Unusual Stereochemistry in the Copper-catalysed Ring Opening of a Carbohydrate Oxirane with Vinylmagnesium Bromide

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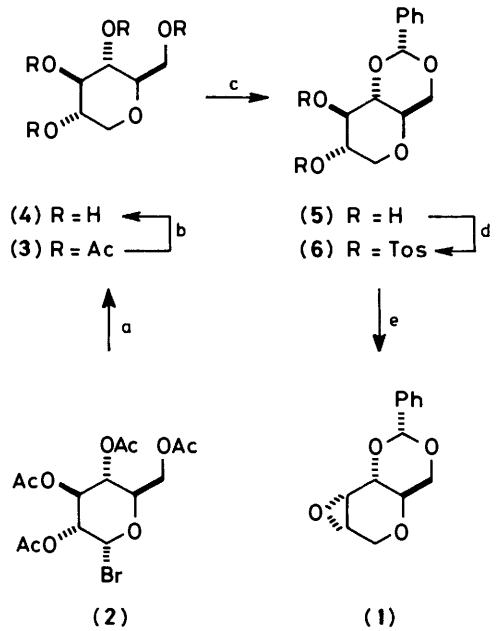
The oxirane ring of 4,6-*O*-benzylidene-1,5:2,3-dianhydro-D-allitol (**1**) opened regio- and stereoselectively at C-2 with Me_2CuLi and allylmagnesium chloride in the presence of catalytic amounts of CuI. With vinylmagnesium bromide, however, the ring opening of (**1**) was regioselective but a mixture of stereoisomers (**10**) and (**12**) was obtained corresponding to retention and inversion at C-2. A mechanism for the formation of the anomolous retention product (**12**) is proposed.

Comparatively few examples of nucleophilic ring opening of carbohydrate oxiranes by organocuprates are known. Good yields have been obtained with homocuprates (R_2CuLi) when R = Me[1,2] but in general the reaction is not efficient owing to the sluggish reactivity of oxiranes. However, the copper-catalysed (CuI) ring opening of oxiranes by Grignard reagents[3] is efficient and has been used successfully with carbohydrates.[4–6] In all the cases examined the expected *trans*-diaxial ring opening of the oxirane occurred with inversion of configuration.[7] As part of a projected synthesis of pseudomonic acid C we have examined the nucleophilic opening of the oxirane of 4,6-*O*-benzylidene-1,5:2,3-dianhydro-D-allitol (**1**)[8] with various carbon nucleophiles. We now report some observations on the reaction of (**1**) with various organocuprates and draw attention to the anomolous stereochemistry obtained with vinylmagnesium bromide–CuI. Sinaÿ[6] has recently applied a similar oxirane cleavage to the synthesis of pseudomonic acid C.

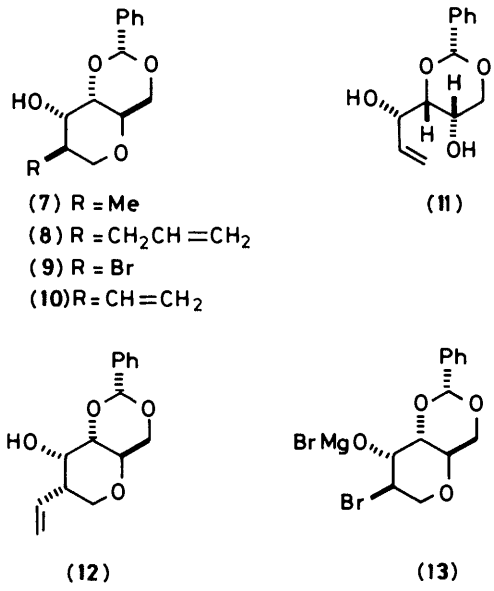


Scheme 1. Ac = Acetyl; Tos = *p*-tolylsulphonyl. *Reagents and conditions:* a, Bu_3SnH/Et_2O, *hv*; b, NaOMe/MeOH; c, $PhCH(OEt)_2$/DMF, H^+; d, TosCl/pyridine; e, NaOMe/MeOH–CH_2Cl_2

The oxirane (**1**) was prepared by a five-step sequence as shown in Scheme 1 starting with 2,3,4,5-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**2**). The photochemically induced reductive debromination[9] of (**2**) to give 1,5-anhydro-D-glucitol tetraacetate (**3**) is noteworthy as the most efficient and reliable means for preparing (**3**). The conversion of (**3**) into (**1**) was then achieved by a modification of known procedures.[8] By this route the highly crystalline oxirane (**1**) could be prepared on a large scale.

