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Deoxygenation of carbohydrates by thiol-catalysed radical-chain redox rearrangement of the derived benzylidene acetals

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Five- or six-membered cyclic benzylidene acetals, derived from 1,2- or 1,3-diol functionality in carbohydrates, undergo an efficient thiol-catalysed radical-chain redox rearrangement resulting in deoxygenation at one of the diol termini and formation of a benzoate ester function at the other. The role of the thiol is to act as a protic polarity-reversal catalyst to promote the overall abstraction of the acetal hydrogen atom by a nucleophilic alkyl radical. The redox rearrangement is carried out in refluxing octane and/or chlorobenzene as solvent at *ca.* 130 °C and is initiated by thermal decomposition of di-*tert*-butyl peroxide (DTBP) or 2,2-bis(*tert*-butylperoxy)butane. The silanethiols $(Bu^tO)_3SiSH$ and Pr^i_3SiSH (TIPST) are particularly efficient catalysts and the use of DTBP in conjunction with TIPST is generally the most effective and convenient combination. The reaction has been applied to the mono-deoxygenation of a variety of monosaccharides by way of 1,2-, 3,4- and 4,6-*O*-benzylidene pyranoses and a 5,6-*O*-benzylidene furanose. It has also been applied to bring about the dideoxygenation of mannose and of the disaccharide α,α-trehalose. The use of *p*-methoxybenzylidene acetals offers no great advantage and ethylene acetals do not undergo significant redox rearrangement under similar conditions. Functional group compatibility is good and tosylate, epoxide and ketone functions do not interfere; it is not necessary to protect free OH groups. Because of the different mechanisms of the ring-opening step (homolytic *versus* heterolytic), the regioselectivity of the redox rearrangement can differ usefully from that resulting from the Hanessian–Hullar (H.–H.) and Collins reactions for brominative ring opening of benzylidene acetals. When simple deoxygenation of a carbohydrate is desired, the one-pot redox rearrangement offers an advantage over H.–H./Collins-based procedures in that the reductive debromination step (which often involves the use of toxic tin hydrides) required by the latter methodology is avoided.

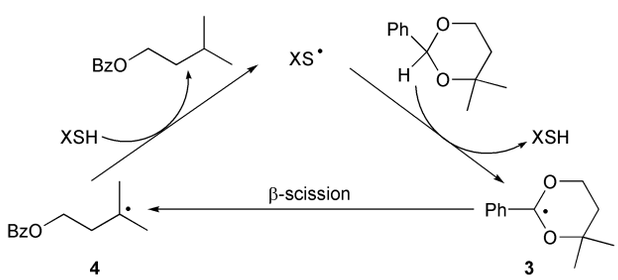
Introduction

Our continuing interest in applications of the principle of polarity-reversal catalysis[1] (PRC) has led us to explore the use of thiols to promote the radical-chain deoxygenation of alcohols[2] and of diols.[3–5] It has proved possible to devise methodology for deoxygenation of the ROH function through the use of suitable derivatives of the general type ROCHXY that can be induced to undergo a thiol-catalysed radical-chain redox decomposition to give RH and XYC=O, without the need for any other stoichiometric reagent.[2] For mono-deoxygenation of 1,2- or 1,3-diol functionality, we have reported[3–5] that the corresponding redox rearrangement of the derived benzylidene acetals,[6,7] as exemplified by the conversion of 2-phenyl-4,4-dimethyl-1,3-dioxane **1** to isopentyl benzoate **2** (Scheme 1),[3] is effectively catalysed by thiols. The propagation stage of the radical-chain mechanism is shown in Scheme 2.

1 **2**

Scheme 1

Provided that the two alternative benzoyloxyalkyl radicals that can result from β-scission of an unsymmetrical 2-phenyl-1,3-dioxanyl radical such as **3** do not interconvert prior to their trapping by the thiol, the selectivity of the overall deoxygenation process is determined by the regioselectivity of this β-scission step. Thus, in Scheme 2 the intermediate dioxanyl radical **3** undergoes highly selective β-scission with cleavage of the C(4)–O(3) bond to give the tertiary radical **4**, in preference to the primary alkyl radical that would arise from C(6)–O(1) bond cleavage, leading to isopentyl benzoate as the final product rather than *tert*-pentyl benzoate. However, the thermodynamic driving forces behind such potentially competitive homolytic cleavage processes do not necessarily always follow the 'expected' order 3°-C–O > 2°-C–O > 1°-C–O and we have recently discussed the various factors that determine the regioselectivity of the β-scission stage.[5]



4 **3**

Scheme 2

The mono-deoxygenation of diol functionality is of particular relevance in the area of carbohydrate chemistry and, in preliminary communications,[3,4] we have described the application of our methodology to the redox rearrangement of some carbohydrate benzylidene acetals. For example, when the glucopyranoside **5** in octane–chlorobenzene (1 : 1) was heated at *ca.* 130 °C for 3 h in the presence of 5 mol% each of 2,2-bis(*tert*-butylperoxy)butane (BBPB, **11**) and tri-*tert*-butoxysilanethiol $[(Bu^tO)_3SiSH]$, with repeat additions of peroxide and thiol after 40 min, the benzylidene acetal was converted essentially quantitatively into the benzoate esters **6** and **7** in the ratio 97 : 3.[3] † Similar results were obtained with the 2,3-di-

† Collidine (2,4,6-trimethylpyridine; 10 mol%) was also present in the reaction mixture.

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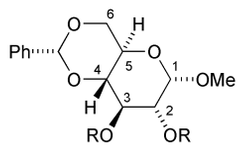
O-methyl derivative **8**, which yielded the deoxybenzoates **9** and **10** in the ratio 93 : 7.[4] The strong preference for cleavage of the primary-C–O bond, rather than the secondary-C–O bond, in the β-scission step is of significant interest from both theoretical and practical standpoints, the latter in that it allows for the ready regioselective formation of 6-deoxyglucose derivatives.

In contrast, the corresponding 2,3-di-*O*-methylgalactopyranoside **14**, a *cis*-fused analogue of the *trans*-fused bicyclic-[4.4.0]glucoside **8**, afforded mainly the 4-deoxybenzoate **10** under the same conditions (**15** : **10** = 38 : 62).[4] In order to identify the factors that govern regioselectivity in these complex bicyclic systems, we have recently investigated the redox rearrangement of a number of model non-carbohydrate benzylidene acetals and carried out density functional theory calculations to aid interpretation of the results.[5] We have also reported an EPR spectroscopic study of the kinetics of the β-scission step in isolation for selected 2-phenyl-1,3-dioxan-2-yl and 2-phenyl-1,3-dioxolan-2-yl radicals.[8] It was concluded that the relative rates of competing modes of bond scission, and thus the regioselectivity of the overall redox rearrangement, were influenced not only by differences in the thermodynamic driving forces, but also by charge-transfer interactions and bond angle/torsional strain effects that operate in the transition states for these β-scission processes.

In the present paper, we explore the scope of the thiol-catalysed radical-chain redox rearrangement of cyclic benzylidene acetals as a practical tool for the mono-deoxygenation of diol functionality in a number of representative carbohydrate derivatives.



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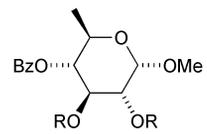

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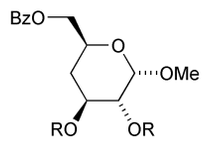

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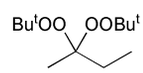

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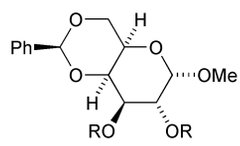

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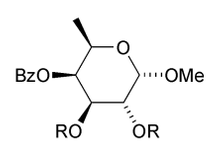


13 R = Ac
15 R = Me

Results and discussion

Our preliminary work [3,4] has shown that silanethiols, especially tri-*tert*-butoxysilanethiol (TBST) and triisopropylsilanethiol (TIPST) which are both very resistant to hydrolysis,[9] are generally more effective catalysts for the redox rearrangement than alkanethiols. Our initial choice of BBPB **11** as initiator, rather than the simpler alternative of di-*tert*-butyl peroxide (Bu^tOOBu^t, DTBP) was influenced by the shorter half-life of the former (*ca*. 1 h for BBPB and *ca*. 10 h for DTBP at 125 °C). However, since DTBP is relatively volatile and thus any excess can be easily removed at the end of the reaction, its longer half-life can be compensated for by using larger amounts of this initiator. Use of DTBP also avoids the need to make further additions of initiator during the reaction, as is sometimes necessary when using BBPB.[3,4] Furthermore, the acidic by-products that appear to be formed during the decomposition of peroxides in the presence of thiols, often prove more of a problem with BBPB, especially if relatively long reaction times are required.

