Halogenated Enolates. Synthesis of 2-Deoxypentose Derivatives from D-Glyceraldehyde

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The reaction of alkyl dihalogenoacetate magnesium enolates (1) with 2,3-*O*-isopropylidene-D-glyceraldehyde (3) to give the hydroxy-esters (4) and (5) has been studied. We found that the production of the *erythro*- isomer (4) is favoured, in agreement with theoretical models. An *erythro* : *threo* ratio of 7 : 3 was obtained with the enolate (1b). This condensation may be an alternative to the lithioacetate condensation method after removal of halogen by Raney nickel- or tributyltin hydride-reduction. The structures of the different products were established after lactonisation which proceeded in good yield. This method constitutes a new entry to 2-deoxy-2-halogeno- and 2-deoxypentono-1,4-lactones.

THE synthesis of deoxypentoses often proceeds by chemical modification of the parent sugar or degradation of a higher one. The synthesis of 2-deoxy-D-*erythro*-pentose was based on these concepts.[1-3] Elegant approaches using chain elongation of a D-erythrose derivative have been also reported.[4,5] Branched and deoxy-sugars have been successfully synthesized from D-glyceraldehyde.[6] We report now our results on the chain extension of D-glyceraldehyde by aldolisation with αα-dichloroacetate magnesium enolates. In previous reports [7,8] we had indicated that Grignard reagents of type (1) react with carbonyl groups to yield the corresponding αα-dihalogeno-β-hydroxy-esters. In the case of a conformationally blocked cyclic ketone, the reaction has proved to be completely stereospecific.[8] We have extended this reaction to a chiral aldehyde in order to examine the degree of asymmetric induction. For this purpose we chose 2,3-*O*-isopropylidene-D-glyceraldehyde,[9] a high degree of stereoselectivity in the Grignard condensation with aldehydes derived from carbohydrates having been widely demonstrated.[10]

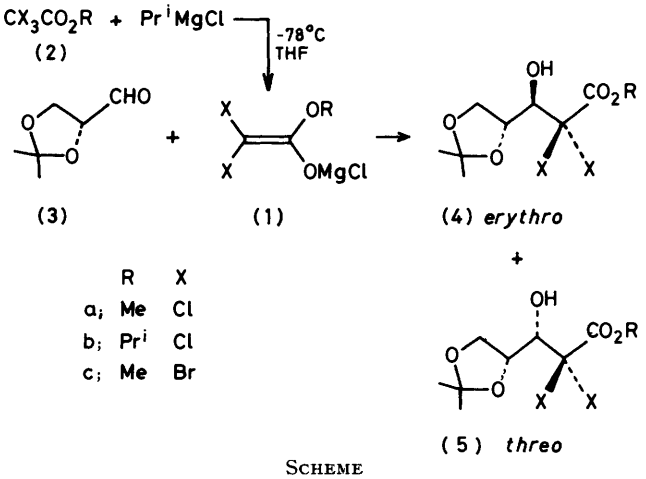
RESULTS

Aldolisation Reactions.—The principle of the reaction is summarized in the Scheme. The magnesium enolates (1a—c) were prepared in dry tetrahydrofuran (THF) by halogen–metal exchange of isopropylmagnesium chloride with the appropriate trihalogenoacetate (2) at −78 °C within 1 h. To this mixture was added a solution of the aldehyde (3) [10] in THF and the mixture kept at −78 °C for 20 min. The temperature was then allowed to reach −20 °C and the mixture was hydrolysed with acid buffer and extracted (ethyl acetate). The corresponding alcohols (4) and (5) were isolated by chromatography over silica gel in 65% total yield.

When enolate (1a) reacted with the aldehyde (3) the alcohols (4a) and (5a) were obtained and could be easily separated by chromatography. It was then possible to determine the diastereoisomeric ratio (3a) : (5a) [*erythro*: *threo*] as 7 : 3.† We confirmed this ratio by 250 MHz ^{1}H n.m.r. spectroscopy: integration of the methyl ester signals, which were well separated, gave an identical ratio.