The oxirane (**1**) reacted with a large excess of Me_2CuLi to give (**7**) in 64% yield but attempts to open the oxirane ring with functionalised carbon chains using the homocuprates prepared in the usual way[10] from allyl-lithium, vinyl-lithium, or 1-(trimethylsilyl)prop-1-enyl-lithium[11] failed. Similarly, the higher order mixed cuprates[12] $R_2Cu(CN)Li_2$ (R = allyl or vinyl) failed to react with (**1**). However, the copper-catalysed ring opening of (**1**) with allylmagnesium chloride in THF occurred rapidly at −30 °C to give (**8**) in 80—88% yield along with *ca.* 5% of (**11**). By contrast, addition of (**1**) to the reagent prepared from allylmagnesium bromide and 10 mol % of CuI in THF at −30 °C gave only the bromohydrin (**9**) in 90% yield. The formation of (**9**) probably involved a Lewis acid-catalysed scission of the oxirane ring since (**1**) reacted rapidly with anhydrous $MgBr_2$ in THF at −30 °C to give (**9**) in 90% yield.

Reaction of (**1**) with vinylmagnesium bromide and 10 mol % CuI in THF at −30 °C gave two isomeric products [(**10**) and (**12**)] in 75% yield. The relative proportion of (**10**) and (**12**) depended on the age of the Grignard reagent. Freshly prepared reagent gave (**10**) and (**12**) in equal amounts, whereas week-old



Scheme 2.

reagent which had been stored at −40 °C gave (**10**) and (**12**) in the ratio of 3:1. Isomer (**10**) was the product of normal *trans*-diaxial ring scission with inversion of configuration at C-2 whereas (**12**), with retention of configuration at C-2, was the product of apparent equatorial attack and as such is anomolous. Isomer (**12**) was probably the result of a two-step mechanism in which competing $MgBr_2$-catalysed scission of the *oxirane ring gave the* bromohydrin derivative (**13**) from which a second copper-catalysed displacement at C-2 by the vinyl group occurred with inversion of configuration to give (**12**) with overall retention. Hence the variation in product ratio can be attributed to the concentration of $MgBr_2$ in solution: the reagent stored at −40 °C had deposited large amounts of $MgBr_2$ thereby removing some of the reagent responsible for the formation of (**12**).

Support for the proposed mechanism was obtained by allowing (**1**) to react with $MgBr_2$ to give (**13**) which was then added to vinylmagnesium bromide–CuI in THF at −30 °C. Isomer (**12**) was isolated in 59% yield uncontaminated by (**10**). The substitution of a secondary bromide by an organocuprate is difficult;[13] therefore it is likely that the oxygen atom at C-3 plays a major role in facilitating the reaction.

Experimental

T.l.c. (thin-layer chromatography) was carried out using Kieselgel GF_{254} and compounds were visualised with 5% H_2SO_4 in EtOH. Column chromatography was carried out on Kieselgel 60 (230—400 mesh). All reactions requiring anhydrous conditions were conducted in flame-dried apparatus under a static atmosphere of dry nitrogen. Organic extracts were dried over $MgSO_4$ and evaporated at aspirator pressure using a Büchi rotary evaporator. Cuprous iodide was extracted overnight with tetrahydrofuran (THF) in a Soxhlet apparatus and then dried at 0.5 mmHg. It was thereafter stored in a desiccator in the dark. The Amberlite IR-120 resin was washed 3 times with dilute HCl followed by distilled water until the washings showed pH 7. The resin was then washed with MeOH and Et_2O. Light petroleum refers to the fraction of b.p. 40—60 °C.

MeOH was dried by distillation from $Mg(OMe)_2$. Et_2O and THF were dried with Na; pyridine and dimethylformamide (DMF) were distilled from CaH_2.