A series of pilot experiments was carried out with the 4,6-*O*-benzylidene acetals **5** and **12** in order to optimise the conditions for the redox rearrangement and selected results are summarised in Table 1. When conversion was essentially quantitative, isolated total yields of benzoate esters were typically around 90%. The silanethiols TBST and TIPST are evidently equally effective as protic polarity-reversal catalysts, although the fact that the latter has recently become available commercially makes it the more convenient choice for general use.

We conclude from the results shown in Table 1 (and others described later) that the use of either DTBP (50 mol%) (method A) or BBPB (5 mol%) (method B) as initiator, in conjunction with TBST or (more conveniently) TIPST as catalyst (5 mol%), is similarly effective for bringing about redox rearrangements that take place relatively rapidly (*i.e.* are complete within 1–2 h). However, on grounds of convenience, method A must be considered the procedure of choice in most cases. For slower reactions, method B requires further additions of BBPB and thiol, and the presence of collidine (as an acid scavenger) is usually essential; method A is usually superior here.

In the absence of a thiol catalyst, using either peroxide initiator, much less rearrangement of **5** or **12** took place (entries 3, 7 and 9). Extending the reaction times and/or adding more peroxide initiator did increase the yields of benzoate esters,[6,7] but large amounts of unchanged benzylidene acetal always remained and a number of unidentified by-products were formed.

Octane proved to be a very suitable solvent for conducting the redox rearrangements, since it is unreactive, non-aromatic, non-toxic and easily removed by evaporation under reduced pressure. For generality, chlorobenzene was always used as a co-solvent or solvent when the benzylidene acetal was insufficiently soluble in octane alone, but more environmentally-friendly substitutes for this could be found on an individual basis.

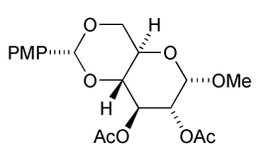
The *p*-methoxybenzylidene acetals **16** and **17** (PMP = *p*-methoxyphenyl) were investigated as analogues of the 4,6-benzylidene pyranosides **5** and **12**, in the expectation that the presence of the *p*-methoxy group on the aromatic ring would facilitate abstraction of the benzylic hydrogen atom by the electrophilic thiyl radical (a polar effect) and, perhaps, also promote the β-scission step (see Scheme 2). By this means it might be possible to carry out the redox rearrangements at lower temperatures. Under the conditions used for the rearrangement of **5** and **12**, the *p*-methoxybenzylidene acetals behaved similarly to their respective unsubstituted parents, both in terms of the rates of rearrangement and regioselectivity (Table 1, entries 12–17). The effects of using milder conditions were investigated briefly. In refluxing benzene, under conditions similar to those of method B, but replacing the BBPB by azobis-(isobutyronitrile) (AIBN) as initiator (2 × 5 mol%) in conjunction with TBST (2 × 5 mol%) as catalyst, 16% of **16** was converted to the benzoate esters **18** and **19** (PMBz = *p*-methoxybenzoyl). Under the same conditions, 10% of the benzylidene acetal **5** was converted to benzoate. Replacing the AIBN with 1,1-di-*tert*-butylperoxycyclohexane as initiator ($t_{½}$ *ca*. 1 h at 117 °C) in refluxing toluene as solvent resulted in 58% conversion of **16** and 20% conversion of **5**. We conclude that the use of *p*-methoxybenzylidene acetals does not usually offer any substantial advantages over the simple benzylidene derivatives.

tert-Butoxyl radicals abstract hydrogen from C(2) in 2-methyl-1,3-dioxolane slightly *more* rapidly than from 2-phenyl-1,3-dioxolane, despite the benzylic stabilisation of the radical

Table 1 Redox rearrangement of 4,6-*O*-benzylidene acetals and related acetals derived from glucose and from galactose[a]

Entry	Acetal	Method[b]	Thiol catalyst	Conversion[c] (%)	Product benzoate composition[c]	Isolated yield (%)
1	**5**	A	TIPST	>98	**6** : **7** = 97 : 3	92 (**6**)
2	**5**	A	TBST	98	**6** : **7** = 97 : 3	91 (**6**)
3	**5**	A	None	11		
4	**5**	B	TBST	87	**6** : **7** = 96 : 4	
5	**5**	B[d]	TBST	98	**6** : **7** = 96 : 4	90 (**6**)
6	**5**	B[d]	TIPST	>98	**6** : **7** = 97 : 3	93 (**6**)
7	**5**	B	None	6		
8	**12**	A	TIPST	>98	**13** : **7** = 38 : 62	32 (**13**), 58 (**7**)
9	**12**	A	None	12		
10	**12**	B	TBST	77	**13** : **7** = 38 : 62	
11	**12**	B[d]	TBST	94	**13** : **7** = 37 : 63	28 (**13**), 55 (**7**)
12	**16**	A	TIPST	<98	**18** : **19** = 96 : 4	90 (**18**)
13	**16**	A	None	9		
14	**16**	B	TBST	91	**18** : **19** = 96 : 4	
15	**16**	B[d]	TBST	98	**18** : **19** = 96 : 4	89 (**18**)
16	**17**	A	TIPST	>98	**20** : **19** = 40 : 60	35 (**20**), 54 (**19**)
17	**17**	B[d]	TBST	>98	**20** : **19** = 41 : 59	34 (**20**), 52 (**19**)
18	**21**	A	TIPST	<4[e,f]		
19	**21**	B[d]	TBST	<4[e]		

[a] The solvent was octane–chlorobenzene (1 : 1 v/v) and the total reaction time was 2 h in each case. [b] Method A: single additions of DTBP (50 mol%) and thiol (5 mol%) at the start of reaction. Method B: one addition of BBPB (5 mol%), thiol (5 mol%) and collidine (10 mol%) at the start of reaction with further additions when indicated. [c] Estimated by ^{1}H NMR spectroscopy. [d] Further additions of initiator (5 mol%) and thiol (5 mol%) were made after 40 min. [e] No product acetate ester could be identified with certainty by ^{1}H NMR spectroscopy. [f] The starting acetate was still essentially unchanged when a further addition of TIPST (5 mol%) was made after 2 h and the mixture was heated for a further 3 h.



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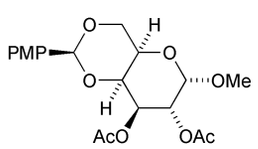

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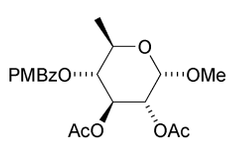

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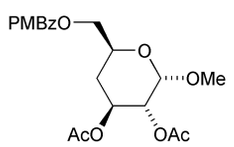

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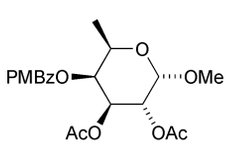

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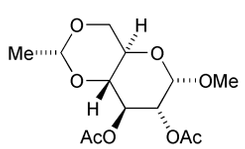
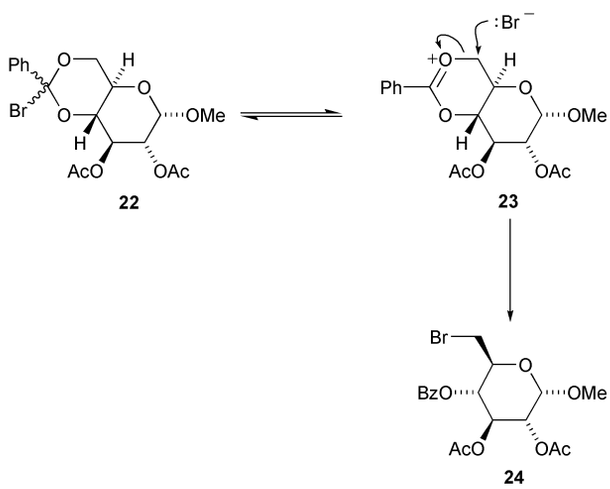


21

derived from the latter.[8] Since the replacement of a 2-phenyl group in 1,3-dioxolan-2-yl or 1,3-dioxan-2-yl radicals (*e.g.* **3** in Scheme 2) by a methyl group should not drastically alter the rate of their β-scission, we were led to investigate the redox rearrangement of the ethylidene acetal **21** to compare with its benzylidene analogue **5**. However, the ethylidene acetal turned out to be much less reactive and very little rearrangement to the corresponding acetates took place under conditions that brought about the complete rearrangement of **5** (Table 1, entries 18 and 19). It seems likely that the rate of hydrogen-atom abstraction by thiyl radicals from C(2) is much more sensitive to the overall thermochemistry of the reaction, and thus to the nature of the substituent at C(2), than the corresponding abstraction by alkoxyl radicals. Abstraction by a silanethiyl radical will be considerably less exothermic and, therefore, presumably proceeds through a much later transition state than the very exothermic abstraction by an alkoxyl radical.

