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Free radical-induced *C*-allylation of α-bromolactones. Synthesis of 2-*C*-allyl-2-deoxy-D-arabinono- and -D-ribono-1,4-lactones*

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ABSTRACT

Application of the Keck *C*-allylation of organic halides to 2-bromo-2-deoxy-D-arabinonolactone resulted in the formation of mixtures of 2-*C*-allyl lactones. The stereochemical preferences observed were dictated by the nature of vicinal and remotely placed substituents in the lactone.

INTRODUCTION

The recent interest in C–C bond formation *via* free radical processes[1] has instigated a number of important applications in the carbohydrate field[1,2]. The facile formation of *C*-allyl derivatives from the reaction of organic halides with allyl tributylstannane[3] was extended by Keck and Yates[4] to polyfunctional molecules. In this seminal work, it was demonstrated that *C*-allylation of a variety of carbohydrate derivatives could be effected at primary, secondary, and anomeric positions. This reaction has been a useful method for *C*-branching, and it has been used as a key step in the synthesis of a number of natural products[5]. In most of the reported cases, stereochemical control was observed, particularly when steric bias was clearly manifested, resulting in an *anti* disposition of the *C*-allyl group relative to the vicinal bulky substituent. Stereochemical control was also seen at the anomeric carbon atom due to stereoelectronic effects associated with the 2-tetrahydropyranyl radical[6], for example. In addition to the versatile allyl group, a number of other groups have been introduced at the anomeric position in carbohydrates *via* radical-mediated processes[7] and with excellent stereocontrol.

Palladium(II)-catalyzed *C*-allylation of organic halides is well known[8], although applications to carbohydrates have not been exploited. One limitation to such *C*-allylation has been the presence, in the halide counterpart, of a β-hydrogen on an sp^3 carbon atom which results in β-elimination subsequent to oxidative addition[9]. A notable exception to this behavior has been reported by Simpson and Stille[10] in the Pd(II)-mediated coupling of 2-bromo-1,4-butanolide and 2-haloesters with allyltribu-

* This paper is dedicated to Prof. S. David on the occasion of his 70th birthday, and wishing him the best in chemistry and in life.

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tylstannane. In the absence of the catalyst, higher temperatures were required for free radical coupling of organotin reagents with α-haloesters[11].

In view of the versatility of the allyl group and the utility of branched-chain deoxy sugar derivatives as chirons in total synthesis, we became interested in exploring the *C*-allylation of readily available 2-bromolactones under free-radical conditions, but in the absence of Pd(II) as a catalyst. Such issues as stereochemical control, compatibility of existing functionality, and overall efficiency were added incentives for this investigation. We have recently shown preparatively useful examples of stereocontrolled free radical *C*-allylation in the penicillin series[12], as well as of the seldom-exploited intramolecular cyclizations of α-haloesters in allylic and homoallylic systems to give enantiomerically pure γ- and δ-lactones[13,14].

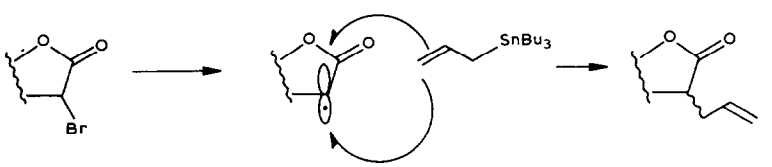
RESULTS AND DISCUSSION

In this paper, we report on the reactions of (±)-2-bromo-4-butanolide, (±)-2-bromo-4-methyl-4-butanolide (**2**), and various *O*-substituted 2-bromo-2-deoxy-D-arabinono-1,4-lactones (**3**–**8**) with allyltributylstannane in the presence of a catalytic quantity of azoisobutyronitrile. In all cases, *C*-allylation took place smoothly and in high yields (Table I, Scheme 1). A general procedure described for (±)-2-bromo-1,4-butanolide (**1**) (Table I, entry a) was applicable to all the other cases studied, with minor variations in the time period of reflux needed to complete the reactions. The most intriguing aspect of these *C*-allylations was the stereochemical outcome in the cases of

TABLE I

C-Allylation of α-bromolactones **1**–**8**

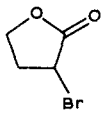
Entry	*α-Bromo-lactone*	*Reflux time (h)*	*Yield (%)*	*2-C-Allyl lactones*	*Ratio*	
					By n.m.r. or h.p.l.c.	*By weight*
a	**1**	2	85	**9**		
b	**2**	3	95	**10** + **11**	1:4	
c	**3**	3	85	**12** + **14**	6:5	
d	**4**	3	92	**13** + **15**		1:2
e	**5**	2	90	**16** + **17**		10:23
f	**6**	2	92	**16** + **17**		10:21
g	**7**	0.75	85	**13** + **15**		5:8
h	**8**	0.75	88	**18** + **19**	1:2	



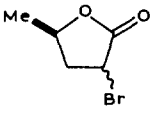
Scheme 1.

substituted 1,4-butanolides. Thus, in entry b (Table I), a *syn* and *anti* mixture of racemic 2-*C*-allyl lactones **10** and **11** was obtained in a 1:4 ratio, as proved by n.O.e. measurements. Since the presence of the 4-methyl substituent cannot be solely responsible for the preponderance of the *anti*-*C*-allyl isomer **11**, it can be surmised that the stabilized radical must have an inherent preference for an *anti* attack, assuming that no epimerization took place from an initially formed *syn* product. In fact, the products **10** and **11** were each configurationally stable under the conditions of the reaction.