† We attributed the *erythro*-configuration to the major isomer (4) on the basis of chemical and spectral data: see *Structural Proof*, below. Compound (5) therefore had the *threo*-configuration.

On the other hand when enolate (1b) was used, we obtained the alcohols (4b) and (5b) which were indistinguishable by t.l.c.; fortunately it was possible to crystallize compound (4b) from the crude mixture. The mother liquors contained a mixture of both epimers (4b) and (5b), the latter being the most abundant (*ca.* 95%). In this case we used ^{1}H n.m.r. spectroscopy to determine the ratio *erythro* : *threo* by integration of the hydroxy-group signals which were two well separated doublets. An *erythro* : *threo* ratio of 7 : 3 was obtained, as in the preceding experiments.

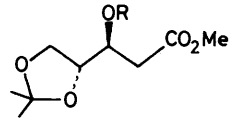


SCHEME

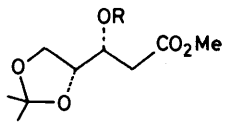
Furthermore, the reaction of the aldehyde (3) with the dibromo-magnesium enolate (1c) was studied. Although the diastereoisomeric ratio (*erythro* : *threo*) determined on the crude reaction mixture by ^{1}H n.m.r. spectroscopy was 85 : 15, we isolated the products (4c) and (5c) in only 15% yield. We did not investigate this reaction further.

It was clear that the nature of the groups R and X in reagents (1a—c) had no major influence on the diastereoisomeric ratio of the product alcohols (4) and (5). A similar aldolisation reaction was reported during the course of our studies.[11] Methyl lithioacetate was treated with the aldehyde (3) to give a mixture of the isomeric esters (6a) and (7a) (85 : 15 based on ^{13}C n.m.r. experiments). The degree of stereoselectivity appeared to be higher than in our present study. In our hands this reaction gave a 55% yield of pure materials, but compounds (6a) and (7a) could be only partially separated by column chromatography. Although the presence of chlorine atoms in reagents (1) did

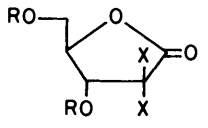
not improve the stereoselectivity, the separation of the diastereoisomeric alcohols (4) and (5) was very easy by chromatography and/or direct crystallisation.



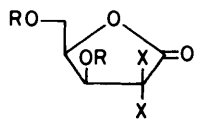
(6) a; R = H
b; R = Ac



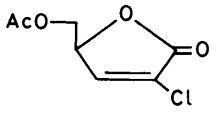
(7) a; R = H
b; R = Ac



	R	X
(8)	a; H	Cl
	b; Ac	Cl
(10)	a; H	H
	b; Ac	H



	R	X
(9)	a; H	Cl
	b; Ac	Cl
(11)	a; H	H
	b; Ac	H



(12)

We turned our attention to the removal of the halogen atoms and the lactonisation reaction. We found that compounds (4) and (5) reacted with tributyltin hydride or with Raney nickel to give the corresponding dehalogenated products (6) and (7) in good yield. On the other hand, compounds (4) and (5) were lactonized when treated with toluene-*p*-sulphonic acid in wet benzene under reflux. The lactones (8a) and (9a) were isolated in virtually quantitative yield. Subsequent reductive dechlorination with Raney nickel afforded the lactones (10a) and (11a), respectively, in 90% yield.

We investigated the reaction of compounds (8a) and (9a) with Zn or triphenylphosphine. Elimination took place giving the unsaturated lactone (12) in moderate yield. A good yield was obtained using tris(dimethylamino)phosphine.

