,6 - anhydro - α - D - glucofuranose (**2**) reacted with the salt **6b** at room temperature to give similar proportions of the unsaturated sugar **17** (analog of **12**) and diselenide **18** (analog of **13b**), e.g. 60:40, as though the epoxide **1** reacted with the salt **6b**.

The reaction of the endocyclic methyl - 2,3 - anhydro - 4,6 - O - benzylidene - α - D - allo pyranoside **3** with the salt (**6b**) takes essentially the same course as with the 5,6-anhydro sugar **1**, giving almost quantitative yields of the corresponding 2,3-unsaturated sugar but, for steric reasons, requires more energetic conditions. In this case prolonged refluxing in benzene solution is necessary.

After 40 hr, 90% of the starting 2,3-allo-epoxide **3** reacted and the yield of the isolated methyl - 4,6 - O - benzylidene - 2,3 - dideoxy - α - D - erythro - hex - 2 - enopyranoside **14** was 85%. The mixture contained a small amount of the diselenide, which was not isolated but whose presence was clearly indicated by ^{31}P NMR spectroscopy. The identity of the isolated olefinic sugar with methyl - 4,6 - O - benzylidene - 2,3 - dideoxy - α - D - erythro - hex - 2 - eno - pyranoside **14** was confirmed on the basis of ^{1}H NMR parameters,[13] the value of the m.p. and of $[\alpha]_D$.[14]

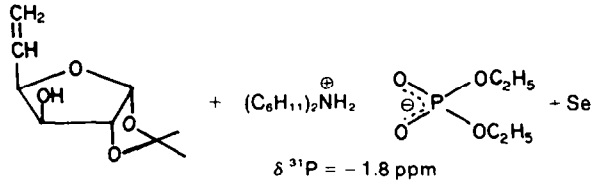
Methyl - 2,3 - anhydro - 4,6 - O - benzylidene - α - D - mannopyranoside **4** reacts with the salt (**6b**) much slower than its configurational "allo" isomer **3**. After 40 hr of refluxing in benzene solution only 40% of the starting salt (**6b**) reacted with the epoxide. The mixture contained the unsaturated sugar in addition to the side-product of the diselenide **13** structure and an unidentified P-containing product ($\delta^{31} = -21.3$ ppm). The ratio of the unsaturated sugar to the diselenide was 2:1.

The reaction of Brigl's anhydride (**5**) with the alkylammonium salt of O,O-diethylphosphoroselenoic acid **6a** in boiling benzene, after 2 hr under argon gives as the



$\delta^{31}P = +48.2$ ppm

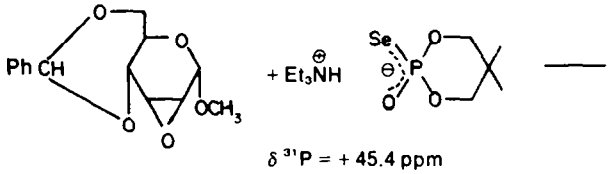
1 **6a**



$\delta^{31}P = -1.8$ ppm

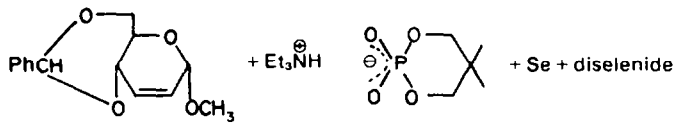
12 **10a**

Scheme 1.



$\delta^{31}P = +45.4$ ppm

3 **6b**



$\delta^{31}P = -3.9$ ppm $\delta^{31}P = -8.8$ ppm

14 **10b** **19**

Scheme 2.