The situation with the 2-bromo-2-deoxy-D-arabinonolactone derivatives[15] **3–8** was significantly different however. Thus, in the unsubstituted lactone **3**, an equal ratio



1



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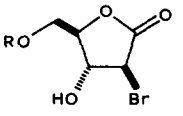
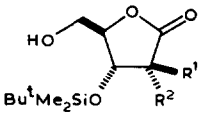


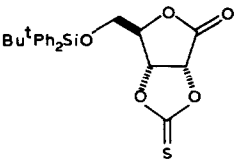
3 R = H

4 R = Bu^tPh_2SiO



5 R^1 = Br, R^2 = H

6 R^1 = H, R^2 = Br



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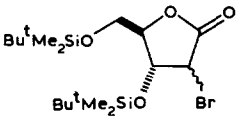
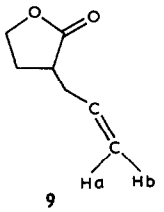


8 (2:1 β:α)



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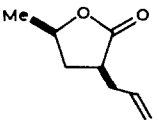

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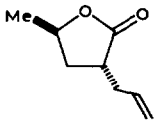

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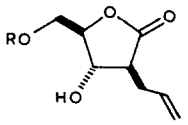
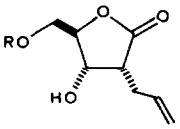


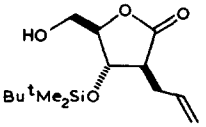
12 R = H

13 R = Bu^tMe_2SiO



14 R = H

15 R = Bu^tMe_2SiO



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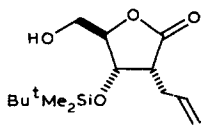

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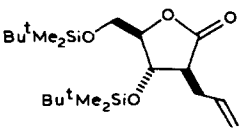

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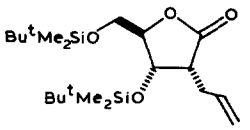
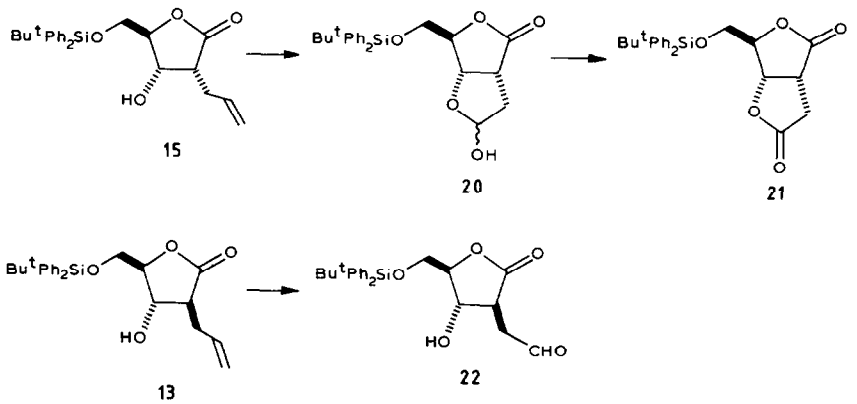


19

of the D-*arabino* isomer **12** and the D-*ribo* isomer **14** was observed. When the steric bulk of the primary hydroxyl group was increased, as in **4**, the favored product was the D-*ribo* isomer **15**, although the ratio was not as impressive as in enolate alkylations of related lactones where steric effects are operative[16]. Changing the polarity of the solvent to a 2:1 mixture of benzene and acetonitrile, in the case of **4**, changed the *arabino*-to-*ribo* ratio to 1:1, thus emphasizing the importance of polar effects. In this and other cases, the use of allyltriphenylstannane resulted in slower reaction rates, but the ratios remained the same as in the case of allyltributylstannane. However, increasing the steric bulk in the immediate vicinity of the forming radical, such as in the *tert*-butyldimethylsilyl derivatives **5**, **6**, and **8** (Table I; entries e, f, and h) did not alter the *arabino*- to-*ribo* ratio, as compared to that in entry d. Thus, unlike the important directing effects of bulky α-substituents in enolate alkylations of 1,4-lactones, the free-radical counterparts shown here are less subject to such effects. The diacetate corresponding to **3** also led to a 1:2 ratio of *arabino*-to-*ribo* isomers. That the original configuration of the bromide had little if any (entries e and f) bearing on the stereochemical outcome of the reaction was demonstrated in the case of **5**, **6**, and **8**, since the same ratio of products was obtained when an epimeric mixture of bromides (entry h) or when individual isomers (entries e and f) were used. Interestingly, the 2,3-thionocarbonate **7** (entry g) also led to a mixture of **13** and **15** where the D-*ribo* isomer was once again the slightly favored isomer.