Structural Proof.—Assuming that lactonisation and subsequent removal of halogen did not affect the stereochemistry of the product, we determined the structures of the derived lactones. In fact, starting from a single isomer [(4) or (5)], only one isomer was obtained in each reaction. Their i.r. spectra indicated that the products [(8a) and (9a)] were γ-lactones (ν_{CO} 1 790 cm^{-1}). The ring size was confirmed by comparing the spectra of the lactones (8a) and (9a) with those of (8b) and (9b), respectively. Acetylation strongly affected the chemical shifts of the 3- and 5-hydrogens. In a six-membered lactone only the 3- and 4-H signals will be shifted because of the presence of acetoxy-groups on C-3 and C-4.

The determination of the $J_{3,4}$ value in the lactones (10) and (11) allowed the assignment of the stereochemistry at C-3 by comparison with literature data.[12] A small value favoured the *erythro*-configuration in which the 3- and 4-H atoms are *trans*, whereas a larger $J_{3,4}$ value favoured a *cis* disposition of 3- and 4-H. We observed values of $J_{3,4}$ = 1.75 Hz for compound (10b) and $J_{3,4}$ = 4.75 Hz for (11b), supporting the *erythro*-configuration for compound (4) and the *threo* configuration for compound (5).

An authentic sample of compound (10b), prepared from 2-deoxy-D-*erythro*-pentose,[13] was identical with our product in every respect.

Conclusions.—We have shown that the addition of *gem*-dihalogeno-magnesium enolates to 2,3-*O*-isopropylidene-D-glyceraldehyde occurs in good yield with some stereoselectivity. The presence of chlorine atoms greatly facilitated the separation of diastereoisomers by chromatography and/or crystallisation. We took advantage of these facts by synthesizing chiral lactones in 50% overall yield from D-glyceraldehyde acetonide.

EXPERIMENTAL

High-field n.m.r. spectra were obtained using a Cameca 250 spectrometer operating at 250 MHz in the continuous-wave mode (^1H), and at 62.86 MHz in the Fourier-transform mode with a pulse width of 4 μS(^{13}C). Unless otherwise stated, the spectra were recorded in $CDCl_3$ with chemical shifts (δ) downfield from $SiMe_4$ as internal standard. I.r. spectra were recorded on a Perkin-Elmer 580 spectrometer. Optical measurements were performed on a Perkin-Elmer 141 automatic polarimeter. T.l.c. was performed on pre-coated Merck plates, with visualisation by H_2SO_4 (50% in MeOH), NH_2OH–$FeCl_3$,[14] or Rhodamine–Na_2CO_3 sprays.* The following developing systems were used (v/v) : ethyl acetate–hexane, 1 : 4 (solvent A); 2 : 3 (solvent B); 1 : 1 (solvent C); 3 : 2 (solvent D). M.p.s were measured on a Kofler block. Solvent evaporation was carried out under reduced pressure below 40 °C. 2,3-*O*-Isopropylidene-D-glyceraldehyde (3) was prepared according to the method of Baer and Fischer.[9] All reactions were conducted under dry argon.

Typical Aldolisation Procedure.—To a 1M solution of isopropylmagnesium chloride in THF (18 ml) cooled to −78 °C was added dropwise the desired trihalogenoacetate (2) (1.1 equiv., 19.8 mmol) in THF. After 1 h at −78 °C a solution of the aldehyde (3) (1.3 g) in THF (10 ml) was added dropwise during 1 h. After 20 min at −78 °C the cooling bath was removed. The mixture was hydrolysed with acetate buffer when the temperature had reached −20 °C. The products were extracted with ethyl acetate (3 × 100 ml) and the extracts were washed with saturated aqueous sodium hydrogen carbonate and then with water. The organic layer was dried (Na_2SO_4), filtered, and concentrated to dryness. The following compounds were prepared after chromatography on silica gel (A as eluant). *Methyl* (3R, 4R)-2,2-*Dichloro*-4,5-O-*isopropylidene*-3,4,5-*trihydroxy-pentanoate* (4a), (1.2 g, 44%), by recrystallisation from hexane, m.p. 100 °C; $[\alpha]_D^{25}$ +3.6° (*c*, 1.39 in ethanol); R_f 0.21 (solvent B); $\nu_{max.}$ (KBr) 3 380 and 1 765 cm^{-1}; δ 1.33 and 1.38 (total 6 H, 2 × s, CMe_2), 3.6 (1 H, d, OH), 3.88 (3 H, s, OMe), 4.12 (1 H, q, $J_{5,5'}$ 9, $J_{4,5'}$ 5.5 Hz, 5′-H), 4.18 (1 H, q,