Melting points were determined with a Reichert hot-stage microscope and are uncorrected. Chemical shifts are reported as δ values in p.p.m. relative to tetramethylsilane (δ 0.0) as an internal standard. ^1H N.m.r. spectra were recorded with a Perkin-Elmer R32 spectrometer operating at 90 MHz or a Bruker WH-400 spectrometer operating at 400 MHz. The terms *ax* and *eq* in the ^1H n.m.r. data denote the axial or equatorial protons respectively assigned from the lowest energy conformation. Carbon n.m.r. spectra were recorded with a JEOL FX90Q spectrometer operating at 22.5 MHz. Inverted signals obtained with a pseudo-INEPT pulse sequence are indicated by an asterisk. I.r. spectra were recorded with a Perkin-Elmer model 1420 spectrometer. Peak intensities were recorded as strong (s), medium (m), or weak (w). Optical resolutions were recorded with a Thorn Automation Type 243 polarimeter using 4 cm cells.

1,5-*Anhydro*-D-*glucitol* (**4**).—To a stirred solution of 0.192M-NaOMe in MeOH (700 cm^3) was added at 0 °C 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-glucitol[9] (**3**) (103 g, 0.310 mol) in one portion. The cooling bath was removed and the mixture stirred at 20 °C for 4 h. The mixture was passed through a 5 cm diameter column containing 250 cm^3 of Amberlite IR-120 resin which was then washed with dry MeOH (3 × 200 cm^3). The combined filtrate and washings were evaporated and the residue recrystallised from EtOH–Et_2O to give (**4**) (43.5 g, 0.265 mol, 85%) as dense white prisms, m.p. 141—143 °C (lit.,[8] 139—141 °C); $[\alpha]_D^{21}$ +41.6° (*c* 1.6 in H_2O) {lit.,[8] $[\alpha]_D^{20}$ +42.5° (*c* 1—2 in H_2O)}.

4,6-O-*Benzylidene*-1,5-*anhydro*-D-*glucitol* (**5**).—A solution of 1,5-anhydro-D-glucitol (10.5 g), benzaldehyde diethyl acetal (17.5 cm^3), and toluene-*p*-sulphonic acid monohydrate (0.5 g) in dimethylformamide (24 cm^3) was stirred at 20 °C for 4 days. Ice–water was added and the product extracted into ethyl acetate. The organic layer was washed with brine, dried, and evaporated to a white solid which was recrystallised from ethyl acetate–light petroleum to give (**5**) (17.8 g, 91%) as fine white needles, m.p. 146—154 °C. Compound (**5**) did not crystallise well and tended to separate from solution as a gelatinous mass. Therefore, (**5**) was used in the next step without further purification. A sample recrystallised slowly from isopropyl alcohol had m.p. 163.7—164.4 °C (lit.,[8] m.p. 164—165 °C); $[\alpha]_D^{21}$ −22.1° (*c* 0.5 in $CHCl_3$) {lit.,[8] $[\alpha]_D^{20}$ −21.2° (*c* 0.5 in $CHCl_3$)}.

2,3-*Di*-O-p-*tolylsulphonyl*-4,6-O-*benzylidene*-1,5-*anhydro*-D-*glucitol* (**6**).—Reaction of the diol (**5**) (10.0 g, 40 mmol) and toluene-*p*-sulphonyl chloride (42.5 g, 220 mmol) in pyridine (125 cm^3) for 4 days as described[8] gave (**6**) (17.6 g, 80%) after recrystallisation from $CHCl_3$–light petroleum: it had m.p. 188—190 °C (lit.,[8] m.p. 185—189 °C); $[\alpha]_D^{21}$ −48.5° (*c* 1.5 in $CHCl_3$) {lit.,[8] $[\alpha]_D^{20}$ −48.5° (*c* 1.5 in $CHCl_3$)}.