The configurational identity of the enantiomerically pure 2-*C*-allyl lactones in the D-*arabino*-to-D-*ribo* series was secured by chemical means (Scheme 2). Thus, oxidative cleavage of **15** with ozone, followed by further oxidation with pyridinium chlorochromate led to lactone **21**, showing the *syn* relationship between the original *C*-allyl group and OH-3. A similar oxidation of **13** gave the corresponding aldehyde derivative **22**, which upon further oxidation with pyridinium chlorochromate did not give a lactone but led to decomposition after prolonged reaction times.

The precise underlying reasons for the variation in the ratios of the D-*arabino*-to-D-*ribo* isomers in entries c–h are not entirely evident. Based on steric grounds alone, one



Scheme 2.

would have expected a larger proportion of the D-*ribo* isomer in entry d, and a preponderance of the D-*arabino* isomer in the reactions of **5** and **6** (entries e and f). We surmise that once a radical is formed at C-2 in these lactones, its reactivity can be a function of several factors, including the resonance-stabilizing effect of the carbonyl group[19], steric bulk[20], dipolar (electronic), and stereoelectronic effects[6,21]In addition, the β-oxygen effect, demonstrated by Barton *et al.*[22], may be operational in stabilizing such radicals. Excluding the existence of a bridging phenomenon by a neighboring oxygen atom[9], the observed stereochemical outcome of these *C*-allylations may be the result of a combination of the aforementioned effects. Thus, a dipolar repulsive effect by O-3 may be responsible for the preponderance of the D-*arabino* isomer in entry c compared to the other entries. This effect is somewhat counterbalanced by the steric bulk of the C-5 substituent in entry d, thus favoring the D-*ribo* isomer. The results in entries e and f are perhaps the most intriguing, since the D-*ribo* isomer is favored by a ratio of 2:1 over the D-*arabino* isomer *in spite of the presence of the bulky substituent at C-3*. It is possible that prior coordination of the organotin species to OH-5 effectively acts as a shield for further attack from the same side. This result would conform with the ratios observed in entry h where steric bulk is present at C-3 and C-5. Coordination to the free hydroxyl groups in the radical formed from **3** (entry c), if operative, most probably involves the primary hydroxyl group. In this case, the dipolar repulsive effect of O-3 directs the *C*-allylation toward the D-*arabino* isomer, counteracting the steric effect of the transient coordinated species. An alternative mechanism to explain the stereochemical outcome of *C*-allylation *syn* to an adjacent hydroxyl group in entries d–h may involve internal transfer of the allyl group from a tin–oxygen coordinated species[23]. This, however, would involve large rings and may be a disfavored intramolecular process.

Regardless of mechanistic aspects, we have demonstrated the utility of the allylstannane method to prepare enantiomerically pure 2-*C*-allyl-2-deoxy-D-pentono-lactones that are not readily accessible by other means. In this regard, free-radical processes present a definitive advantage over enolate anion alkylations, since these would be prone to β-elimination unless the OH-3 derivatives are utilized, hence the need to work with dianions[24–26]. Examples of the alkylations of such dianions are rare in the carbohydrate series[24]. Furthermore, the compatibility of the reaction conditions with the presence of unprotected hydroxyl groups presents a definite operational asset in free-radical reactions.

EXPERIMENTAL

Genral methods. — Melting points were determined using a Büchi melting point apparatus and are uncorrected. Optical rotations were measured on a Perkin–Elmer 231 polarimeter. I.r. spectra were recorded with a Perkin–Elmer 781 spectrometer. ^{1}H-N.m.r. spectra were recorded either with a 300 MHz Varian VXR-300, or a 400 MHz Brüker WH-400 spectrometer at room temperature; chemical shifts (δ) were recorded relative to chloroform (δ 7.265) as the standard. Mass spectra were recorded with a VG

Micromass 1212 low-resolution instrument, or a AEI-MS 902 instrument for high resolution. All reactions were monitored by t.l.c., and the products were detected by either H_2MoO_4–$Ce(SO_4)_2$ solution, or $KMnO_4$–M H_2SO_4 as the indicator. T.l.c. was done on commercial precoated plates (Merck, 0.25 mm thick, Kieselgel $60F_{254}$), and flash chromatography, according to Still *et al.*[25], on silica gel (Merck No. 9385, 230–400 mesh). Microanalyses were performed at the Guelp Chemical Laboratories Ltd., Guelph, Ont., Canada.

General procedure for the free-radical allylation of 2-bromolactones. — To a solution of the lactone (1 mmol) in dry benzene (5 mL) were added, in succession, allyltributylstannane (1.1 mmol) and a catalytic amount (10 mg) of azoisobutyronitrile. The solution was refluxed until the starting material was consumed, then it was concentrated *in vacuo* to a syrup which was purified by flash column chromatography.