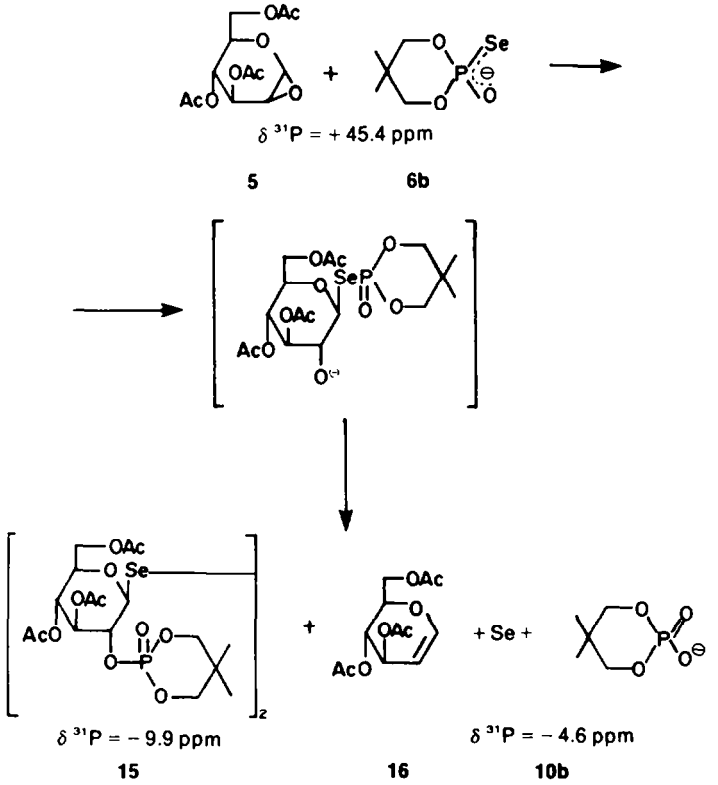
only product 3,4,6-tri-O-acetyl-D-glucal **16** (Table 1). When 1,2-anhydrohexopyranoside **5** was allowed to react with the salt **6b**, at room temperature for 6 days, the 1,2-unsaturated sugar **16**, together with the diselenide **15** (Scheme 3) were obtained. In Table 1 the reaction conditions and the yields of the 1,2-alkene **16** and of the diselenide **15** are given.

The usual work-up procedure resulted in isolation of D-glucal which physical properties were in agreement with those of an authentic sample of 3,4,6-tri-O-acetyl-D-glucal.[15] The structure of the diselenide **15** was established on the basis of elemental analysis, ^{1}H NMR, ^{31}P NMR, IR and $[\alpha]_D$. The low $[\alpha]_D$ value and the pattern of the ^{1}H NMR spectrum indicate the β-configuration of the glycosyl diselenide **15** (Scheme 3). The deoxygenation of epoxides by O,O-dialkylphosphoroselenoates follows substantially the same mechanistic scheme as the epoxide–episulphide transformation by O,O-dialkylphosphorothioates and dithioates. The formation of the unsaturated sugar **12** is a consequence of the instability of the episelenide **11** formed in the course of this reaction. The correctness of the proposed mechanism was confirmed by isolation of the diselenide **13** which was formed under oxidative conditions from **9**. The mechanism of this reaction is proposed in Scheme 4.

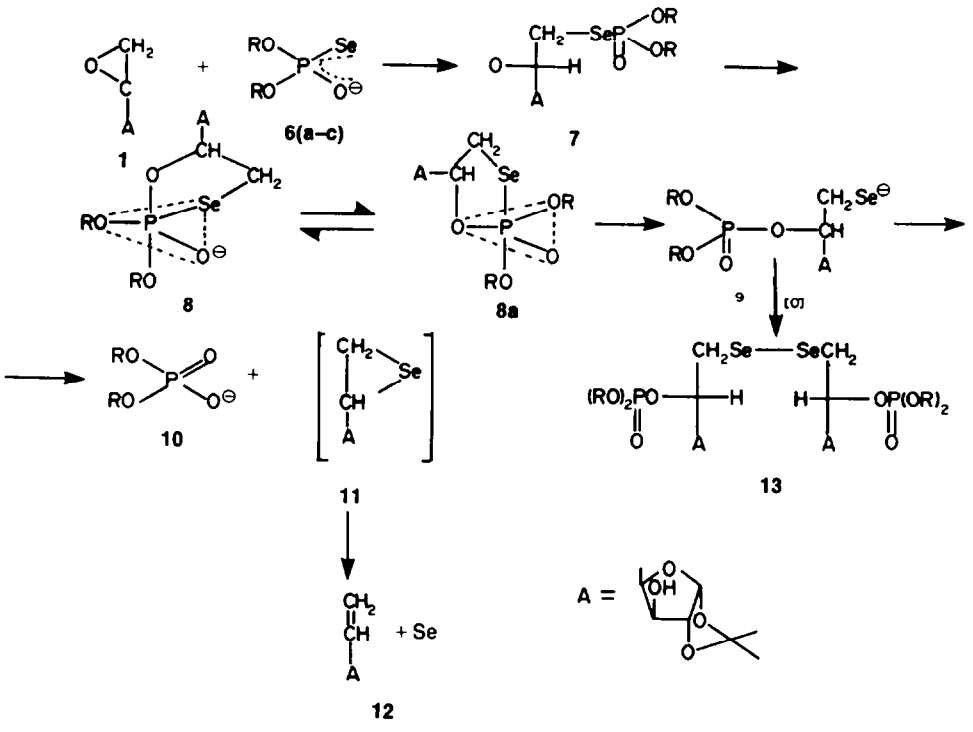
Table 1. The reaction of 1,2-anhydro-3,4,6-tri-O-acetyl-α-D-glucopyranose **5** with alkylammonium salts **6a** and **6b**