4,6-O-*Benzylidene*-1,5:2,3-*dianhydro*-D-*allitol* (**1**).—To a 2.33M-solution of NaOMe in MeOH (60 cm^3) was added 2,3-di-*O*-*p*-tolylsulphonyl-4,6-*O*-benzylidene-1,5-anhydro-D-glucitol (**6**) (4.00 g, 17.1 mmol) in CH_2Cl_2 (140 cm^3). After 17 h at 20 °C the mixture was washed with cold water (3 × 75 cm^3), dried, and evaporated. The residue was recrystallised from CH_2Cl_2–light petroleum to give (**1**) (1.54 g, 97%) as fine white needles, m.p. 122—125 °C (lit.,[8] m.p. 127—129 °C); $[\alpha]_D^{21}$ +33.5° (*c* 0.56 in $CHCl_3$) {lit.,[8] $[\alpha]_D^{20}$ +35° (*c* 0.5 in $CHCl_3$)}; $\nu_{max.}$(CCl_4) 3 020, 1 215, and 760 cm^{-1} (all s); δ_H (400 MHz, $CDCl_3$) 7.50—7.53 and 7.32—7.41 (2 H and 3 H, m), 5.59 (1 H, s, PhC*H*), 4.18 (1 H, ddd, J_{gem} 10, $J_{6eq,5}$ 4.8, $J_{6eq,3}$ 0.8 Hz, 6-H_{eq}), 4.108 (1 H, dd, J_{gem} 13.4, $J_{1ax,2}$ 3.0 Hz, 1-H_{ax}), 4.061 (1 H, ddd, J_{gem} 13.4, $J_{1eq,2}$ 0.8, $J_{1eq,3}$ 0.8 Hz, 1-H_{eq}), 4.026 (1 H, dd, $J_{4,6}$ 8.8, $J_{4,3}$ 1.2 Hz, 4-H), 3.74 (1 H, ddd, $J_{5,6ax}$ 10.2, $J_{5,4}$ 8.8, $J_{5,6eq}$ 4.8 Hz, 5-H), 3.65 (1 H, dd, J_{gem} = $J_{6ax,5}$ = 10.2 Hz, 6-H_{ax}), 3.57 (1 H, dddd, $J_{3,2}$ 4.8, $J_{3,1eq}$ 0.8, $J_{3,4}$ 1.2, $J_{3,6eq}$ 0.8 Hz, 3-H), and 3.44 (1 H, ddd, $J_{2,3}$ 4.8, $J_{2,1ax}$ 3.0, $J_{2,1eq}$ 0.8 Hz, 2-H) (Found: C, 66.9; H, 6.2. Calc. for $C_{13}H_{14}O_4$: C, 66.7; H, 6.0%).

If $CHCl_3$ is used as solvent as prescribed,[8] the reaction does not go to completion because $CHCl_3$ reacts with NaOMe.

2-*Deoxy*-2-C-*methyl*-4,6-O-*benzylidene*-1,5-*anhydro*-D-*altritol* (**7**).—To a stirred suspension of CuI (1.2 g, 6 mmol) in Et_2O (5 cm^3) was added dropwise at 0 °C 9.0 cm^3 of a 1.4M-solution of MeLi in Et_2O. After 20 min, the oxirane (**1**) (0.234 g, 1.0 mmol) in THF (10 cm^3) was added. The mixture was stirred at 0 °C for 15 h whereupon saturated aqueous NH_4Cl (10 cm^3) was added. The organic layer was washed with water, dried, and evaporated. The residue was chromatographed on Kieselgel with EtOAc–light petroleum (1:9) as eluant to give 0.16 g (64%) of (**7**) after recrystallisation from EtOH: it had m.p. 110—113 °C; $[\alpha]_D^{22}$ −12.5° (*c* 0.1 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.45—7.52 and 7.34—7.42 (2 H and 3 H, m), 5.64 (1 H, s, PhC*H*), 4.31 (1 H, dd, J_{gem} 10.5, J_{vic} 5 Hz, 6-H_{eq}), 4.06 (1 H, dd, J_{gem} 12, J_{vic} 3 Hz, 1-H_{ax}), 3.98 (1 H, broadened dd, $J_{3,4}$ 3, $J_{3,2}$ 3 Hz, 3-H), 3.91 (1 H, ddd, $J_{5,6\beta}$ 10.5, $J_{5,4}$ 10, $J_{5,6\alpha}$ 5 Hz, 5-H), 3.78 (1 H, dd, $J_{4,5}$ 10, $J_{4,3}$ 3 Hz, 4-H), 3.72 (1 H, dd, J_{gem} 10, J_{vic} 10 Hz, 6-H_{ax}), 3.53 (1 H, dt, J_{gem} 12, J_{vic} 1 Hz, 1-H_{eq}), 2.32 (1 H, br, D_2O exchange), 2.04 (1 H, m, 2-H), and 1.19 (3 H, d, *J* 7.5 Hz, 2-Me) (Found: C, 66.95; H, 7.2. $C_{14}H_{18}O_4$ requires C, 67.2; H, 7.2%).

