A Novel Method for the Synthesis of Anomerically Allylated *C*-Glycofuranosides. An Unusual Lewis Acid-catalysed Rearrangement of an Oxetanosyl-*N*-glycoside† to Furanosyl-*C*-glycosides

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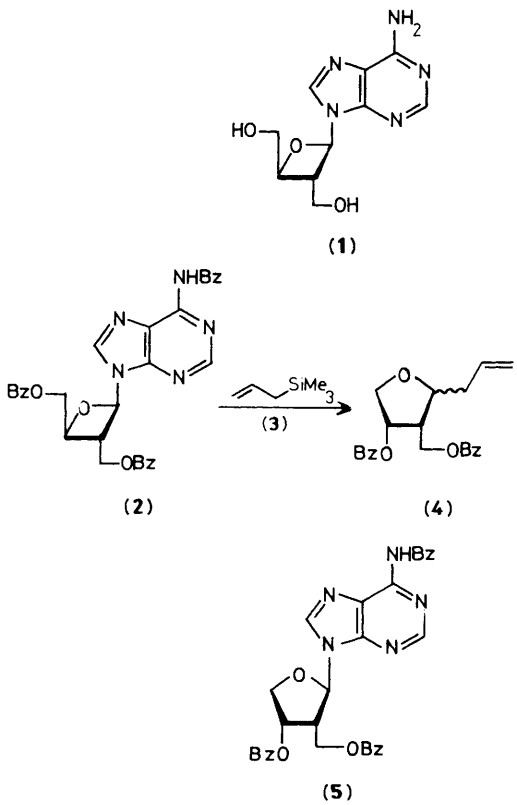
An oxetanosyl-*N*-glycoside is converted into furanosyl-*C*-allylglycosides with allyltrimethylsilane in the presence of Lewis acid.

Many reactions of allylic trimethylsilanes involve electrophilic substitution with allylic rearrangement and loss of the trimethylsilyl group to make a carbon–carbon bond. Recently these bond formation reactions have been applied to the synthesis of *C*-glycosides, particularly *C*-allylglycosides,[1] owing to the potential use of such materials in the total synthesis of natural products such as the pseudomonic acids[2] and palytoxin.[3] Further, epoxides[4] and oxetanes[5] react with allylic trimethylsilanes in the presence of Lewis acids to give homoallylic alcohols and hex-5-en-1-ols, respectively.

In continuation of our studies on the chemical properties of the oxetane ring of oxetanocin (**1**),[6] we have found that the oxetanosyl-*N*-glycoside was converted into furanosyl-*C*-allylglycosides with allyltrimethylsilane.

When *N*-benzoyloxetanocin dibenzoate (**2**) was treated with allyltrimethylsilane (**3**) in the presence of $SnCl_4$ or BF_3–OEt_2 in MeCN, 2-deoxy-2-hydroxymethyl-D-erythrofuranosyl-1-allylglycoside dibenzoates, α- and β-(**4**),‡ were obtained in moderate yields (Scheme 1). In the absence of (**3**), however, N^6-benzoyl-2-deoxy-2-hydroxymethyl-β-D-erythrofuranosyladenine dibenzoate (**5**)‡ was isolated as the sole product (Table 1). As expected, (**5**) could not be converted into (**4**)



Scheme 1. Bz = PhCO.

† Oxetanosyl is taken to refer to the four-membered sugar ring, analogous to furanosyl.

‡ ^{1}H N.m.r. data (400 MHz, $CDCl_3$) for α-(**4**): δ 2.42—2.50 (2H, complex), 2.82 (1H, m), 3.91 (1H, dd, *J* 2.93, 10.74 Hz), 4.25—4.34 (2H, complex), 4.43 (1H, dd, *J* 5.86, 10.74 Hz), 4.61 (1H, dd, *J* 5.86, 11.23 Hz), 5.14 (1H, dd, *J* 1.95, 10.26 Hz), 5.21 (1H, dd, *J* 1.47, 17.09 Hz), 5.58 (1H, m), 5.91 (1H, m), 7.43—7.47 (4H, complex), 7.55—7.61 (2H, complex), and 8.03—8.09 (4H, complex). β-(**4**): δ 2.53—2.61 (3H, complex), 3.91 (1H, dd, *J* 6.84, 12.69 Hz), 4.07 (1H, dd, *J* 4.88, 10.74 Hz), 4.15 (1H, dd, *J* 1.46, 10.74 Hz), 4.48 (1H, dd, *J* 5.86, 11.23 Hz), 4.54 (1H, dd, *J* 6.35, 11.23 Hz), 5.12—5.21 (2H, complex), 5.45—5.47 (1H, m), 5.88—5.94 (1H, m), 7.41—7.48 (4H, complex), 7.55—7.61 (2H, complex), and 8.02—8.07 (4H, complex). (**5**): δ 3.64—3.74 (1H, m), 4.51 (1H, dd, *J* 2.89, 10.80 Hz), 4.58 (1H, dd, *J* 4.36, 10.80 Hz), 4.69 (1H, dd, *J* 6.12, 11.49 Hz), 4.80 (1H, dd, *J* 5.70, 11.49 Hz), 5.64 (1H, ddd, *J* 2.53, 2.89, 4.36 Hz), 6.47 (1H, d, *J* 3.26 Hz), 7.37—7.66 (9H, complex), 7.85—7.92 (2H, complex), 7.96—8.09 (4H, complex), 8.34 (1H, s), 8.69 (1H, s), and 9.07 (1H, br.s).

Table 1. Lewis acid catalysed rearrangement of (**2**).

Entry	(**2**) (mmol)	(**3**) (mmol)	Acid (mmol)	Products[a]	Ratio α/β[b]	Total yield (%)[c]
1	1	10	$SnCl_4$ (5)[d]	(**4**)	1/5	43
2	1	10	BF_3OEt_2 (5)[d]	(**4**)	1/6	52
3	1	0	$SnCl_4$ (2)[e]	(**5**)	—	16
4	1	0	BF_3–OEt_2 (2)[f]	(**5**)	—	48

[a] All new compounds α- and β-(**4**), and (**5**) exhibited satisfactory analytical and spectral data. [b] Anomeric configuration was confirmed by ^{1}H n.m.r. data given by COSY, long-range COSY, and NOESY (400 MHz). [c] Yield of chromatographically purified products. [d] 30 min at 0 °C. [e] 85 min at room temp. [f] 120 min at room temp.

under the conditions used in entries 1 and 2 of Table 1. These results show that the oxetane ring in (**1**) was easily cleaved by a Lewis acid to give furanosyl compounds by a ring expansion accompanying transglycosidation. All attempts to react (**2**) with other silyl nucleophiles such as Me_3SiN_3, Me_3SiCN, and ketene silylacetals were unsuccessful and only (**5**) was obtained.

In conclusion, this is to the best of our knowledge the first example of the preparation of *C*-allylglycosides from an *N*-glycoside.§

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§ Similar results were obtained with allyltributyltin. The reaction mechanism has not been clarified yet.

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