O,O-dialkyl-phosphoro-selenoic acids salts	Reaction conditions	3',4,6-tri-O-acetyl-D-glucal (16) Yield (%)	Diselenide (15) Yield (%) [x]
6a	Benzen, 24°C 6 days	50	50
6a	Benzen, 80°C 2 hrs, argon	100	-
6b	Benzen, 24°C 6 days	40	60

[x] Yields were determined by ^{31}P NMR spectroscopy. The yields of the unsaturated sugar (16) were determined by integration of the ^{31}P signal corresponding to the phosphate anion formed.



Scheme 3.



Scheme 4.

The first step is the nucleophilic attack of O,O-dialkylphosphoroselenoate on the 3-membered anhydro-ring with formation of the transient adduct **7** which then rearranges into the penta-coordinate intermediate **8**. On turn **8** via permutational isomerisation affords **8a** which then decomposes into **9**. The phosphate **9** undergoes internal nucleophilic displacement at the C-5 atom leading to the episelenide and the phosphate anion **10**. The episelenide **11** decomposes spontaneously† with the extrusion of elemental Se and formation of the unsaturated sugar **12**. In the presence of oxygen the phosphate **9** is oxidised to the diselenide **13**.

Summarising the results obtained in the present investigations we conclude the following: The deoxy genation reaction of sugar epoxides by O,O-dialkylphosphoroselenoic acids alkylammonium salts presents a new, effective way of the synthesis of unsaturated sugars. Highest yields of the unsaturated sugar were obtained when the reaction was performed by refluxing of the reactants in benzene or at room temperature in oxygen-free atmosphere. Although pure phosphoroselenoic acids salts are easily accessible we have demonstrated that this reagent can be prepared *in situ* from O,O-dialkylphosphites and elemental Se in the presence of a secondary or tertiary amine. Monitoring of the reaction course by ^{31}P NMR enables precise adjusting of the time of the reaction in each particular case judging from the disappearance of the ^{31}P NMR signal ascribed to the starting selenoate and appearance of that ascribed to the phosphoric acid anion formed. Deposition of elemental Se in the form of a black powder visualises the progress of the deoxygenation reaction. O,O-Diethylphosphoroselenoate is the reagent of choice for the transformation of sugar epoxides into unsaturated sugars excluding the cases when prolonged heating is necessary, which causes decomposition of the organophosphorus reagent. Deoxygenation reaction can be performed with unprotected OH groups of the sugar moiety.[16] Under the conditions applied we did not observe any polimerisation or degradation process of the olefinic products. We presume that the new deoxygenation procedure described here will find general synthetic application.

†Episelenides are known to be formed as intermediate products in deoxygenation reactions described by other authors.[17,18] The episelenides could not be isolated but their presence was indicated by spectroscopic methods.