* T.l.c. plates were first impregnated with fluorescein sodium salt, and were then sprayed with solutions of Rhodamine B in ethanol (0.5% w/v) and 10% aqueous sodium carbonate. Spots were detected by examination under u.v. light (320 nm).

$J_{4,5}$ 5.5 Hz, 5-H), 4.32 (1 H, q, $J_{3,4}$ 6, $J_{3,OH}$ 6 Hz, 3-H), and 4.35 (1 H, t, 4-H) (Found: C, 39.85; N, 5.05; Cl, 27.8. $C_9H_{14}Cl_2O_5$ requires C, 39.56; H, 5.13; Cl, 26.01%).

Methyl (3S,4R)-2,2-*Dichloro*-4,5-O-*isopropylidene*-3,4,5-*trihydroxypentanoate* (5a) (545 mg, 20%), an oil; $[\alpha]_D^{25}$ −10.6 (*c*, 1.39 in ethanol); R_f 0.27 (solvent B); the i.r. spectrum was identical with that of the isomer (4a); δ 1.42 and 1.44 (total 6 H, 2 × s, CMe_2), 3.7 (1 H, d, OH), 3.90 (3 H, s, OMe, 3.90 (1 H, t, $J_{5,5'}$ 6.5, $J_{4,5'}$ 7 Hz, 5'-H), 4.20 (1 H, q, $J_{3,4}$ 2.5, $J_{3,OH}$ 9 Hz, 3-H), 4.22 (1 H, t, $J_{4,5}$ 6.5 Hz, 5-H), and 4.56 (1 H, sext, 4-H) (Found: C, 38.8; H, 5.05; Cl, 26.5. $C_9H_{14}Cl_2O_5$ requires C, 39.56; H, 5.13; Cl, 26.01%).

Isopropyl (3R,4R)-2,2-*Dichloro*-4,5-O-*isopropylidene*-3,4,5-*trihydroxypentanoate* (4b). After concentration of the reaction mixture, compound (4b) crystallized on storage in a refrigerator (1.36 g, 45%), m.p. 84 °C; $[\alpha]_D^{25}$ +3.6° (*c*, 0.1 in $CHCl_3$); R_f 0.27 (solvent A); $\nu_{max.}$ (KBr) 3 500, 3 390, and 1 720 cm^{-1}; δ 1.35 (6 H, d, $CHMe_2$), 1.36 and 1.40 (total 6 H, 2 × s, CMe_2), 3.3 (1 H, d, OH), 4.11 (1 H, q, $J_{5,5'}$ 8.5, $J_{4,5'}$ 6 Hz, 5'-H), 4.16 (1 H, q, $J_{4,5}$ 5.5 Hz, 5-H), 4.37 (1 H, q, $J_{3,4}$ 5 Hz, 4-H), 4.42 (1 H, t, $J_{3,OH}$ 5.5 Hz, 3-H), and 5.09 (1 H, sept, $J_{H,Me}$ 6 Hz, $CHMe_2$) (Found: C, 44.0; H, 6.0; Cl, 23.65. $C_{11}H_{18}Cl_2O_5$ requires C, 43.99; H, 6.0; Cl, 23.34%).