The thiol-catalysed redox rearrangement described here should be compared with the well-known brominative ring-opening reactions undergone by 1,3-dioxacyclanes. In carbohydrate chemistry the synthetically useful cleavage of benzylidene acetals by *N*-bromosuccinimide to give β- or γ-bromo benzoates is known as the Hanessian–Hullar (H.–H.) reaction.[10,11] The benzylidene acetal is usually treated with NBS in refluxing carbon tetrachloride and in the case of the glucoside **5** gives the 6-bromo-4-benzoate **24**, as shown in Scheme 3. The reaction probably proceeds initially *via* a classical radical benzylic bromination to give **22**, followed by C–Br heterolysis and S_N2-attack by Br^- at the primary C(6) in the delocalised benzoxonium ion **23**.[11] A rather milder variant of the H.–H. reaction, that has advantages in some situations, has been introduced by Collins and co-workers.[12,13] Here the initial benzylic bromination is brought about at ambient temperature by UV irradiation of a carbon tetrachloride solution containing $CBrCl_3$ and the benzylidene acetal. The quite different mechanisms for opening of the 1,3-dioxacyclane ring that operate in H.–H./Collins reactions and in our thiol-catalysed radical reaction would be expected to lead to interesting and useful differences in the regiochemical outcomes of the two types of reaction. Furthermore, when overall monodeoxygenation of the diol function is desired, use of the thiol-catalysed redox rearrangement methodology obviates the need for reductive removal of the bromine from the bromo ester that results from the H.–H./Collins procedures. Since this debromination is often



22 **23** **24**

Scheme 3

Table 2 Redox rearrangement of the 1,2-*O*-benzylidene acetal **26** as a function of thiol concentration[a]

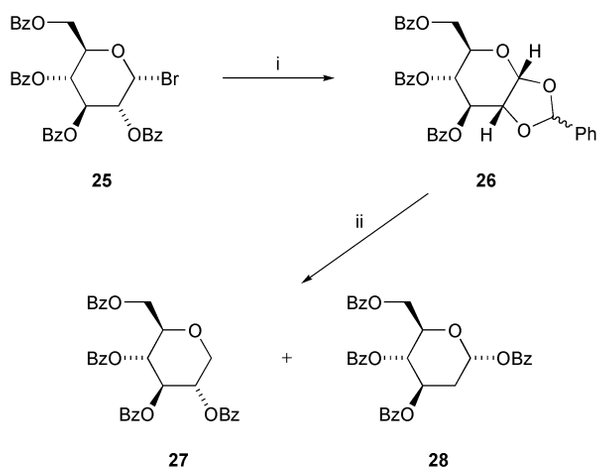
Entry	TBST (mol%)	[TBST]/M	Conversion (%)	Product ratio[b] [**28**] : [**27**]
1	0	0	28	[c]
2	2	0.0023	96	54.6
3	4	0.0054	≥98	29.8
4	5	0.0061	≥98	24.0
5	15	0.0210	≥98	13.0
6	30	0.0320	≥98	8.5

[a] The solvent was octane–chlorobenzene (1 : 1 v/v) and all reactions were carried out under reflux. The concentration of the starting acetal **26** varied between 0.11 and 0.15 M. Additions of BBPB (5 mol%) were made initially, after 40 min and again after 80 min. Single additions of thiol and collidine (10 mol%) were made at the start of the reaction. [b] Estimated by ^{1}H NMR analysis of the crude reaction product. [c] The 1-deoxy isomer **27** was not detectable alongside the relatively small amount of **28** present in the crude reaction mixture.

accomplished by treatment with toxic tributyltin hydride, the ability to dispense with this step is desirable not only on grounds of efficiency.

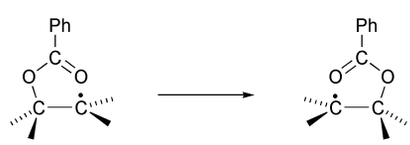
Redox rearrangement of 1,2-benzylidene acetals

Collins and co-workers have successfully applied their methodology to the brominative ring opening of a number of 1,2-*O*-benzylidene glycopyranose derivatives[12] and we have also investigated the thiol-catalysed redox rearrangement of some representative 1,2-*O*-benzylidene pyranoses. These compounds are conveniently prepared by treatment of 1-bromo-2-*O*-benzoylpyranoses with tetrabutylammonium borohydride (or sodium borohydride in conjunction with tetrabutylammonium iodide),[14,15] sometimes in the presence of silver triflate, as illustrated in Scheme 4 for the preparation of the glucoside **26** from the pyranosyl bromide **25**.[15] When the acetal **26** was heated in the absence of thiol under argon in refluxing octane–chlorobenzene (1 : 1) for a total of 4 h, in the presence of BBPB (3 × 5 mol%) added initially, after 40 min and again after 80 min, partial redox rearrangement did take place to give the 2-deoxy benzoate **28** containing <1% of the isomer **27**, but 72% of the starting material remained. However, when the reaction was repeated in the presence of TBST (5 mol%) as catalyst, the redox rearrangement proceeded cleanly to completion and gave a mixture of the benzoates **27** and **28** in the ratio 4 : 96.



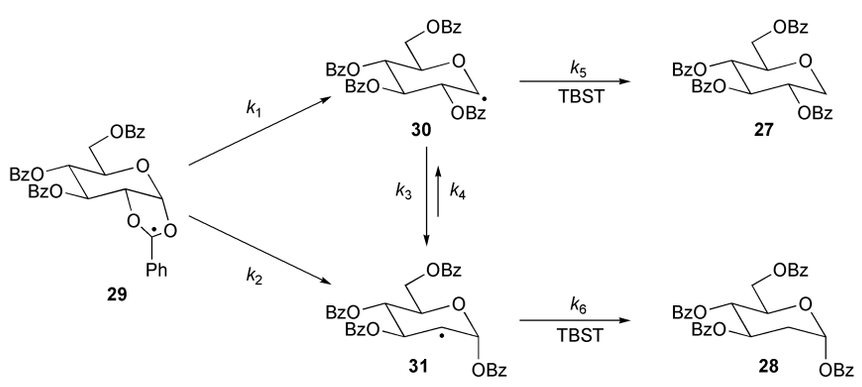
Scheme 4 *Reagents and conditions*: (i) Bu_4NBH_4, AgOTf in $MeNO_2$–toluene (1 : 1), −25 °C. (ii) BBPB (3 × 5 mol%), collidine (10 mol%), TBST (5 mol%) in refluxing octane–chlorobenzene (1 : 1).

For the redox rearrangement of a benzylidene acetal derived from a 1,2-diol, it is important to consider the extent to which the overall regiochemistry is influenced by the 1,2-migration of the benzoate group that is a characteristic of 2-benzoyloxyalkyl radicals [eqn. (1)].[16,17] If this radical rearrangement process competes with trapping of the benzoyloxyalkyl radicals by the thiol, then the distribution of end products may not reflect the regioselectivity of the β-scission step. In order to determine the significance of this 1,2-shift in the present context, the regioselectivity of the redox rearrangement of **26** was investigated as a function of thiol concentration; the results are summarised in Table 2. It is evident that a single addition of 2–4 mol% TBST is sufficient to induce complete conversion of the acetal **26** to the benzoates **27** and **28**, but that the proportion of the 1-deoxy isomer **27** increases as the thiol concentration increases. Evidently, the radical **31** is more stable than the radical **30** (in accord with previous observations on related radicals[16]) and rearrangement of the latter to give the former is competing with trapping by the thiol (see Scheme 5). If clean production of the 2-deoxy sugar is desired then the minimum concentration of thiol that gives complete conversion should be used.