EXPERIMENTAL

M.ps (Kofler) are uncorrected. ^1H NMR spectra were recorded for solns in $CDCl_3$ with a Varian 60 MHz instrument. ^{31}P NMR spectra were recorded for solns in $CHCl_3$ (external 85% H_3PO_4) with a Jeol 60 MHz FT instrument. The chemical shifts are reported as δ values (± 1 ppm). IR spectra were recorded for KBr discs with a Unicam SP-200G spectrometer. Optical rotations were determined on solns in $CHCl_3$ with a Polamat A polarimeter. Analyses were performed at the Microanalytical Laboratories of the Centre of Molecular and Macromolecular Studies (Lodz) and the Institute of Organic Chemistry of the Polish Academy of Sciences (Warsaw). The course of the reactions was followed by ^{31}P NMR. The yields of the alkenes formed were evaluated from the intensity of the signal corresponding to the "deselenated" acid salt. The signs of the ^{31}P chemical shifts are given according to the new convention.

Reaction of **1** *with* **6a**. 5,6 - *Dideoxy* - 1,2 - O - *isopropylidene* - D - *xylo* - *hex* - 5 - *enofuranose* (**12**)

Method A. A soln of **1** (1.5 g, 7.42 mmol) and **6a** (2.95 g, 7.42 mmol) in benzene (30 ml) was stirred at 40° for 12 hr, and then 36 hr at 25°. The ppt elemental Se was filtered off, the filtrate evaporated *in vacuo*, and the yellow syrup placed on a column of Kieselgel, 200–400 mesh (0.2–0.5 mm) and eluated with a 3:2 mixture of light petroleum (60–80°) and ethyl ether. Product **12** was obtained (1.1 g, 79%), m.p. 63–64°. δ ^1H NMR: 5.95 (d, H-1), 5.9 – 5.27 (m, H-5, 6, 6'), 4.72 (q, H-4), 4.56 (d, H-2), 4.09 (d, H-3), 2.73 (s, OH), 1.5, 1.33 (2 × s, CMe_2). (Found: C, 58.17; H, 7.57.

$C_9H_{14}O_4$ requires: C, 58.05; H, 7.57). The physical data and spectra of 12 were identical to 5,6 - dideoxy - 1,2 - O - isopropylidene - α - D - xylo - hex - 5 - enofuranose prepared by Horton and Turner.[6a]

Method B. A soln of 1 (0.2 g, 0.99 mmol) and **6a** (0.39 g, 0.99 mmol) in benzene (5 ml) was refluxed for 2 hr under argon. ^{31}P NMR spectrum showed only 1 signal: −2.0 (**10a**).

Method C. A mixture of O,O-diethyl phosphite (0.138 g, 1 mmol), Se black (0.079 g, 1 mmol) and Et_3N (0.101 g, 1 mmol) was stirred for 6 hr at ambient temperature and left thereat for 18 hr. The anhydro sugar 1 (0.2 g, 1 mmol) was then added. Through the reaction flask argon was passed for 4 hr and the mixture was left at room temperature for additional 20 hr under argon. ^{31}P NMR spectrum taken after 24 hr showed 2 signals: +51 (**6a**) and −1.9 (**10a**) integrated as 1:2.

Reaction of 1 *with* **6b**. 6,6' - *Diselenobis* [6 - *deoxy* - 5 - (5",5" - *dimethyl* - 2" - *oxo* - 1",3",2" - *dioxaphosphorinanyloxo*) - 1,2 - O - *isopropylidene* - α - D - *glucofuranose*] (**13b**) *and* 12

Procedure A. A soln of 1 (1.3 g, 6.43 mmol) and **6b** (2.3 g, 6.43 mmol) in benzene (40 ml) was stirred at 40° for 14 hr, then 34 hr at 25°. ^{31}P NMR spectrum showed 2 signals: −3.8 and −7.4 (6:4). The mixture was washed with water dried ($MgSO_4$) and concentrated *in vacuo*. Addition of a few ml of ethyl ether to the syrupy residue gave **13b** as colourless needles, m.p. 147–149° (0.6 g, 19.8%). δ ^{31}P NMR: −7.4. Recrystallisation from $CHCl_3$–ethyl ether gave analytically pure **13b**, m.p. 151–152°; $[\alpha]_D^{25}$: +100.7° (C = 0.46). IR: $\nu_{P=O}$ = 1260 cm^{-1}, ν_{OH} = 3400 cm^{-1}; δ ^1H NMR: 5.9 (d, H-1), 4.52 (d, H-2), 0.9, 1.35 (2s, 5,5-di-Me), 1.3, 1.5 (2s, CMe_2). (Found: C, 38.77; H, 5.81; P, 7.18). $C_{28}H_{48}O_{16}P_2Se_2$ requires: C, 39.07; H, 5.62; P, 7.18). The filtrate after separation of **13b** was concentrated, the syrupy residue was subjected to column chromatography (as above) and 0.6 g of 12 isolated (50.4%) m.p. 64–65°.