(±)-*2-Allyl-1,4-butanolide* (**9**). — From (±)-2-bromo-1,4-butanolide (**1**; 165 mg, 1 mmol) was obtained **9** after flash column chromatography (solvent gradient, 0→20% ethyl acetate in hexane). The product was then distilled at 125–135°/8 mmHg (Kugelrohr) to give **9**[10] (113 mg, 90%); ν_{max}^{NaCl} 2920, 1770, 1645, 1160, and 1025 cm^{-1}; ^{1}H-n.m.r. (300 MHz, $CDCl_3$); δ 5.78 (m, 1 H, C*H*=CH_2), 5.12 (dm, 1 H, *J* 19.9 Hz, Ha of –CH=CH_2), 5.11 (dm, 1 H, *J* 9.1 Hz, Hb of –CH=CH_2), 4.33 (tdd, 1 H, *J* 8.8, 3.2, 0.9, H-4), 4.20 (tdd, 1 H, *J* 9.3, 6.9, 0.9 Hz, H-4'), 2.62 (m, 1 H, C*H*H'CH=CH_2), 2.38 (m, 1 H, CH*H'*CH=CH_2), 2.17 (m, 1 H, H-3), and 1.96 (m, 1H, H-3'); m.s.: *m/z* 127 (100, M + 1); *m/z* 126.0682 (M^+), (calc. for $C_7H_{10}O_2$, 126.0681).

(±)-2-*Allyl-4-methyl*-threo-*1,4-butanolide* (**10**) *and* (±)-*2-allyl-4-methyl*-erythro-*butanolide* (**10**) — Commercially available (±)-2-bromo-4-methyl-1,4-butanolide (**2**; 280 mg, 1.5 mmol), as a 1:1 mixture of *erythro* and *threo* isomers, gave after flash column chromatography (1:9 ethyl acetate–hexane) and distillation at 165–170°/8mm an inseparable syrupy mixture of **10** and **11** (200 mg, 92%); ν_{max}^{NaCl} 2980, 1770, 1645, and 1170 cm^{-1}; ^{1}H-n.m.r. (400 MHz, $CDCl_3$): δ 5.85 (m, C*H*=CH_2, **10** and **11**), 5.10 (dm, *J* 13.3 Hz, Ha of –CH=CH_2, **10** and **11**), 5.08 (dm, *J* 5.7 Hz, Hb of –CH=CH_2, **10** and **11**), 4.65 (m, H-4, **10**), 4.50 (m, H-4, **11**), 2.75 (m, H-2, **10**), 2.73 (m, H-2, **11**), 2.63 (m, C*H*H'–CH–CH_2, **11**), 2.55 (m, C*H*H'–CH=CH_2, **10**), 2.45 (ddd, *J* 12.5, 8.4, 5.6 Hz, H-3 *syn* to Me, **11**), 2.29 (m, CH*H'*–CH=CH_2, **10**), 2.26 (m, CH*H'*–CH=CH_2, **11**), 2.16 (dt, *J* 13.1, 7.7 Hz, H-3 *anti* to Me, **10**), 1.98 (ddd, *J* 16.1, 11.6, 7.2 Hz, H-3 *syn* to Me, **10**), 1.56 (m, H-3 *anti* to Me, **11**), 1.45 (d, *J* 4.5 Hz, H-5, **11**), and 1.35 (d, *J* 4.7 Hz, H-5, **10**); m.s.: *m/z* 141 (100, M + 1).

Anal. Calc. for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.52, H, 8.51.

*2-Bromo-5-*O-tert-*butyldiphenylsilyl-2-deoxy-*D-*arabinono-1,4-lactone* (**4**). — In a dry flask under Ar were placed **3** (2.2 g, 10 mmol), *N,N*-dimethylformamide (50 mL), and imidazole (2.18 g, 32 mmol). The solution was cooled in an ice bath, and *tert*-butylchlorodiphenylsilane (2.95 g, 11 mmol) was added in portions over a period of 15 min. The solution was stirred at 0° for 1.5 h., and then poured into ether, washed twice with water, three times with 10% HCl solution, twice with sat. $NaHCO_3$ solution, and three times with sat. NaCl. After drying ($MgSO_4$) and concentrating *in vacuo*, the resulting oil was purified by flash chromatography (1:4 ethyl acetate–hexane) to give **4**

(3.5 g, 75%), $[\alpha]_D^{25}$ +27° (*c* 1.7, $CHCl_3$); ν_{max}^{NaCl} 3470, 2930, 1780, 1430, 1115, and 705 cm^{-1}; ^{1}H-n.m.r. (400 MHz, $CDCl_3$): δ 7.69–7.64 (arom.), 7.48–7.40 (arom.), 4.73 (m, 1 H, H-3), 4.50, (d, 1 H, *J* 7.6 Hz, H-2), 4.33 (m, 1 H, H-4), 3.99 (dd, 1 H, *J* 11.8, 3.5 Hz, H-5a), 3.90 (dd 1 H, *J* 11.9, 3.6 Hz, H-5b), 2.86 (br. s, 1H, OH), and 1.08 (s 9H, Bu^{t}Si).