(1)

A steady-state kinetic analysis based on the mechanism shown in Scheme 5 leads to eqn. (2) which relates the relative yields of 1- and 2-deoxy sugars to the thiol concentration (assumed to remain constant during the reaction). The derivation of eqn. (2) also makes the reasonable assumption that k_4 may be neglected in relation to k_6[XSH] (*i.e.* that the only fate of radical **31** is to give the 2-deoxy product **28**). A plot of the

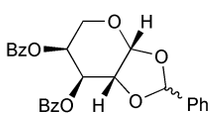


Scheme 5

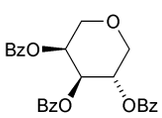
relative yields of **28** and **27** against 1/[XSH] gives a good straight line with a slope of 0.112 M and an intercept of 6.74, indicating that β-scission of the radical **29** with cleavage of the C(2)–O bond occurs about 7 times faster than cleavage of the C(1)–O bond at 130 °C. From the magnitude of the slope we can estimate that k_3/k_5 is *ca.* 1.4×10^{-2} M. The rate constants for abstraction of hydrogen from TBST by the radicals **30** and **31** are probably in the region of 2×10^7 M^{-1} s^{-1} at 130 °C,[9,18]‡ indicating that k_3 is around 3×10^5 s^{-1} at this temperature, a value in accord with expectation for this type of rearrangement.[16,17]

$$\frac{\text{Yield}\mathbf{28}}{\text{Yield}\mathbf{27}} = \frac{k_3}{k_5[\text{XSH}]}\left(1+\frac{k_2}{k_1}\right)+\frac{k_2}{k_1} \qquad (2)$$

To explore further the application of the thiol-catalysed redox rearrangement to 1,2-*O*-benzylidene acetals, the diastereoisomeric L-arabinose derivatives **32** and **33** were examined. Reductive cyclisation of the pyranosyl bromide with borohydride afforded a mixture of the benzylidene acetals **32** and **33** in the ratio 37 : 63, although complete chromatographic separation of these was not possible. The stereochemical assignments were made on the basis of nuclear Overhauser enhancement (NOE) experiments. Thus, the signals from H-1 and H-2 showed strong enhancement when the benzylidene proton was irradiated in the major isomer, confirming this as the *endo*-compound **33**. Only the signal from H-3 showed (now weaker) enhancement during the corresponding irradiation in the minor isomer, showing that this is the *exo*-form **32**.



32 *exo*-Ph
33 *endo*-Ph



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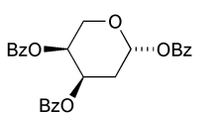


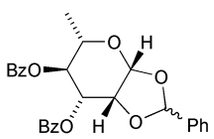
35

When the isomeric mixture of **32** and **33** was heated under reflux in chlorobenzene for 2 h in the presence of DTBP (50 mol%) and TIPST (5 mol%) (method A), complete conversion to the benzoate esters **34** and **35** (61 : 39) took place and these were isolated in a combined yield of 92%. When the amount of thiol was reduced to 2 mol%, under otherwise identical conditions, conversion was 95% while the yields of the 1- and 2-deoxy compounds were now very similar (**34** : **35** = 49 : 51). These results again show that rearrangement of the intermediate β-benzoyloxyalkyl radical is competitive with its trapping by the thiol. Application of eqn. (2) indicates that β-scission of the intermediate dioxolanyl radical with cleavage of the C(1)–O bond now takes place 2–3 times *more* rapidly than cleavage of the C(2)–O bond, in contrast with the behaviour of the radical **29**. In the absence of thiol, conversion was only 25% after 2.5 h and the product ratio **34** : **35** was 45 : 55. When the reaction time was extended to 6 h, the conversion increased to *ca.* 45%, but unidentified by-products were now also formed in addition to **34** and **35**.

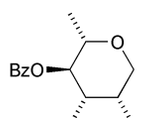
The relative reactivity of the *exo*- and *endo*-acetals towards abstraction of the benzylidene hydrogen atom by $Pr^i_3SiS^\bullet$ was estimated by determining the change in the epimeric ratio after partial conversion of the acetal and applying eqn. (3). Starting with benzylidene acetal for which **32** : **33** was 37 : 63, this ratio had changed to 85 : 15 at 83% conversion, which was achieved after heating for 35 min. This result implies that the *endo*-isomer **33** is about 6 times more reactive than the *exo*-isomer **32**, presumably as a result of the greater accessibility of the *exo*-benzylidene hydrogen atom in the former compound.

$$\ln\left(\frac{[endo]_0}{[endo]_t}\right) = \left(\frac{k_{endo}}{k_{exo}}\right)\ln\left(\frac{[exo]_0}{[exo]_t}\right) \qquad (3)$$

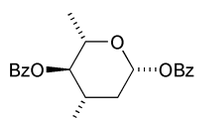
The corresponding diastereoisomeric 1,2-*O*-benzylidene acetals **36** and **37**, derived from L-rhamnose, were also examined. These compounds were prepared initially as a 90 : 10 mixture of *exo*- and *endo*-epimers that was chromatographically enriched to 96 : 4, also providing a 55 : 45 mixture from the faster-running fractions. The stereochemical assignments were made on the basis of the chemical shifts of the benzylidene protons, since (as we have confirmed in the present work) the *endo*-proton in *exo*-1,2- and 3,4-*O*-benzylidene acetals reliably appears downfield by 0.3–0.5 ppm from the *endo*-proton in the *exo*-isomer.[20] The redox rearrangement of any of these isomeric mixtures catalysed by TIPST (5 mol%) under the conditions of method A afforded the same mixture of isomeric benzoates **38** and **39** in the ratio 68 : 32. Reducing the amount of thiol to 2 mol% caused the benzoate ratio to shift towards the 2-deoxy isomer, such that **38** : **39** became 52 : 48. Conversion was essentially quantitative in both cases and the 1- and 2-deoxybenzoates were separately isolated in yields of 45% and 42%, respectively, from the rearrangement in the presence of 2 mol% TIPST. These results parallel those obtained with the L-arabinosides **32** and **33** and show that migration of the benzoate group to the 1-position competes with radical trapping of the 2-benzoyloxypyranosyl radical by TIPST. In common with **32** and **33**, partial redox rearrangement of the 55 : 45 *exo*–*endo* mixture of benzylidene acetals showed that the *endo*-isomer (**37**) was also the more reactive towards $Pr^i_3SiS^\bullet$, again by a factor of *ca.* 6 at 130 °C.



36 *exo*-Ph
37 *endo*-Ph

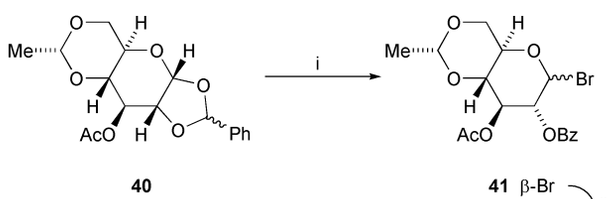


38



39

It is interesting to compare the thiol-catalysed redox rearrangement of 1,2-*O*-benzylidene acetals with the brominative ring-opening methodology first applied to these compounds by Collins and co-workers in 1988.[12] For example,[12] the glucoside **40** afforded initially the β-anomer of the 1-bromo-1-deoxy benzoate **41** in essentially quantitative yield when subjected to radical bromination by $CBrCl_3$, as shown in Scheme 6. However, the β-anomer is unstable and rearranges slowly on standing (or rapidly in the presence of tetrabutylammonium bromide) to give the α-anomer **42**. Thus, the Collins reaction is complementary to the thiol-catalysed redox rearrangement of the glucoside **26**, which affords the 2-deoxy benzoate **28** almost exclusively, reflecting the different mechanisms for opening of the dioxolane ring in the two types of reaction. It is noteworthy that the ethylidene acetal function in **40** survives the radical



40 **41** β-Br **42** α-Br

Scheme 6 *Reagents and conditions*: (i) $CBrCl_3$ in CCl_4, *hν*, ambient temp. (ii) On standing or, more rapidly, in the presence of Bu_4NBr.