Reaction of the Oxirane (**1**) *with Vinylmagnesium Bromide–*CuI.—To a stirred suspension of CuI (0.25 g, 1.3 mmol) in THF (8 cm^3) at −30 °C was added dropwise a solution of vinylmagnesium bromide in THF (25 cm^3, *ca.* 1M-reagent prepared in the usual way and stored at −10 °C for 24 h to precipitate as much $MgBr_2$ as possible). After 5 min at −30 °C, the oxirane (**1**) (1.00 g, 4.3 mmol) in THF (17 cm^3) was added and the mixture maintained at −30 °C for 1 h and 0 °C for 2 h by which time t.l.c. analysis [Et_2O–light petroleum (1:1)] indicated the absence of (**1**). The mixture was diluted with Et_2O (50 cm^3) and washed with NH_4Cl–NH_4OH. The aqueous layer was extracted with Et_2O (3 × 50 cm^3) and the combined extracts dried and evaporated. The solid residue (0.87 g) was chromatographed on Kieselgel with Et_2O–light petroleum (1:3) as eluant to give 2-*deoxy*-2-C-*vinyl*-4,6-O-*benzylidene*-1,5-*anhydro*-D-*altritol* (**10**) (0.35 g, 1.33 mmol, 31%), m.p. 52—53 °C (from Et_2O–light petroleum); $[\alpha]_D^{22}$ −8.4° (*c* 0.354 in CH_2Cl_2); $\nu_{max.}$(film) 3 459m, 2 880m, 1 450m, 1 370m, 1 100—1 000s, 750m, and 700s cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.45—7.50 and 7.35—7.41 (2 H and 3 H, m), 6.02 (1 H, ddd, *J* 18, *J'* 11, *J''* 7 Hz, H_2C=C*H*), 5.61 (1 H, s, PhC*H*), 5.31 [1 H, ddd, *J* 18, *J'* 1.5, *J''* 1.5 Hz, (*H*)HC=C], 5.25 [1 H, ddd, *J* 11, *J'* 1.5, *J''* 1.5 Hz, (*H*)HC=C], 4.31 [1 H, dd, J_{gem} 10, J_{vic} 5 Hz, 6-H_{eq}], 4.10 (1 H, narrow m, 3-H), 4.08 (1 H, dd, J_{gem} 12, J_{vic} 3 Hz, 1-H_{ax}), 3.95 (1 H, ddd, $J_{5,4}$ = $J_{5,6ax}$ = 10, $J_{5,6eq}$ 5 Hz, 5-H), 3.79 (1 H, d with fine splitting, *J* 12 Hz, 1-H_{eq}), 3.76 (1 H, dd, $J_{4,5}$ 10, $J_{4,3}$ 3 Hz, 4-H), 3.71 (1 H, dd, J_{gem} = J_{vic} = 10 Hz, 6-H_{ax}), 2.59 (1 H, m, 2-H), and 2.03 (1 H, br, OH); δ_C (22.5 MHz, $CDCl_3$) 137.3*, 136.6, 129.2, 128.3, 126.2, 117.4*, 102.0, 77.6, 69.3*, 69.1, 67.0, 66.1*, and 45.1 (Found: C, 68.45; H, 7.1. $C_{15}H_{18}O_4$ requires C, 68.7; H, 6.9%) and 2-*deoxy*-2-C-*vinyl*-4,6-O-*benzylidene*-1,5-*anhydro*-D-*allitol* (**12**), m.p. 128—130 °C (from Et_2O–light petroleum); $[\alpha]_D^{22}$ −37.8° (*c* 0.05 in CH_2Cl_2); $\nu_{max.}$(film) 3 400s, 2 970s, 2 860s, 1 640m, 1 460s, 1 385s, 1 280m, 1 050s, 1 000—860s, 760s, and 700s cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.46—7.52 and 7.33—7.41 (2 H and 3 H, m), 5.86 (1 H, ddd, *J* 18, *J'* 9, *J''* 7.5 Hz, H_2C=C*H*), 5.67 (1 H, s, PhC*H*), 5.19 [1 H, ddd, *J* 18, *J'* ~ 1, *J''* ~ 1 Hz, (*H*)HC=C], 5.18 [1 H, ddd, *J* 9, *J'* ~ 1, *J''* ~ 1 Hz, (*H*)HC=C], 4.34 (1 H, dd, J_{gem} 10, J_{vic} 5 Hz, 6-H_{eq}), 4.18 (1 H, dd, $J_{3,2}$ = $J_{3,4}$ = 2 Hz, 3-H), 3.93 (1 H, ddd, $J_{5,4}$ = $J_{5,6ax}$ = 10, $J_{5,6eq}$ 5 Hz, 5-H), 3.81 (1 H, dd, J_{gem} = J_{vic} = 11 Hz, 1-H_{ax}), 3.70 (1 H, dd, J_{gem} = J_{vic} = 10 Hz, 6-H_{ax}), 3.68 (1 H, dd, J_{gem} 11, J_{vic} 5 Hz, 1-H_{eq}), 3.63 (1 H, dd, $J_{4,5}$ 10, $J_{4,2}$ 2 Hz, 4-H), 2.63 (1 H, m, 2-H), and 1.95 (1 H, br s, OH); δ_C (22.5 MHz, $CDCl_3$) 137.3*, 134.3, 129.1, 128.2, 126.2, 117.6*, 101.8, 80.4, 69.4*, 68.0, 66.1*, 65.8, and 45.1 (Found: C, 68.85; H, 7.00. $C_{15}H_{18}O_4$ requires C, 68.7; H, 6.9%).