Procedure B. A soln of 1 (0.15 g, 0.74 mmol) and **6b** (0.24 g, 0.72 mmol) in benzene (15 ml) was heated under reflux for 3 hr. ^{31}P NMR spectrum showed 1 signal: −3.8 (**10b**).

Procedure C. Through the soln of 1 (0.15 g, 0.74 mmol) and **6b** (0.24 g, 0.72 mmol) in CH_2Cl_2 (5 ml) O_2 was passed for 3 hr and the mixture kept at room temperature for additional 3 days under O_2. ^{31}P NMR spectrum showed 2 signals: −3.8 (**10a**) and −7.3 (**13b**) integrated as 4:6.

The reaction of 1 *with* **6c**. 6,6'-*Diselenobis* [6 - *deoxy* - 5 - O - (O,O - *dineopentylphosphinyl*) - 1,2 - O - *isopropylidene* - α - D - *gluco* - *furanose*] (**13c**)

Procedure A. A soln of 1 (0.5 g, 2.47 mmol) and **6c** (1 g, 2.48 mmol) in benzene was stirred at room temperature for 48 hr. ^{31}P NMR shows 2 signals: −0.4 and −0.8 (4:6). The ppt of elemental Se was filtered off, the filtrate evaporated *in vacuo*. Addition of a few ml of light pertroleum (b.p. 60–80°) to the yellow syrupy residue gave 13c as colourless needles, m.p. 130–133° (0.4 g, 32%). On recrystallisation from light-petroleum-benzene m.p. 132–133°; $[\alpha]_D^{21}$: +91.6° (*c*, 0.24); $\delta^{31}P$ NMR: −0.4. IR: $\nu_{P=O}$ = 1250 cm^{-1} and ν_{OH} = 3300 cm^{-1}; δ ^1H NMR: 5.9 (d, H-1), 4.5 (d, H-2), 1.0 (s, 6 × CH_3), 1.3 and 1.5 (2 s, CMe_2). (Found: C, 45.67; H, 7.36, $C_{38}H_{72}O_{16}P_2Se_2$ requires: C, 45.43; H, 7.22).

Procedure B. A soln of 1 (0.15 g, 0.74 mmol) and **6c** (0.3 g, 0.74 mmol) in benzene (5 ml) was heated under reflux for 2 hr. ^{31}P NMR spectrum showed 1 signal: −1.2 (**10c**).

5,6 - *Anhydro* - 1,2 - O - *cyclohexylidene* - α - D - *glucofuranose* (2)

To the cooled (−10°) soln of 6 - O - tosyl - 1,2 - O - cyclohexylidene - α - D - glucofuranose (9.5 g, 2.3 mmol) in 25 ml of anhyd CH_2Cl_2, 0.54 g of Na dissolved in 11 ml of abs MeOH were added. The reactants were kept at −10° for 15 min and then at ambient temperature for 30 min. The thick, gelatineous mass was diluted with water (50 ml) and extracted with CH_2Cl_2 (3 × 50 ml). The extracts were dried ($MgSO_4$) and concentrated *in vacuo*. Addition of petroleum ether and light petroleum to the oily residue gave colourless needles of 2 (3 g, 54%) m.p. 90–90.5°. δ ^1H NMR: 5.95 (d, H-1), 4.5 (d, H-2), 4.3 (d, H-3), 3.85 (q, H-4), 2.72–3.05 (m, H-6,6'), 1.55–1.65 (m, cyclohexyl). (Found: C, 59.55; H, 7.52. $C_{12}H_{18}O_5$ requires: C, 59.50; H, 7.43).