‡ Because of the favourable polar effect of the oxygen atom directly attached to the radical centre in **30**, which will render the latter more nucleophilic than **31**, k_5 would be expected to be somewhat larger than k_6.[19]

Table 3 Redox rearrangement of the 4,6-*O*-benzylidene acetals **49**–**52** and the 5,6-*O*-benzylidene acetal **57**[a]

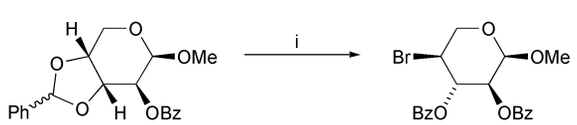
Entry	Benzylidene acetal	Method[b]	Solvent[c]	Conversion (%)	Product ratio 6-deoxy : 4-deoxy[d]	Isolated yield (%)
1	**49**	A	C	97	97 : 3	92 (**53**)
2	**50**	A	C	96	96 : 4	90 (**54**)
3	**50**	B	O + C (1 : 1)	≥98	98 : 2	93 (**54**)
4	**51**	A	C	83	97 : 3	—
5	**51**	A[e]	C	93[f]	97 : 3	90 (**55**)
6	**51**	B	O + C (1 : 1)	97	97 : 3	85 (**55**)
7	**52**	A[e]	C	88[g]	96 : 4	88 (**56**)
8	**57**	A	O + C (1 : 1)	≥98	88 : 12[h]	79 (**58**)

[a] The total reaction time was 2 h in each case, unless stated otherwise. [b] Method A: single additions of DTBP (50 mol%) and TIPST (5 mol%) at the start of reaction. Method B: one addition of BBPB (5 mol%), TBST (5 mol%) and collidine (10 mol%) at the start of reaction with further additions of initiator (5 mol%) and thiol (5 mol%) after 40 min and after 80 min. [c] O = octane, C = chlorobenzene. [d] Estimated by ^{1}H NMR spectroscopic analysis of the crude reaction product. [e] Collidine (10 mol%) added initially. [f] The conversion was 96% after 4 h when a further addition of TIPST (5 mol%) was made after 2 h. The isolated yield refers to this reaction. [g] The conversion was 98% after 6 h when a further addition of TIPST (5 mol%) was made after 4 h. The isolated yield refers to this reaction. [h] Ratio 5-deoxy : 6-deoxy.

bromination stage intact, paralleling the low reactivity of ethylidene acetals in the thiol-catalysed redox rearrangement (see above).

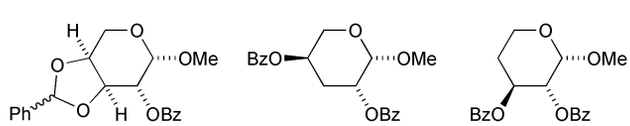
Redox rearrangement of 3,4-benzylidene acetals

Collins has reported that brominative ring opening of the 3,4-*O*-benzylidene acetal **43** using bromotrichloromethane affords the 4-bromo-4-deoxy benzoate **44** selectively and in high yield (Scheme 7).[13] For comparison, we have examined the thiol-catalysed redox rearrangement of methyl 2-*O*-benzoyl-3,4-*O*-benzylidene-β-L-arabinopyranoside, the antipode of **43**. The acetal was obtained initially as a 33 : 67 mixture of the *exo*- and *endo*-epimers **45** and **46** from which both compounds were isolated as crystalline solids.[20a,21] The structure of the less-abundant *exo*-isomer **45** was confirmed unambiguously by single-crystal X-ray diffraction[22] and exhibited the characteristic downfield chemical shift of the *endo* acetal proton, compared with the corresponding *exo* proton in **46**.



43 **44**

Scheme 7 *Reagents and conditions*: (i) $CBrCl_3$ in CCl_4, *hv*, ambient temp.



45 *exo*-Ph
46 *endo*-Ph
47 **48**

Treatment of either epimer with DTBP and TIPST (5 mol%) in refluxing octane (method A) afforded quantitatively a 64 : 36 mixture of **47** and **48**, from which the individual isomers were isolated as a syrup and a crystalline solid, respectively. Changing the amount of TIPST to 2 mol% or to 10 mol% did not alter the relative yields of the 3- and 4-deoxybenzoates, implying either that the intermediate β-benzoyloxyalkyl radicals are present in the equilibrium ratio or that migration of the benzoate group does not compete with radical trapping by thiol, even with 2 mol% TIPST.

Functional group compatibility

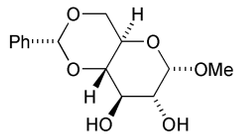
To explore the compatibility of some typical functional groups with the thiol-catalysed redox rearrangement, the reactions of the 4,6-*O*-benzylidene acetals **49**–**52** were investigated and the results are summarised in Table 3. The reactions of **49** and **50** proceeded smoothly to high conversion under the conditions of method A, although method B was also successful for the redox rearrangement of **50**. Method B worked well for the epoxide **51**, but method A was less effective unless collidine was also present. However, method A with collidine gave higher conversion than method B for the ketone **52**. In all cases, the 6-deoxy benzoates **53**–**56** were formed in marked preference to the 4-deoxy isomers (*ca*. 97 : 3) and isolated yields were very good. As demonstrated by the clean reaction of the diol **49**, there is no need to protect the free hydroxy function. The tosylate groups in **50** do not interfere, the epoxide ring in **51** survives intact in the benzoate **55** and the carbonyl group in **52** has no influence on the redox rearrangement process. The 5,6-*O*-benzylidene-D-glucofuranoside **57** afforded an 88 : 12 mixture of the two benzoates **58** and **59**, in which the isopropylidene acetal function is unaffected.

Multiple deoxygenation of carbohydrates

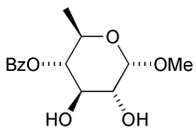
In order to explore the application of the thiol-catalysed redox rearrangement methodology to the multiple deoxygenation of carbohydrate polyols, two di-*O*-benzylidene acetals were examined. Methyl 2,3:4,6-di-*O*-benzylidene-α-D-mannopyranoside is commercially available as the isomer **60**, in which the phenyl group on the dioxolane ring is *exo*.[20a,23] Treatment of this compound with DTBP (50 mol%) and TIPST (5 mol%) in refluxing chlorobenzene, according to method A, resulted in its quantitative conversion to a 41 : 59 mixture of the 2,6-dideoxy benzoate **61** and the 3,6-dideoxy isomer **62**. The conversion decreased to 89% when the amount of thiol was reduced to 2 mol%, under otherwise similar conditions, and the product ratio moved slightly towards the 2,6-dideoxy isomer (45 : 55). Compounds **61** and **62** were each isolated in a pure state by column chromatography.

The partly rearranged intermediates **63**–**65** were identified in the reaction mixture using ^{1}H NMR spectroscopy. The two benzylidene protons in the starting material **60** appear at δ 6.30 and δ 5.67. In NOE experiments, when the proton at δ 5.67 was irradiated the signals from both H-4 and H-6_{axial} were strongly enhanced, indicating that this benzylidene proton is on the 6-membered dioxane ring. However, when the proton at δ 6.30 was irradiated, only the signal from H-4 showed (weaker) enhancement, indicating that this proton is on the 5-membered dioxolane ring.

The redox rearrangement was carried out under the conditions of method A (50 mol% DTBP + 5 mol% TIPST) and the reaction mixture was examined after 30 min, 60 min and 2.5 h. After 30 min, two new PhC*H* resonances appeared at δ 5.64 and δ 5.66, very close to the chemical shift of the corresponding proton on the dioxane ring of **60**. After 60 min, the intensities



49



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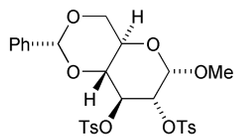

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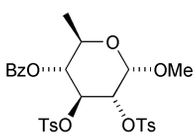

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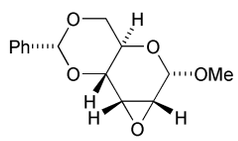

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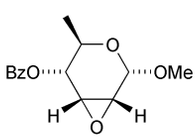

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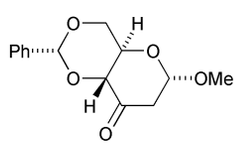

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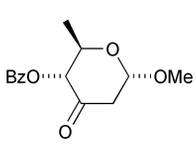

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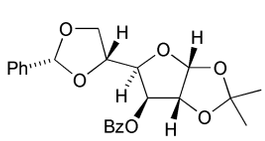

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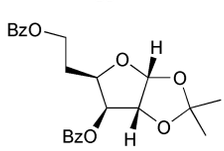

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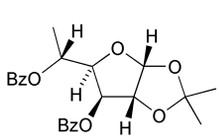

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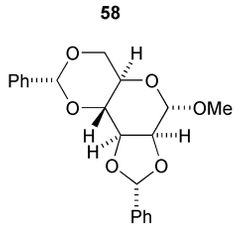

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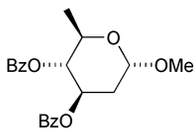

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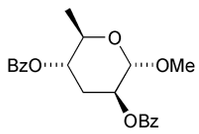

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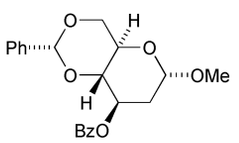

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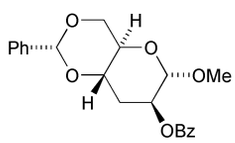
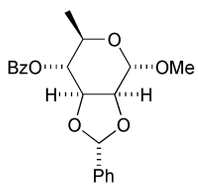


64



65

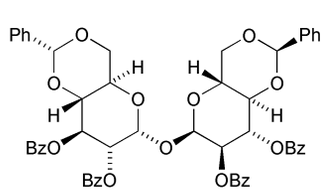
of both new peaks had increased relative to that from the dioxane benzylidene proton in **60**, but the new peaks had disappeared after 2.5 h when only the final products **61** and **62** could be detected. These new peaks are assigned to the benzylidene protons in the intermediate products **63** and **64**. It is assumed that no epimerisation takes place at the benzylidene centres on the dioxolane rings.