Isopropyl (3S,4R)-2,2-*Dichloro*-4,5-O-*isopropylidene*-3,4,5-*trihydroxypentanoate* (5b). This was isolated as a mixture containing *ca.* 5% of the epimer (4b) (900 mg, 20%); R_f 0.27 (solvent A); the i.r. spectrum was identical with that of compound (4a); δ 1.34 (6 H, d, *J* 6 Hz, $CHMe_2$), 1.38 and 1.40 (total 6 H, 2 × s, CMe_2), 3.4 (1 H, d, OH), 3.90 (1 H, q, $J_{5,5'}$ 8.5, $J_{4,5'}$ 7.2 Hz, 5'-H), 4.20 (1 H, q, $J_{3,4}$ 2.5, $J_{3,OH}$ 9.5 Hz, 3-H), 4.22 (1 H, q, $J_{4,5}$ 6 Hz, 5-H), 4.55 (1 H, oct, 4-H), and 5.08 (1 H, sept, $CHMe_2$).

General Procedure for Dehalogenation of the Esters (4a) *and* (5a).—(*a*) *Using tributyltin hydride.* To a solution of the dihalogeno-derivative (5 mmol) in dry THF (5 ml) was added tributyltin hydride (3.15 g, 10 mmol) at 0 °C. After 24 h at room temperature the solvent was evaporated off. The crude residue was chromatographed on silica gel. The yield was 65%.

(*b*) *Using Raney nickel.* To a solution of the substrate (5 mmol) in dry methanol were added triethylamine (1.01 g, 10 mmol) and Raney nickel (0.5 g) under hydrogen. After 3 h of vigorous stirring, the catalyst was filtered off. After evaporation of the filtrate the residue was taken up in ethyl acetate and the solution was washed with water and then dried (Na_2SO_4). The yield after work-up was 90%.

Compounds (4a) and (5a) were reduced to the esters (6a) and (7a), respectively by these methods. Their respective acetates (6b) and (7b) have been fully characterized. *Methyl* (3S,4R)-3-O-*acetyl*-4,5-O-*isopropylidene*-3,4,5-*trihydroxypentanoate* (6b) was an oil; $[\alpha]_D^{25}$ +22.2° (*c*, 1.2 in ethanol); R_f 0.38 (solvent C); $\nu_{max.}$ (film) 1 745 cm^{-1}; δ 1.34 and 1.43 (total 6 H, 2 × s, CMe_2), 2.06 (3 H, s, COMe), 2.67 (1 H, d, $J_{2',3}$ 7.5 Hz, 2'-H), 2.68 (1 H, d, $J_{2,3}$ 5.5 Hz, 2-H), 3.68 (3 H, s, OMe), 3.80 (1 H, q, $J_{5,5'}$ 8.7, $J_{4,5'}$ 5.5 Hz, 5'-H), 4.02 (1 H, q, $J_{4,5}$ 6.7 Hz, 5-H), 4.28 (1 H, dq, $J_{3,4}$ 4 Hz, 4-H), and 5.35 (1 H, dq, 3-H).

Methyl (3R,4R)-3-O-*acetyl*-4,5-O-*isopropylidene*-3,4,5-*trihydroxypentanoate* (7b) was an oil; $[\alpha]_D^{25}$ −3.9° (*c*, 0.92 in ethanol); R_f 0.4 (solvent C); the i.r. spectrum was identical with that of the epimer (6b); δ 1.34 and 1.43 (total 6 H, 2 × s, CMe_2), 2.06 (3 H, s, COMe, 2.63 (1 H, q, $J_{2,2'}$ 16, $J_{2',3}$ 7.7 Hz, 2'-H), 2.73 (1 H, q, $J_{2,3}$ 4.5 Hz, 2-H), 3.68 (3 H, s, OMe), 3.80 (1 H, q, $J_{5,5'}$ 8.7, $J_{4,5'}$ 5.5 Hz, 5'-H), 4.06 (1 H, q, $J_{4,5}$ 6.7 Hz, 5-H), 4.22 (1 H, q, $J_{3,4}$ 6 Hz, 4-H), and 5.25 (1 H, q, 3-H).