The 3,5-dinitrobenzoate derivatives of (**10**) and (**12**) gave m.p. 143.6—145.7 °C and 153.5—154.5 °C respectively (from Et_2O–light petroleum).

Reaction of the Oxirane (**1**) *with Allylmagnesium Chloride–*CuI.—To a stirred suspension of CuI (32 mg) in THF (1 cm^3) was added at −30 °C a solution of allylmagnesium chloride (15 cm^3) prepared from Mg (4.78 g, 196 mg-atom) and allyl chloride (4.0 cm^3, 49 mmol) in THF (50 cm^3). To the resultant olive green solution was added the oxirane (**1**) (200 mg, 0.9 mmol) in THF (2 cm^3). The mixture was kept at −30 °C for 1 h after which t.l.c. (Et_2O–light petroleum, 1:1) showed no starting material and a single major product. The reaction mixture was poured into a solution of NH_4Cl and NH_4OH with rapid stirring and Et_2O (200 cm^3) was added. The organic layer was dried, evaporated, and the solid residue chromatographed on Kieselgel with Et_2O–light petroleum (1:4) as eluant to give 2-*deoxy*-2-C-*allyl*-4,6-O-*benzylidene*-1,5-*anhydro*-D-*altritol* (**8**) (217 mg, 85%) as white plates after recrystallisation from Et_2O–light petroleum; it had m.p. 65.2—68.2 °C; $[\alpha]_D^{22}$ −16.1° (*c* 0.018 in CH_2Cl_2); $\nu_{max.}$(film) 3 500m, 3 020m, 2 885m, 1 640w, 1 230s, 1 120s, 1 100s, 1 060s, 1 000s, 720m, 700m, and 670 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.46—7.51 and 7.35—7.42 (2 H and 3 H, m), 5.79 (1 H, 10-line symmetrical m, H_2C=C*H*), 5.63 (1 H, s, PhC*H*), 5.075—5.16 (2 H, m, H_2C=CH), 4.31 (1 H, dd, J_{gem} 10.5, J_{vic} 5 Hz, 6-H_{eq}), 4.07 (1 H, dd, $J_{3,4}$ = $J_{3,2}$ = 3 Hz, 3-H), 3.99 (1 H, dd, J_{gem} 11.5, J_{vic} 3 Hz, 1-H_{ax}), 3.92 (1 H, ddd, $J_{5,4}$ 10.5, $J_{5,6ax}$ 10, $J_{5,6eq}$ 5 Hz, 5-H), 3.725 (1 H, dd, $J_{4,5}$ 10, $J_{4,3}$ 3 Hz, 4-H), 3.72 (1 H, dd, J_{gem} = J_{vic} = 10 Hz, 6-H_{ax}), 3.65 (1 H, d with fine splitting, *J* 11.5 Hz, 1-H_{eq}), 2.21—2.42 (2 H, m, H_2C=CH–CH_2), 2.31 (1 H, br, OH), and 1.91—1.97 (1 H, m, 2-H); δ_C (22.5 MHz, $CDCl_3$) 137.4*, 136.0, 129.2, 128.3, 126.2, 117.0*, 102.0, 77.6, 69.3*, 68.35, 67.3, 65.8*, 41.3, and 34.1* (Found: C, 69.85; H, 7.45. $C_{16}H_{20}O_4$ requires C, 69.5; H, 7.3%).