During the reaction a multiplet (ddd, J 13.0, 11.2 and 3.8) appeared at δ 1.94 and this can be assigned to H-2_{axial} in the intermediate **63**, on the basis that the chemical shift, relative peak intensities and coupling constants are very similar to those for H-2_{axial} in the final product **61**. Another multiplet (d[t], J 13.5 and 4.0) at δ 2.32 can be assigned similarly to H-$3_{equatorial}$ in the intermediate **64**, by comparison with the spectrum of the final product **62**. After 60 min, integration of these two multiplets showed that **63** : **64** was *ca*. 42 : 58, essentially the same as the final ratio of **61** : **62** obtained at the end of the reaction (41 : 59). Using these integrals, it was possible to assign the CH_3O singlets at δ 3.41 and 3.50 to **63** and **64**, respectively. Similarly, the peaks at δ 5.66 and 5.64 can be assigned to the benzylidene protons in **63** and **64**, respectively.

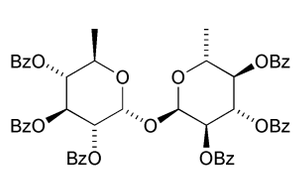
After 60 min, the ^{1}H NMR spectrum of the reaction mixture showed a total of six singlets in the CH_3O region, presumably corresponding to the methoxy groups in **60**–**65**, while after 2.5 h only the two singlets assigned to **61** (δ 3.43) and **62** (δ 3.49) remained. Because of the complexity of the composite spectrum the presence of the intermediate **65** could be established only indirectly. Thus, after 60 min the PhC*H* resonance at δ 5.67, due to the benzylidene proton on the dioxane ring in residual **60**, gave an integration corresponding to only *ca*. 64% of the single PhC*H* resonance at δ 6.30. Evidently, the latter peak arises from overlap of the dioxolane benzylidene proton signals from **60** and **65**, which are present in the ratio *ca*. 64 : 36. This was the same as the ratio of the integrals of the CH_3O singlets due to **60** at δ 3.46 and the only unassigned singlet at δ 3.44, confirming that the latter arises from **65**. Integration of the six methoxy singlets provided the most accurate estimate of the concentrations of **60**–**65**, which were in the ratio 18 : 18 : 27 : 11 : 16 : 10 after 60 min.

We conclude that, as expected,[8] both the five- and six-membered benzylidene acetal functions in **60** participate in the first stage of the redox rearrangement of **60**. The two benzylidene hydrogen atoms are probably abstracted at similar rates,[8] although of the two resulting benzylic radicals the dioxanyl radical is likely to undergo β-scission rather faster than its dioxolanyl counterpart.[8]

The disaccharide derivative 2,2′,3,3′-tetra-*O*-benzoyl-4,6:4′,6′-di-*O*-benzylidene-α,α-trehalose **66** also underwent stepwise redox rearrangement, in refluxing chlorobenzene in the presence of DTBP (50 mol%) and TIPST (2 × 5 mol%), to give ultimately the 6,6′-dideoxy compound **67**. After 1 h, immediately before the second addition of TIPST was made, ^{1}H NMR analysis of a sample of the reaction mixture revealed two 5-methyl doublets (J 6.1 Hz) at δ 0.71 and 0.76 in the ratio 42 : 58. The latter doublet arises from the final product **67**, while the former is assigned to the partially rearranged compound; about 40% of the starting material was still present at this stage. After the second addition of TIPST, the reaction mixture was heated under reflux for a further 1.5 h to complete the rearrangement to **67**. The isolated yield of the 6,6′-dideoxytrehalose was 88%.



66



67

It is important to remember that, as radical-chain reactions, these redox rearrangements are subject to inhibition by small

(even trace) quantities of compounds that can act as efficient scavengers of the chain-propagating radicals. This very property is, of course, exploited to establish such a mechanism. However, it does mean that care must be taken to ensure that potential scavengers are not present as impurities in the reactants, even as very minor contaminants that might be acceptable in the non-chain heterolytic processes that are the main stay of organic synthesis. For example, when the redox rearrangement of the trehalose derivative **66** was attempted using material that had not been adequately purified, but contained only trace impurities, the reaction was more sluggish and did not proceed to completion under the conditions described before. Although a detailed examination of the problem was not attempted, a pyridine derivative (arising from the pyridine used in the benzoylation step) appeared to be present as a trace impurity in **66**. Although the culprit did not appear to be pyridine hydrochloride itself, when the redox rearrangement of pure **66** (^{1}H NMR clean) was repeated in the presence of 5 mol% of this salt, the reaction was considerably slower and did not now proceed to completion.

Conclusion

We conclude that the thiol-catalysed redox rearrangement of the derived benzylidene acetals provides a simple method for the partial deoxygenation of carbohydrates. This radical-chain reaction is complementary to the well-established Hanessian–Hullar and Collins procedures for the brominative ring opening of carbohydrate benzylidene acetals. Because of the different mechanisms (homolytic *versus* heterolytic) that operate in the ring-opening stages, the regiochemistry of the redox rearrangement and the brominative cleavage processes can differ in useful ways. When simple deoxygenation without further functionalisation of the carbohydrate is desired, the redox rearrangement offers the advantage that a reductive debromination step (often requiring the use of toxic tin hydrides) can be avoided. It should also be possible readily to scale up the one-pot, thiol-catalysed redox rearrangement process.

Experimental

NMR spectra were recorded using a Bruker AVANCE 500 instrument (500 MHz for ^{1}H, 125.7 MHz for ^{13}C). The solvent was $CDCl_3$ and chemical shifts are reported relative to residual $CHCl_3$ (δ_H = 7.26) or to $CDCl_3$ (δ_C = 77.0 ppm); *J* values are quoted in Hz and the use of [multiplet] indicates an apparent multiplet associated with an observed line spacing. Column chromatography and TLC were carried out using Merck Kieselgel 60 (230–400 mesh) and Kieselgel 60 F_{254} aluminium-backed pre-coated plates, respectively. Optical rotations were measured on an AA Series Polaar 2000 polarimeter (Optical Activity Ltd.) using a 1 dm cell and are given in units of 10^{-1} deg cm^2 g^{-1}.

All manipulations and reactions of air-sensitive materials were carried out under an atmosphere of dry argon or nitrogen and all extracts were dried over anhydrous $MgSO_4$. Petroleum refers to the fraction of bp 40–60 °C.

Materials

Anhydrous octane, anhydrous chlorobenzene, 2,2-bis(*tert*-butylperoxy)butane (50% w/w in mineral oil) and di-*tert*-butyl peroxide (98%) were obtained commercially (Aldrich) and were used as received. Tri-*tert*-butoxysilanethiol was prepared according to a modification of the literature method,[24] as described previously,[25] and triisopropylsilanethiol was prepared according to the method of Soderquist and co-workers[26] or obtained commercially (Aldrich). Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside **49** and methyl 2,3:4,6-di-*O*-benzylidene-α-D-mannopyranoside **60** were obtained from Aldrich.

Preparation of starting acetals

Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside[27] **5**, methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-galactopyranoside[28] **12**, methyl 2,3-di-*O*-acetyl-4,6-*O*-*p*-methoxybenzylidene-α-D-glucopyranoside[27,29] **16**, methyl 2,3-di-*O*-acetyl-4,6-*O*-ethylidene-α-D-glucopyranoside[30] **21** were prepared as reported in the literature. Methyl 2,3-di-*O*-acetyl-4,6-*O*-*p*-methoxybenzylidene-α-D-galactopyranoside **17** was prepared by acetylation of methyl 4,6-*O*-*p*-methoxybenzylidene-α-D-galactopyranoside[31] using sodium acetate in acetic anhydride, as described for the preparation of **16**.