The reaction of 2 *with* **6b**. 6,6' - *Diselenobis*[6 - *deoxy* - 5 - (5",5" - *dimethyl* - 2" - *oxo* - 1",3",2" - *dioxaphosphorinanyloxo*) - 1,2 - O - *cyclohexylidene* - α - D- *-glucofuranose*] (**18**)

A soln of 2 (1 g, 4 mmol) and **6b** (1.4 g, 4 mmol) in benzene (30 ml) was stirred at room temperature for 48 hr. The ppt of elemental Se was filtered off, the filtrate washed with water, dried ($MgSO_4$) and concentrated *in vacuo*. Addition of few mls of ethyl ether to the yellow, semi-crystalline residue gave **18** as colourless needles (0.4 g, 21%) m.p. 155–156°; $[\alpha]_D^{25}$: +93; δ ^{31}P NMR: −7.4; δ ^1H NMR: 5.9 (d, H-1), 0.9 and 1.35 (2 s, 5,5-dimethyl), 1.5–1.7 (m, cyclohexyl). (Found: C, 43.32; H, 6.08. $C_{34}H_{56}O_{16}P_2Se_2$ requires: C, 43.40; H, 6.00).

The reaction of 3 *with* **6b**

Methyl - 4,6 - O - *benzylidene* - 2,3 - *dideoxy* - α - D - *erythro* - *hex* - 2 - *enopyranoside* (**14**). A soln of 3 (1 g, 3.78 mmol) and **6b** (1.25 g, 3.78 mmol) in benzene was refluxed for 31 hr. The mixture was washed with water, dried ($MgSO_4$) and the solvent removed *in vacuo*. On addition of a few ml of ethyl ether a colourless crystalline ppt (0.1 g, m.p. 191–197°) was filtered off. The product was identified as unreacted 3. On evaporation of the filtrate 0.8 g of colourless crystals were obtained which on recrystallisation from hexane gave 14, m.p. 118–119° (0.72 g, 85%); $[\alpha]_D^{29.6}$: +127° (*c*, 1.04). δ ^1H NMR: 4.88 (H-1), 5.75 (H-2), 6.14 (H-3), 7.14 (H-4), 3.85 (H-5), 3.72 (H-6a), 4.3 (6-6e), 5.55 (methin proton), 3.49 (O-Me), 7.3–7.49 (Ph). The physical data and spectra of **14** were identical to those of methyl - 4,6 - O - benzylidene - 2,3 - dideoxy - α - D - erythro - hex - 2 - enopyranoside described by Iley and Fraser-Reid.[13]

Reaction of 4 *with* **6b**

A soln of 4 (0.5 g, 1.9 mmol) and **6b** (0.6 g, 1.8 mmol) in benzene (35 ml) was refluxed for 40 hr. The solvent was evaporated *in vacuo* and the syrupy residue was subjected to ^{31}P NMR. The ^{31}P NMR spectrum showed signals: 45.4 (**6b**), −3.2 (**10b**), −9.9, −21.3, integrated as 10:2:1:2, respectively.

Reaction of 5 *with* **6a**

Procedure A. A soln of 5 (0.5 g, 1.73 mmol) and **6a** (0.6 g, 1.5 mmol) in benzene (15 ml) was refluxed for 2 hr under argon. ^{31}P NMR spectrum showed 1 signal: −2.8 (**10a**).

Procedure B. A soln of 5 (0.9 g, 3.12 mmol) and **6a** (1.24 g, 3.11 mmol) in benzene (15 ml) was kept at room temperature for 6 days. ^{31}P NMR spectrum showed 2 signals: −2.0 (**15a**) and −2.8 (**10a**).

Reaction of 5 *with* **6b**. 1,1' - *Diselenobis*[1 - *deoxy* - 2 - (5",5" - *dimethyl* - 2" - *oxo* - 1",3",2" - *dioxaphosphorinanyloxo*) - 3,4,6 - *tri* - O - *acetyl* - β - D - *glucopyranose*] (**15b**) *and* 3,4,6 - *tri* - O - *acetyl* - D - *glucal* (**16**)