General Procedure for the Lactonisation of the Halogeno-esters (4) *and* (5) .—The halogeno-ester (4a,b) or (5a,b) (1 mmol) was dissolved in wet benzene (50 ml) containing toluene-*p*-sulphonic acid (25 mg). The mixture was heated at reflux for 10 h. Thus prepared were (3R, 4R)-2,2-*dichloro*-3,5-*dihydroxy*-γ-*valerolactone* (8a) (179 mg, 89%), which was crystallized directly from benzene, m.p. 118 °C; $[\alpha]_D^{25}$ +112.2° (*c*, 1.08 in CH_3CN); R_f 0.18 (solvent D); $\nu_{max.}$ (KBr) 3 420 and 1 775 cm^{-1}; δ(CD_3CN) 3.3 (2 H, m, 2 × OH), 3.76 (1 H, q, $J_{5,5'}$ 13, $J_{4,5'}$ 4 Hz, 5'-H), 3.98 (1 H, q, $J_{4,5}$ 2.2 Hz, 5-H), 4.27 (1 H, dq, $J_{3,4}$ 8.5 Hz, 4-H), and 4.56 (1 H, d, 3-H) (Found: C, 29.85; H, 2.85; Cl, 35.7. $C_5H_6Cl_2O_4$ requires C, 29.85; H, 2.98; Cl, 35.32%).

(3S, 4R)-2,2-*Dichloro*-3,5-*dihydroxy*-γ-*valerolactone* (9a) (182 mg, 90%) was an oil; $[\alpha]_D^{25}$ +32.8° (*c*, 0.63 in CH_3CN); R_f 0.12 (solvent D); $\nu_{max.}$ (film) 3 240 and 1 800 cm^{-1}; δ (CD_3CN) 3.3 (2 H, m, 2 × OH), 3.89 (1 H, d, $J_{4,5}$ 6.7 Hz, 5-H), 3.89 (1 H, d, $J_{4,5'}$ 5.2 Hz, 5'-H), 4.58 (1 H, d, $J_{3,4}$ 3.4 Hz, 3-H), and 4.86 (1 H, dq, 4-H) (Found: C, 29.8; H, 3.0; Cl, 35.25. $C_5H_6Cl_2O_4$ requires C, 29.85; H, 2.98; Cl, 35.32%).

Conventional acetylation of the diols (8a) and (9a) afforded the diacetates (8b) and (9b) respectively. (3R, 4R)-3,5-*Diacetoxy*-2,2-*dichloro*-γ-*valerolactone* (8b) (276 mg, 94%) had m.p. 91 °C; $[\alpha]_D^{25}$ +90.5° (*c*, 1.1 in $CHCl_3$); R_f 0.39 (solvent D); $\nu_{max.}$ (KBr) 1 810 and 1 740—1 775 cm^{-1}; δ 2.05 and 2.15 (total 6 H, 2 × s, 2 × COMe), 4.32 (1 H, d, $J_{4,5'}$ 4.4 Hz, 5'-H), 4.42 (1 H, d, $J_{5,4}$ 2 Hz, 5-H), 4.58 (1 H, sext, $J_{4,3}$ 7.5 Hz, 4-H), and 5.70 (1 H, d, 3-H).

(3S, 4R)-3,5-*Diacetoxy*-2,2-*dichloro*-γ-*valerolactone* (9b) (269 mg, 95%) was an oil; $[\alpha]_D^{25}$ +63.2° (*c*, 0.96 in ethanol); R_f 0.39 (solvent D); $\nu_{max.}$ (film) 1 810 and 1 750—1 770 cm^{-1}; δ 2.08 and 2.18 (total 6 H, 2 × s, 2 × COMe), 4.33 (2 H, d, $J_{4,5'} = J_{4,5}$ = 6 Hz, 5- and 5'-H), 5.1 (1 H, sext, $J_{3,4}$ 3.8 Hz, 4-H), and 5.81 (1 H, d, 3-H).