3,4,6-Tri-*O*-benzoyl-1,2-*O*-benzylidene-α-D-glucopyranose[32] **26** was prepared as a mixture of *exo*- and *endo*- epimers by treatment of 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl bromide **25** with silver triflate and tetrabutylammonium borohydride, as described by Garegg *et al.*[15] On the basis of the chemical shifts of the benzylidene protons the *exo–endo* ratio was estimated to be 35 : 65.

The epimeric 1,2-benzylidene acetals **32**[14] and **33**[14] derived from L-arabinose were prepared in a similar fashion from 2,3,4-tri-*O*-benzoyl-β-L-arabinopyranosyl bromide,[33] without the use of silver triflate, according to the method described by Betaneli *et al.*[14] The corresponding 1,2-benzylidene acetals **36**[14] and **37**[14] derived from L-rhamnose were prepared in the same way from 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl bromide.[34]

The *exo*- and *endo*-diastereoisomers of methyl 2-*O*-benzoyl-3,4-*O*-benzylidene-β-L-arabinopyranoside **45**[21] and **46**[20a,21] were prepared by benzoylation [using PhC(O)Cl in pyridine] of methyl 3,4-*O*-benzylidene-β-L-arabinopyranoside,[35] itself prepared from methyl β-L-arabinopyranoside.[36]

Methyl 4,6-*O*-benzylidene-2,3-di-*O*-toluenesulfonyl-α-D-glucopyranoside[37] **50**, methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside[30,38] **51**, methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexopyranosid-3-ulose[39] **52** and 3-*O*-benzoyl-5,6-*O*-benzylidene-1,2-*O*-isopropylidene-α-D-glucofuranose[40] **57** were prepared as described in the literature. Compound **57** appeared from its ^{1}H/^{13}C NMR spectra to be a single isomer in which the benzylidene phenyl group is *trans* to H-5. This assignment was made on the basis of NOE experiments in which the signals from H-5 (δ 4.50) and from one of the protons attached to C(6) (δ 4.17) were enhanced when the benzylidene proton (δ 6.00) was irradiated. The signal from H-2 (δ 4.66) also showed strong enhancement, because H-1 is nearly isochronous (δ 6.01) with the benzylidene proton.

The disaccharide diacetal **66**[41] was prepared by benzoylation of 4,6:4′,6′-di-*O*-benzylidene-α,α-trehalose[42a] by treatment with benzoyl chloride in pyridine.

Details of the preparation and characterisation of these acetals are given below where appropriate when the compounds are incompletely described in the literature.

Methyl 2,3-di-*O*-acetyl-4,6-*O*-*p*-methoxybenzylidene-α-D-galactopyranoside 17[31]

Mp 67 °C (from diethyl ether–hexane); $[a]_D^{22}$ +193.9 (*c* 2.3, $CHCl_3$); δ_H 2.07 (3 H, s, Ac), 2.09 (3 H, s, Ac), 3.42 (3 H, s, OMe), 3.74 (1 H, m, H-5), 3.81 (3 H, s, OMe), 4.04 (1 H, dd, *J* 12.5 and 1.7, H-6A), 4.26 (1 H, dd, *J* 12.5 and 1.6, H-6B), 4.44 (1 H, dd, *J* 3.2 and 1.1, H-4), 5.08 (1 H, d, *J* 3.2, H-1), 5.31 (1 H, dd, *J* 10.9 and 3.2, H-3), 5.36 (1 H, dd, *J* 10.9 and 3.2, H-2), 5.47 (1 H, s, PhC*H*), 6.89 (2 H, m, Ph), 7.43 (2 H, m, Ph); δ_C 20.9, 21.0, 55.3, 55.5, 62.0, 68.1, 68.5, 69.0, 73.9, 97.7, 100.8, 113.5, 127.5, 130.1, 160.1, 170.2, 170.6 (Found: C, 57.4; H, 6.2. $C_{19}H_{24}O_9$ requires C, 57.6; H, 6.1%).

3,4-Di-*O*-benzoyl-1,2-*O*-benzylidene-L-arabinopyranoside 32 (*exo*) and 33 (*endo*)

2,3,4-Tri-*O*-benzoyl-β-L-arabinopyranosyl bromide was prepared from tetra-*O*-benzoyl-L-arabinopyranose and HBr

(30% w/w in acetic acid) according the literature method;[33] δ_H 4.23 (1 H, dd, *J* 12.8, and 2.0, H-5A), 4.47 (1 H, d, *J* 12.8, H-5B), 5.70 (1 H, dd, *J* 10.5 and 3.8, H-2), 5.83 (1 H, dd, *J* 3.5 and 2.0, H-4), 6.00 (1 H, dd, *J* 10.5 and 3.4, H-3), 6.93 (1 H, d, *J* 3.8, H-1), 7.20–7.70 (9 H, m, Ph), 7.80–8.20 (6 H, m, Ph).

3,4-Di-*O*-benzoyl-1,2-*O*-benzylidene-L-arabinopyranoside was prepared as a syrup by treatment of the pyranosyl bromide with sodium borohydride in the presence of tetrabutylammonium iodide, as described in the literature.[14] ^{1}H NMR analysis showed the product to consist of a mixture of the *exo*- and *endo*-isomers in a ratio of 37 : 63.

***exo*-Isomer 32.** δ_H 4.07 (1 H, dd, *J* 12.5, and 5.1, H-5A), 4.34 (1 H, dd, *J* 12.5 and 4.3, H-5B), 4.63 (1 H, dd, *J* 5.8 and 3.6, H-2), 5.71 (1 H, ddd, *J* 5.1, 4.3 and 3.3, H-4), 5.82 (1 H, d, *J* 3.6, H-1), 5.84 (1 H, dd, *J* 5.8 and 3.2, H-3), 6.42 (1 H, s, PhC*H*), 7.20–7.72 (9 H, m, Ph), 7.81–8.11 (6 H, m, Ph); δ_C 62.7, 67.4, 68.8, 76.1, 97.7, 103.9, 126.4, 128.4, 128.5, 129.6, 129.7(8), 129.8(2), 133.5, 137.0, 165.4, 165.5 (because of overlap, only 8 peaks were detected for the 12 different aromatic carbon nuclei).

***endo*-Isomer 33.** δ_H 4.06 (1 H, dd, *J* 12.4, and 5.8, H-5A), 4.30 (1 H, dd, *J* 12.4 and 4.4, H-5B), 4.46 (1 H, dd, *J* 4.7 and 3.8, H-2), 5.56 (1 H, ddd, *J* 5.6, 4.4 and 3.8, H-4), 5.72 (1 H, d, *J* 3.8, H-1), 5.88 (1 H, [t], *J* 4.7, H-3), 6.04 (1 H, s, PhC*H*), 7.20–7.71 (9 H, m, Ph), 7.82–8.20 (6 H, m, Ph); δ_C 62.3, 66.9, 69.1, 76.2, 96.9, 104.4, 126.8, 128.5, 128.6, 129.3, 129.8, 133.4, 136.3, 165.3, 165.4 (because of overlap, only 7 peaks were detected for the 12 different aromatic carbon nuclei).

3,4-Di-*O*-benzoyl-1,2-*O*-benzylidene-β-L-rhamnopyranose 36 (*exo*) and 37[14] (*endo*)

These acetals were prepared as described[14] from 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl bromide[34] to give a mixture of *exo* and *endo*-isomers in the ratio 10 : 90 (total yield 55%).

The *exo*-isomer **36** was isolated by flash chromatography as a syrup from the earlier fractions, using petroleum–diethyl ether as eluent (10 : 1, then 5 : 1); $[\alpha]_D^{22}$ +188.2 (*c* 1.1, $CHCl_3$); δ_H 1.40 (3 H, d, *J* 6.2, Me), 3.85 (1 H, dq, *J* 9.0 and 6.2, H-5), 4.73 (1 H, dd, *J* 3.7 and 2.2, H-2), 5.59 (1 H, dd, *J* 9.8 and 3.7, H-3), 5.63 (1 H, dd, *J* 9.8 and 9.0, H-4), 5.70 (1 H, d, *J* 2.2, H-1), 6.51 (1 H, s, PhC*H*), 7.32–7.45 (10 H, complex, Ph), 7.51 (1 H, m, Ph), 7.98 (4 H, m, Ph); δ_C 17.6, 69.8, 70.9, 71.9 (2 C), 97.7, 105.5, 126.3, 128.3, 128.4 (2 C), 129.1, 129.3, 129.4, 129.7 (2 C), 129.9, 133.3 (2 C), 133.4, 165.6, 166.0.