Anal. Calc. for $C_{21}H_{25}BrO_4Si$; C, 51.12; H, 5.61. Found: C, 50.86: H, 5.32.

*2-C-Allyl-5-*O-tert-*butyldiphenylsilyl-2-deoxy-*D-*arabinono-1,4-lactone* (**13**) *and 2-C-allyl-5-*O-tert-*butyldiphenylsilyl-2-deoxy-*D-*ribono-1,4-lactone* (**15**). — From **4** (449 mg, 1 mol) in dry benzene containing (5 mL) allyltributylstanne (400 mg, 1.2 mmol) and azoisobutyronitrile (15 mg) were obtained, after flash chromatography (1:9 ethyl acetate–hexane), **13** (143 mg (35%) and **15** (242 mg, 59%).

Compound **13**. $[\alpha]_D^{25}$ +25° (*c* 0.4, $CHCl_3$); ν_{max}^{NaCl} 3450, 3170, 2930, 1775, 1645, 1595, 1490, and 1115 cm^{-1} ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 7.96 (m, 4 H, arom.), 7.42 (m, 6 H, arom.), 5.86 (m, 1 H, C*H* = CH_2), 5.2 (dm, 1H, *J* 18 Hz, Ha of –CH = CH_2), 5.15 (dm, 1H, *J* 10 Hz, Hb of –CH = CH_2), 4.38 (br. t, 1 H, *J* 8.9 Hz, H-3), 4.19 (dt, 1H, *J* 7.4, 4.2 Hz, H-4), 3.94 (d, *J* 1H, 10 Hz, H-5a), 3.91 (d, 1H, *J* 4.2 Hz, H-5b), 2.78–2.62 (m, 2 H, H-2 and C*H*H'CH = CH_2), 2.41 (m, 1 H, CH*H'*CH = CH_2) 1.96 (br. s, 1 H, OH), and 1.07 (s, 9H, Bu^{t}Si); m.s.: *m/z* 411 (22.0, M + 1), 255 (60.0, Bu^tMe_2SiO).

Anal. Calc. for $C_{24}H_{30}O_4Si$: C, 70.21; H, 7.35. Found: C, 69.87; H, 7.22.

Compound **15**. $[\alpha]_D^{25}$ +14° (*c* 0.8, $CHCl_3$); ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 7.63 (m, 4 H, arom.), 7.41 (m, 6H, arom.), 5.94 (m, 1H, C*H* = CH_2), 5.21 (dq, 1 H, *J* 16.0 Hz, Ha of –CH = CH_2), 5.16 (d, 1H, *J* 10.0 Hz, Hb of –CH = CH_2), 4.69 (d, 1 H, *J* 6.3 Hz, H-3), 4.30 (t, 1H, *J* 3.2 Hz, H-4), 3.86 (d, 1H, *J* 3.7 Hz, H-5a), 3.83 (d, 1H, *J* 3.2 Hz, H-5b), 3.05 (m, 1H, H-2), 2.69 (dm, 1H, *J* 15 Hz, C*H*H'CH = CH_2), 2.47 (dq, 1H, *J* 15.0, 8.0 Hz, CH*H'*CH = CH_2), 1.92 (br. s, 1 H, OH), and 1.02 (s, 9H, Bu^{t}Si).

Anal. Calc. for $C_{24}H_{30}O_4Si$: C, 70.21; H, 7.35. Found: C, 69.93; H, 7.27.

*Mixture of 2-bromo-3,5-*O-*di(*tert-*butyldimethysilyl)-2-deoxy-*D-*arabinono-1,4-lactone and-*D-*ribono-1,4-*lactone (**8**). — In a dry flask were placed **3** (386 mg, 1.8 mmol), *N,N*-dimethylformamide (5.6 mL), *tert*-butychlorodimethylsilane (703 mg, 4.7 mmol), and imidazole (613 mg, 9 mmol). The solution was stirred for 12 h at room temperature, and then poured into ether, washed sequentially with 10% HCl, sat. $NaHCO_3$ solution, and finally with water to neutrality. After drying ($MgSO_4$) and concentrating *in vacuo*, the resulting oil was purified by flash chromatography (3:97 ethyl acetate–hexane) to give **8** (683 mg, 85%) as an inseparable mixture of epimers at C-2 (2:1 ratio of *arabino*-to-*ribo* epimers); ν_{max}^{NaCl} 2950, 1800, 1430, 1260, 1150, 840, and 785 cm^{-1}; ^{1}H-n.m.r. (400 MHz, $CDCl_3$): δ 4.70 (dd, *J* 6.1, 6.1 Hz, H-3 of D-*arabino*), 4.50 (d, *J* 5.8 Hz, H-2 of D-*ribo*), 4.42 (dd, *J* 5.8, 5.8 Hz, H-3 of D-*ribo*), 4.40 (d, *J* 6.2 Hz, H-2 of D-*arabino*), 4.34 (m, H-4 of D-*ribo*), 4.24 (m, H-4 of D-*arabino*), 3.96 (m, H-5a of D-*arabino* and D-*ribo*), 3.81 (m, H-5b of D-*arabino* and D-*ribo*), 0.93, 0.89, (Bu^{t}Si of D-*ribo*), 0.91, 0.90 (of D-*arabino* Bu^{t}Si), and 0.20–0.08 (Me_3Si).