The dichloro-lactones (8a) and (9a) were reductively dehalogenated by the method described above for compounds (4) and (5) to afford the lactones (10) and (11a), respectively, which were characterized as their acetates (10b) and (11b), respectively. (3S, 4R)-3,5-*Diacetoxy*-γ-*valerolactone* (10b) was an oil; $[\alpha]_D^{25}$ −5.2° (*c*, 0.93 in ethanol); R_f 0.26 (solvent B); $\nu_{max.}$ (film) 1 790 and 1 740 cm^{-1}; δ 2.62 (1 H, q, $J_{2,2'}$ 18.5, $J_{2',3}$ 2 Hz, 2'-H), 3.03 (1 H, q, $J_{2,3}$ 7.25 Hz, 2-H), 4.28 (1 H, q, $J_{5,5'}$ 12, $J_{4,5'}$ 3.75 Hz, 5'-H), 4.38 (1 H, q, $J_{4,5}$ 3.25 Hz, 5-H), 4.69 (1 H, sext, $J_{3,4}$ 1.75 Hz, 4-H), and 5.29 (1 H, sext, 3-H) (Found: C, 50.05; H, 5.4. $C_9H_{12}O_6$ requires C, 50.00; H, 5.55%).

(3R, 4R)-3,5-*Diacetoxy*-γ-*valerolactone* (11b) was an oil; $[\alpha]_D^{25}$ +39.2° (*c*, 0.91 in ethanol); R_f 0.26 (solvent B); the i.r. spectrum was identical to that of the epimer (10b); δ 2.63 (1 H, q, $J_{2,2'}$ 18, $J_{2',3}$ 2.25 Hz, 2'-H), 2.94 (1 H, q, $J_{2,3}$ 6.5 Hz, 2-H), 4.38 (1 H, q, $J_{4,5'}$ 6.5 Hz, 5'-H), 4.39 (1 H, q, $J_{4,5}$ 4.75 Hz, 5-H), 4.82 (1 H, sext, $J_{3,4}$ 4.75 Hz, 4-H), and 5.57 (1 H, sept, 3-H) (Found: C, 50.0; H, 5.6. $C_9H_{12}O_6$ requires C, 50.00; H, 5.55%).

(4S)-5-*Acetoxy*-2-*chloropent*-2-*en*-4-*olide* (12).—To a solution of the dichloro-lactone (8b) or (9b) (1.425 g, 5 mmol) in dry THF (30 ml) was added hexamethylphosphorous triamide (0.815 g, 5 mmol) at room temperature. T.l.c. after 5 min showed complete disappearance of the starting material. The mixture was diluted with diethyl ether and was then washed with 1 M HCl and water and then dried ($MgSO_4$). The crude product (12) was obtained, after

evaporation of the solvent, as an oil (951 mg, 98%); $[\alpha]_D^{25}$ −65.3° (*c*, 0.96 in ethanol); $\nu_{max.}$ (film) 1 800 and 1 630 cm^{-1}; δ 2.06 (3 H, s, COMe), 4.33 (total 2 H, d, $J_{4,5} = J_{4,5'} = 4.6$ Hz, 5- and 5′-H), 5.22 (1 H, q, $J_{3,4}$ 2 Hz, 4-H), and 7.33 (1 H, d, 3-H) (Found: C, 44.05; H, 3.95; Cl, 18.7. $C_7H_7ClO_4$ requires C, 44.09; H, 3.67; Cl, 18.63%).

Comparison Between the Lactone (10a) *and the Lactone prepared from* 2-*Deoxy*-D-erythro-*pentose*.—2-Deoxy-D-*erythro*-pentose (1 g) was oxidised with bromine according to the method in ref. **13**. The lactone product was immediately acetylated to give an oil; $[\alpha]_D^{25}$ −4.8° (*c*, 1 in ethanol). The lactone (10b) (see above) has $[\alpha]_D^{25}$ −5.2° (*c*, 1 in ethanol); δ_C 20.58, 34.78, 63.33, 71.12, 82.00, 170.00, and 173.78 p.p.m.

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