A 20-fold scale-up of the reaction gave (**8**) (4.16 g, 88%) and a second minor component which eluted from the Kieselgel column with EtOAc. The minor component [210 mg from 4.0 g of (**1**), 5% yield] was identified as (2R,4R,5S)-2-*phenyl*-4-[(1S)-1-*hydroxyprop*-2-*enyl*]-5-*hydroxy*-1,3-*dioxane* (**11**), m.p. 90—91.5 °C (fine needles from Et_2O–light petroleum); $[\alpha]_D^{22}$ −64.7° (*c* 0.032 in CH_2Cl_2); δ_C (22.5 MHz, CD_3OD) 138.9*, 137.4, 129.5, 128.7, 127.1, 117.5*, 101.8, 84.9, 74.1, 71.7*, and 63.4 (Found: C, 66.15; H, 6.6. $C_{13}H_{16}O_4$ requires C, 66.1; H, 6.8%).

Acetylation of (**11**) in the usual way with Ac_2O–pyridine gave an oily diacetate: δ_H (90 MHz, $CDCl_3$) 7.2—7.6 (5 H, m), 5.97 (1 H, ddd, *J* 18, *J'* 9, *J''* 7 Hz, H_2C=C*H*), 5.47 (1 H, s, PhC*H*), 5.37—5.15 (3 H, m, H_2C=CH and AcO–C*H*), 4.94 (1 H, ddd, *J* = *J'* = 11, *J''* 6 Hz, AcOC*H*), 4.34 [1 H, dd, *J* 11, *J'* 6 Hz, OC*H*(H)], 4.01 (1 H, dd, *J* 11, *J'* 2.5 Hz, PhCH–O–C*H*), 3.59 [1 H, dd, *J* = *J'* = 11 Hz, OCH(*H*)], 2.07 (6 H, s).

Treatment of the Oxirane (**1**) *with Allylmagnesium Bromide.*—The oxirane (**1**) was added to allylmagnesium bromide–CuI in THF at −30 °C as described above for allylmagnesium chloride. After chromatography on Kieselgel, unchanged oxirane (**1**) (40 mg) was recovered along with 2-*deoxy*-2-*bromo*-4,6-O-*benzylidene*-1,5-*anhydro*-D-*altritol* (**9**) (240 mg, 90%), m.p. 120—123 °C (from Et_2O–light petroleum); $[\alpha]_D^{22}$ −0.6° (*c* 0.016 in CH_2Cl_2); $\nu_{max.}$(film) 3 350m, 3 020m, 1 225s, 1 120m, 1 100m, 1 000m, and 750s cm^{-1}; δ_H (90 MHz, $CDCl_3$) 7.15—7.7 (5 H, m), 5.60 (1 H, s, PhC*H*), 3.50—4.60 (8 H, m), and 2.90—3.20 (1 H, m) (Found: C, 49.1; H, 4.85. $C_{13}H_{15}BrO_4$ requires C, 49.5; H, 4.8%).

Generation of (**13**) *and its Reaction with Vinylmagnesium Bromide–*CuI.—To a stirred suspension of Mg (51 mg, 2.1 mg-atom) in THF (1 cm^3) was added dropwise 1,2-dibromoethane (192 mg, 1.02 mmol) in THF (1 cm^3). After 30 min, the oxirane (**1**) (245 mg, 1.05 mmol) in THF (3 cm^3) was added at 0 °C and the mixture stirred for 30 min by which time t.l.c. (Et_2O–light petroleum, 1:1) indicated complete conversion of (**1**). The mixture was then added dropwise *via* a syringe to a stirred mixture of *ca.* 1M-vinylmagnesium bromide (4 cm^3) and CuI (76 mg, 0.4 mmol) in THF at −30 °C. After 1 h at −30 °C and 2 h at 0 °C, the mixture was poured into NH_4Cl–NH_4OH and worked-up as above to give (**12**) (162 mg, 59%) identical with the sample previously prepared by t.l.c. and ^1H n.m.r.

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