*2-Bromo-3-*O-tert-*butyldimethylsilyl-2-deoxy-*D-*arabinono-1,4-lactone* (**5**) *and 2-bromo-3-*O-tert-*butyldimethylsilyl-2-deoxy-*D-*ribono-1,4-lactone* (**6**). — The preceding mixture **8** (672 mg, 1.5 mmol) was placed in a flask containing oxolane (2.5 mL), water (2.5 mL), and acetic acid (4.8 mL). The solution was stirred for 5 days, poured into ether,

washed with water, $NaHCO_3$ solution, and water again. After drying ($MgSO_4$) and concentrating *in vacuo*, the two epimers were separated by flash chromatography (1:9 ethyl acetate–hexane), providing **5** (247 mg, 51%) and **6** (185 mg, 38%).

Compound **5**. $[\alpha]_D^{25}$ + 32° (*c* 1.4, $CHCl_3$); ν_{max}^{NaCl} 3460, 2940, 1800, 1155, 840, and 780 cm^{-1}; ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 4.63 (dd, 1H, *J* 7.6, 6.8 Hz, H-3), 4.46 (d, 1H, *J* 7.6 Hz, H-2), 4.27 (ddd, 1H, *J* 6.5, 3.6, 2.7 Hz, H-4), 4.02 (ddd, 1H, *J* 13.0, 5.1, 2.6 Hz, H-5a), 3.77 (ddd, 1H, *J* 13.0, 7.8, 3.6 Hz, H-5b), 0.91 (s, 9 H, Bu^{t}Si), 0.22 (s, 3 H, MeSi), and 0.16 (s, 3H, MeSi).

Anal. Calc. for $C_{11}H_{21}BrO_4Si$; C, 40.62; H, 6.51. Found C, 40.69; H, 6.81.

Compound **6**. M.p. 60–62°; $[\alpha]_D^{25}$ + 110° (*c* 0.6, $CHCl_3$); ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 4.44 (d, 1H, *J* 10.0 Hz, H-2), 4.43 (t, 1H, *J* 10.0 Hz, H-3), 4.37 (m, 1H, H-4), 4.07 (ddd, 1H, *J* 13.0, 4.8, 2.2 Hz, H-5a), 3.76 (ddd, 1H, *J* 13.0, 7.7, 2.4 Hz, H-5b), 0.93 (s, 9H, Bu^{t}Si), 0.16 (s, 3H, MeSi), and 0.14 (s, 3H, MeSi).

2-C-Allyl-3-O-tert-butyldimethylsilyl-2-deoxy-D-arabinono-1,4-lactone (**16**) *and 2-C-allyl-3-O-tert-butyldimethylsilyl-2-deoxy-D-ribono-1,4-lactone* (**17**). — From **5** or **6** (322 mg, 1 mmol) in dry benzene (5 mL) containing allyltributylstannane (400 mg) and azoisobutyronitrile (10 mg) were obtained, after flash column chromatography (1:4 ethyl acetate–hexane), **16** (76 mg, 27%) and **17** (177 mg, 63%).

Compound **16**. $[\alpha]_D^{25}$ + 36° (*c* 0.8, $CHCl_3$); ν_{max}^{NaCl} 3460, 2920, 1780, 1150, 1130, 840, and 780 cm^{-1}; ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 5.80 (m, 1H, C*H* = CH_2), 5.19 (dm, 1H, *J* 15.0 Hz, Ha of –CH = CH_2), 5.15 (d, 1H, *J* 9.0 Hz, Hb of –CH = CH_2), 4.31 (dd, 1H, *J* 8, 6.0 Hz, H-3), 4.19 (m, 1H, H-4), 3.99 (ddd, 1 H, *J* 13.1, 5.7, 2.4 Hz, H-5a), 4.71 (ddd, 1H, *J* 13.1, 7.8, 4.2 Hz, H-5b), 2.75 (dt, 1H, *J* 7.0, 6.0 Hz, H-2), 2.58 (m, 1H, C*H*H′CH = CH_2), 2.49 (m, 1H, CH*H*′CH = CH_2), 0.91 (s, 9H, Bu^{t}Si), 0.13 (s, 3H, MeSi), and 0.12 (s, 3H, MeSi); m.s.: *m/z* 287 (45, M + 1), 115 (45, Bu^{t}Me$_2$Si), and 73 (100).

Anal. Calc. for $C_{14}H_{26}O_4Si$: C, 58.70; H, 9.15. Found: C, 58.59; H, 9.11.