Procedure A. A soln of 5 (1 g, 3.47 mmol) and **6b** (1.14 g, 3.45 mmol) in benzene (25 ml) was stirred at room temperature for 6 days. ^{31}P NMR showed 2 signals: −3.9 (**10b**) and −9.9 (**15b**). The mixture was washed with water, dried ($MgSO_4$) and concentrated *in vacuo*. Addition of a few ml of ethyl ether to the syrupy residue gave **15b**, as colourless needles, m.p. 164–167° (0.6 g, 33.5%). Recrystallisation from $CHCl_3$–ethyl ether gave pure **15b** m.p. 173–175°. $[\alpha]_D^{29}$: −1.61 (*c*, 1.51); δ ^{31}P NMR: −9.9; δ ^1H NMR: 2.05, 2.1, 2.12 (3 × Ac, 3 s), 0.9 and 1.25 (5,5-di-Me, 2 s): ν_{max}^{KBr} 1250 (P=O) and 1750 (Ac). (Found: C, 39.05; H, 5.26. $C_{34}H_{52}O_{22}P_2Se_2$ requires: C, 39.54; H, 5.07). The filtrate after separation of the diselenide **15b** was concentrated, the syrupy residue was triturated with ethyl ether and light petroleum ether. Colorless, crystalline product **16** was obtained, m.p. 51–52° (0.3 g, 31.9%). The ^1H NMR and IR spectra of **16** were identical to those of 3,4,6-tri-O-acetyl-D-glucal.

Dicyclohexylammonium salt of O,O-*diethylphosphoroselenoic and* (**6a**)

Into the cooled (0–5°) mixture of O,O-diethylphosphite (6.9 g, 0.05 mole) in benzene (40 ml) elemental Se (4 g, 0.05 mole) was

added portionwise with efficient stirring. Stirring was continued for 4 hr at 0–5° and then the mixture was kept at room temperature for 16 hr. The unreacted Se was filtered off, and the residue was evaporated to give 12 g (60%) of colourless, thick crystals of **6a** m.p. 157–158°; δ ^{31}P NMR: 48.2 ppm.

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REFERENCES

[1]W. Kudelska and M. Michalska, *Carbohydr. Res.* **83**, 43–49 (1980).
[2]W. Kudelska and M. Michalska, *Ibid.* **90**, 1–6 (1981).
[3]M. Michalska, J. Michalski and I. Orlich-Krezel, *Polish J. Chem.* **53**, 253 (1979).
[4]T. Adachi, Y. Yamada and I. Inioue, *Carbohydr. Res.* **73**, 113 (1979).
[5]N. Zylber, J. Zylber and A. Gaudemer, *J. Chem. Soc., Chem. Comm.* 1084 (1978); Refs. 1 and 2.
[6]L. M. Lerner, *Carbohydr. Res.* **44**, 13 (1975); Ref. 11; [a]D. Horton and W. N. Turner, *Ibid.* **1**, 444 (1966).
[7]J. R. McCarthy, Jr., R. K. Robins and M. J. Robins, *J. Am. Chem. Soc.* **90**, 4993 (1968); [a]L. M. Lerner, *Carbohydr. Res.* **44**, 13 (1975).
[8a]H. Suzuki, T. Fuchita, A. Iwasa and T. Mishina, *Synthesis* 905 (1978) and Refs. therein; [b]D. L. J. Clive and S. M. Menchen, *J. Chem. Soc., Chem. Commun.* 658 (1977); [c]P. I. Garegg, D. Papadimas and B. Samuelsson, *Carbohydr. Res.* **80**, 354 (1980); [d]H. Paulsen, F. R. Heiker and J. Feldmann, *Synthesis* 636 (1980); [e]P. E. Sonnet, *Tetrahedron* 557 (1980).
[9]See Experimental.
[10]See Experimental.
[11]W. Stec and B. Uznanski, *Synthetic Comm.* 473 (1979).
[12]P. Lipka and M. Michalska, unpublished results.
[13]D. E. Iley and B. Fraser-Reid, *Can. J. Chem.* **57**, 653 (1957).
[14]J. E. Christensen and L. Goodmann, *J. Am. Chem. Soc.* **83**, 3827 (1961).
[15]W. Roth and W. Pigman, *Methods in Carbohydr. Chem.* **2**, 405 (1963).
[16]W. Kudelska and M. Michalska, unpublished results.
[17]D. S. J. Clive and C. V. Denyer, *J. Chem. Soc., Chem. Comm.* 253 (1973) and Ref. 7.
[18]T. H. Chan and J. R. Finkenbine, *Tetrahedron Letters* 2091 (1974) and Refs. therein.