Compound **17**. M.p. 76–78° (from hexane), $[\alpha]_D^{25}$ – 8.3° (*c* 1.2, $CHCl_3$); ν_{max}^{KBr} 3320, 2960, 1760, 1060, 840, and 780 cm^{-1}; ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 5.9 (m, 1H, C*H* = CH_2), 5.15 (d, 1H, *J* 16.7 Hz, Ha of –CH = CH_2), 5.09 (d, 1H, *J* 9.5 Hz, Hb of –CH = CH_2) 4.50 (dd, 1H, *J* 5.7, 1.8 Hz, H-3), 4.31 (m, 1H, H-4), 3.90 (dd, 1H, *J* 12.5, 5.7 Hz, H-5a), 3.78 (ddd, 1H, *J* 12.5, 6.6, 5.7 Hz, H-5b), 2.82 (dt, 1H, *J* 9.6, 6.3 Hz, H-2), 2.51 (m, 2H, CH_2CH = CH_2), 0.92 (s, 9H Bu^{t}Si), 0.14 (s, 3H, MeSi), and 0.12 (s, 3H, MeSi); m.s.: same as for **16**.

Anal. Calc. for $C_{14}H_{26}O_4Si$: C, 58.70; H, 9.15. Found: C, 58.64; H, 9.02.

2-C-Allyl-2-deoxy-D-arabinono-1,4-lactone (**12**) *and 2-C-allyl-2-deoxy-D-ribono-1,4-lactone* (**14**). — *From* **13** *and* **15**. A solution of **13** (62 mg, 0.15 mmol) in oxolane (3 mL) containing acetic acid (40 μL) and M tetrabutylammonium fluoride in oxolane (200 μL) was stirred for 12 h. The solvent was evaporated *in vacuo* and the oily residue was purified by flash column chromatography (2:1 ethyl acetate–hexane) to give **12** (21 mg, 81%), white solid, m.p. 43–45°, $[\alpha]_D^{25}$ + 77° (*c* 0.5, ethyl acetate); ν_{max}^{NaCl} 3405, 2930, 1760, 1645, 1180, and 1050 cm^{-1}; ^{1}H-n.m.r. (300 MHz, CD_3OD): δ 5.87 (m, 1H, C*H* = CH_2), 5.28 (dq, 1H, *J* 17.0, 2.3 Hz, Ha of –CH = CH_2), 5.09 (dm, 1H, *J* 10.0 Hz, Hb of –CH = CH_2), 4.88 (s, OH), 4.15 (t, 1H, *J* 1.3 Hz, H-4), 4.13 (t, 1H, *J* 0.9 Hz, H-3), 3.87

(dd, 1H, *J* 12.6, 2.0 Hz, H-5a), 3.65 (dd, 1H, *J* 12.7, 3.9 Hz, H-5b), 2.69 (m, 1H, H-2), and 2.48 (m, 2H, $CH_2CH=CH_2$); m.s.: *m/z* 173 (100, M + 1).

Anal. Calc. for $C_8H_{12}O_4$: C, 55.81; H, 7.02;. Found: C, 55.78; H, 6.88.

In the same manner, **14** was obtained from **15** (74%) as a white solid, m.p. 43–44°, $[\alpha]_D^{25}$ − 10.5° (*c* 0.5, ethyl acetate); ν_{max}^{NaCl} same as for **12**; ^{1}H-n.m.r. (300 MHz, CD_3OD): δ 5.95 (m, 1H, $CH=CH_2$), 5.26 (dq, 1H, *J* 17.0, 1.8 Hz, Ha of $-CH=CH_2$), 5.04 (dm, 1H, *J* 10.0 Hz, Hb of $-CH=CH_2$), 4.89 (s, OH), 4.39 (d, 1H, *J* 6.0 Hz, H-4), 4.32 (td, 1H, *J* 3.9, 0.9 Hz, H-3), 3.73 (dd, 1H, *J* 12.4, 4.25 Hz, H-5a), 3.71 (dd, 1H, *J* 12.4, 4.03 Hz, H-5b), 2.87 (dt, 1H, *J* 6.6, 7.5 Hz, H-2), and 2.42 (t, 2H, *J* 7.4 Hz, $CH_2CH=CH_2$); m.s.: same as for **12**.

Anal. Calc. for $C_8H_{12}O_4$: C, 55.81; H, 7.02. Found: C, 55.73; H, 6.81.

From **3**. To a solution containing **3** (211 mg, 1 mol) in benzene (5.5 mL) and acetonitrile (3 mL) were added allyltributylstannane (497 mg, 1.5 mol) and azoisobutyronitrile (10 mg). After being heated at reflux for 3h, the solution was processed as usual to give an inseparable mixture of **12** and **14** (220 mg, 85%).

C-*Allylation of* **7**. — A solution of **7** (72 mg, 0.17 mmol) in benzene (3 mL) was treated with allyltributylstannane (77 mg, 0.23 mmol) and azoisobutyronitrile. Refluxing for 45 min and the usual processing gave **13** (23 mg, 32%) and **15** (37 mg, 53%).

C-*Allylation of* **8**. — A solution of **8** (154 mg, 0.35 mmol) in benzene (2 mL) was treated with allyl tributylstannane (136 mg, 0.42 mmol) and azoisobutyronitrile (7 mg) at reflux for 45 min. The usual processing gave **18** and **19** (123 mg, 88%) as an inseparable mixture; ν_{max}^{NaCl} 3080, 2960, 2930, 1785, 1643, 1255, 1130, 840, and 760 cm^{-1}; ^{1}H-n.m.r. (400 MHz, $CDCl_3$): δ 5.88 (m, $CH=CH_2$, **19**), 5.78 (m, $CH=CH_2$, **18**), 5.16 (dd, *J* 19.7, 1.8 Hz, Ha $-CH=CH_2$, **19**), 5.12 (dd, *J* 11.0, 1.2 Hz, Hb of $-CH=CH_2$ **18**), 5.11 (dd, *J* 18.2, 2.3 Hz, Ha $-CH=CH_2$, **18**), 5.01 (dd, *J* 14.3, 0.9 Hz, Hb of $-CH=CH_2$ **19**), 4.46 (d, *J* 6.0 Hz, H-3, **19**), 4.42 (dd, *J* 6.6, 5.7 Hz, H-3, **18**), 4.28 (t, *J* 2.4 Hz, H-4, **19**), 4.13 (m, H-4, **18**), 3.92 (dd, *J* 12.5, 3.6 Hz, H-5a, **18**), 3.78 (d, *J* 4.8 Hz, H-5a, **19**), 3.77 (d, *J* 4.2 Hz, H-5b, **19**), 3.76 (dd, *J* 12.5, 1.5 Hz, H-5b, **18**), 2.83 (m, H-2, **19**), 2.70 (m, H-2, **18**), 2.60–2.39 (m, $CH_2CH=CH_2$, **18** and **19**), 0.91, 0.90 (Bu^{t}Si, **18**), 0.89, 0.88 (Bu^{t}Si, **19**), 0.10 (s, MeSi, **18** and **19**), 0.09 (s, MeSi, **18** and **19**), 0.081, 0.080 (MeSi, **18**), and 0.07, 0.06 (MeSi, **19**); m.s.: *m/z* 401 (100, M + 1), and 269 (65, Bu^{t}Me$_2$SiO).

Oxidative cleavage of **15** *and synthesis of* 5-O-tert-*butyldiphenylsilyl-2-deoxy*-D-*ribono-1,4-lactone-2,3-carbolactone*. — A solution containing **15** (200 mg, 0.5 mmol) in dichloromethane (10 mL) was cooled to − 78° and a stream of O_3 was bubbled in to it for 10 min. Dimethyl sulfide was added and the temperature was allowed to rise to 25°. Evaporation of the solvent gave the lactol **20** (61%) as a 2:1 mixture of epimers (δ 5.60, d, *J* 4.4 Hz, major anomer; δ 5.70, d, *J* 5.0 Hz, minor anomer). The lactol (123 mg, 0.3 mmol) was oxidized with pyridinium chlorochromate (193 mg, 0.9 mmol) in dichloromethane (3 mL) containing 4A molecular sieves (500 mg). After 5 h, the mixture was filtered over Celite, the fitrate was concentrated to dryness, and the residue was purified by flash column chromatography (1: 4 ethyl acetate–hexane) to give **21** (101 mg, 82%), $[\alpha]_D^{25}$ − 29° (*c* 0.9, $CHCl_3$); ν_{max}^{NaCl} 2960, 1785, 1060, 840, and 780 cm^{-1}; ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 7.63–7.61 (arom.), 7.49–7.40 (arom.), 5.19 (d, 1H, *J* 6.6 Hz, H-3), 4.73

(t, 1H, *J* 2.0 Hz, H-4), 3.99 (dd, 1H, *J* 11.7, 2.4 Hz, H-5a), 3.86 (dd, 1H, *J* 11.7, 1.8 Hz, H-5b), 3.59 (ddd, 1H, *J* 9.3, 6.6, 3.2 Hz, H-2), 2.97 (dd, 1H, *J* 18.5, 9.3 Hz, H of acetyl *endo*), 2.94 (dd, 1H, *J* 18.5, 3.2 Hz, H of acetyl *exo*), and 1.05 (s, 9 H, Bu'Si).

Anal. Calc. for $C_{23}H_{26}O_5Si$: C, 67.29; H, 6.38. Found: C, 67.01; H, 6.22.

Ozonolysis of **13** under the same conditions gave the corresponding lactone aldehyde, 5-*O*-*tert*-butyldiphenyl-2-deoxy-2-*C*-formylmethyl-D-*arabinono*-1,4-lactone (**22**; 58%), $[\alpha]_D^{25}$ + 32° (*c* 0.6, $CDCl_3$); ν_{max}^{NaCl} 1770 and 1715 cm^{-1}; ^{1}H-n.m.r. (400 MHz, $CDCl_3$): δ 9.85 (s, CHO).

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