The *endo*-isomer **37** was enriched to 96% by flash chromatography; $[\alpha]_D^{22}$ +213.4 (*c* 1.7, $CHCl_3$); δ_H 1.38 (3 H, d, *J* 6.2, Me), 3.67 (1 H, dq, *J* 9.2 and 6.2, H-5), 4.66 (1 H, dd, *J* 3.3 and 2.5, H-2), 5.52 (1 H, d, *J* 2.5, H-1), 5.64 (1 H, dd, *J* 9.7 and 3.3, H-3), 5.69 (1 H, dd, *J* 9.7 and 9.2, H-4), 5.99 (1 H, s, PhC*H*), 7.22–7.45 (10 H, complex, Ph), 7.50 (1 H, m, Ph), 7.98 (4 H, m, Ph); δ_C 17.7, 69.8, 71.1, 71.5, 78.4, 96.2, 105.9, 127.7, 128.4, 128.5 (2 C), 129.0, 129.3, 129.7 (2 C), 129.8, 130.0, 133.3, 133.4, 165.6, 166.1.

Methyl 2-*O*-benzoyl-3,4-*O*-benzylidene-*β*-L-arabinopyranoside 45[21] (*exo*) and 46[20a,21] (*endo*)

Methyl 3,4-*O*-benzylidene-β-L-arabinopyranoside (6.50 g), prepared as a mixture of *exo* and *endo* isomers according to the literature method[35] from methyl β-L-arabinopyranoside,[36] was benzoylated in the usual way by stirring overnight with benzoyl chloride (20 mL) and pyridine (60 mL). After the standard work-up, ^{1}H NMR spectroscopy showed the *exo* : *endo* ratio to be 33 : 67.

From this mixture, the *endo*-isomer **46** was isolated by slow crystallisation from diethyl ether at 4 °C; mp 118–120 °C, $[\alpha]_D^{22}$ +264.1 (*c* 1.8, $CHCl_3$) {lit.[21] mp 119–120 °C; $[\alpha]_D$ +224 (*c* 1.0, $CHCl_3$)}; δ_H 3.40 (3 H, s, OMe), 4.06 (1 H, dd, *J* 13.5 and 3.0, H-5A), 4.20 (1 H, d, *J* 13.5, H-5B), 4.40 (1 H, dd, *J* 6.3 and 3.0, H-4), 4.67 (1 H, dd, *J* 7.4 and 6.3, H-3), 5.03 (1 H, d, *J* 3.5, H-1), 5.20 (1 H, dd, *J* 7.4 and 3.5, H-2), 5.94 (1 H, s, PhC*H*), 7.35–7.65 (8 H, m, Ph), 8.10 (2 H, m, Ph); δ_C 55.8, 58.4, 72.8, 73.6, 75.9, 97.1, 104.5, 126.8, 128.3, 128.5, 129.6, 129.7, 130.0, 133.2, 136.7, 166.0.

The more soluble *exo*-isomer **45** was isolated from the mother liquor by flash chromatography using petroleum–diethyl ether (10 : 1, then 5 : 1, then 5 : 2) as eluent. Mp 127–128 °C; $[\alpha]_D^{22}$ +202.2 (*c* 1.1, $CHCl_3$) {lit.[21] mp 125–127 °C, $[\alpha]_D$ +168 (*c* 1.0, $CHCl_3$)}; δ_H 3.42 (3 H, s, OMe), 3.97 (1 H, dd, *J* 13.4 and 2.5, H-5A), 4.12 (1 H, d, *J* 13.4, H-5B), 4.32 (1 H, dd, *J* 5.3 and 2.5 H-4), 4.81 (1 H, dd, *J* 8.3 and 5.3, H-3), 5.06 (1 H, d, *J* 5.3, H-1), 5.31 (1 H, dd, *J* 8.3 and 3.5, H-2), 6.27 (1 H, s, PhC*H*), 7.37 (3 H, m, Ph), 7.46 (4 H, m, Ph), 7.58 (1 H, m, Ph), 8.13 (2 H, m, Ph); δ_C 55.8, 58.5, 70.1, 73.6, 74.3, 97.3, 102.9, 126.1, 128.3(9), 128.4(1), 129.1, 129.6, 130.0, 133.3, 138.7, 166.2 (Found: C, 67.5; H, 5.7. $C_{20}H_{20}O_6$ requires C, 67.4; H, 5.7%).

2,3,2′,3′-Tetra-*O*-benzoyl-4,6:4′,6′-di-*O*-benzylidene-α,α-trehalose 66[41]

This was prepared from 4,6:4′,6′-di-*O*-benzylidene-α,α-trehalose,[42a] itself prepared from the α,α-trehalose and benzaldehyde dimethyl acetal in *N*,*N*-dimethyl formamide, using toluene-*p*-sulfonic acid as catalyst.[42b] Compound **66** was purified by flash chromatography using petroleum–diethyl ether–dichloromethane (5 : 1 : 1) as eluent, followed by careful recrystallisation from dichloromethane–diethyl ether–hexane; mp 238–239 °C; $[\alpha]_D^{22}$ +240.3 (*c* 1.5, $CHCl_3$) {lit.[41] mp 240–241 °C; $[\alpha]_D$ +239 (*c* 1.0, $CHCl_3$)}; δ_H 3.50 (4 H, m, H-6 and -6′), 3.85 (2 H, [t], *J* 9.8, H-4 and -4′), 4.00 (2 H, [t]d, J 9.8 and 7.4, H-5 and -5′), 5.36 (2 H, s, 2 PhCH), 5.37 (2 H, dd, J 9.8 and 4.0, H-2 and -2′), 5.58 (2 H, d, J 4.0, H-1 and -1′), 6.10 (2 H, [t], *J* 9.8, H-3 and -3′), 7.2–7.55 (22 H, complex, Ph), 8.00 (4 H, m, Ph), 8.10 (4 H, m, Ph); δ_C 63.4, 68.1, 69.3, 71.8, 78.8, 94.4, 101.4, 126.3, 127.9, 128.2, 128.3, 128.9 (2 C), 129.6, 129.7(5), 128.8(1), 133.0, 133.7, 136.8, 165.2, 165.9.

General procedures for redox rearrangement

Method A. The acetal (1.0 mmol), dry octane and/or chlorobenzene (1.5 mL), DTBP initiator (0.5 mmol) and thiol catalyst (0.05 mmol) were successively introduced into an argon-filled 10 mL two-necked round-bottomed flask, containing a dry magnetic stirrer bar and fitted with a condenser through which a slow downward flow of argon was maintained. The side neck was closed with a stopper and the flask was immersed in an oil bath that had been pre-heated to 140–145 °C. The mixture was stirred under reflux for 1–3 h, allowed to cool and the volatile material was removed by evaporation under reduced pressure. The crude product was examined by ^{1}H NMR spectroscopy to determine its composition and estimate the extent of conversion to benzoate esters, before the latter were isolated by flash chromatography (usually using petroleum–diethyl ether eluent, first 10 : 1, then 5 : 1, then 5 : 2). When further additions of thiol were made to the reaction mixture, the flask was raised from the oil bath and allowed to cool briefly before the reagent was added quickly through the side neck.

Method B. The procedure was similar to that for method A, except that BBPB (initially 0.05 mmol) was present as initiator in place of DTBP, together with collidine (0.10 mmol) and the thiol catalyst (initially 0.05 mmol). After 40 min, further additions of BBPB and thiol (0.05 mmol of each) were made and these additions were repeated at 40 min intervals, if necessary to drive the reaction to completion. Reflux was continued for 0.5–1 h after the last addition.

Rearrangement products. The benzoate esters **6**,[7] **7**,[7] and **13**[7] showed optical rotations and NMR spectroscopic data in

accord with those reported in the literature. The properties of rearrangement products that have not been reported previously, or are inadequately described in the literature, are given below.

Methyl 2,3-di-*O*-acetyl-4-*O*-*p*-methoxybenzoyl-6-deoxy-α-D-glucopyranoside 18

Oil, $[\alpha]_D^{18}$ +33.2 (*c* 1.7, $CHCl_3$); δ_H 1.23 (3 H, d, *J* 6.3, Me-5), 1.88 (3 H, s, Ac), 2.08 (3 H, s, Ac), 3.42 (3 H, s, OMe), 3.85 (3 H, s, OMe), 4.00 (1 H, dq, *J* 9.8 and 6.3, H-5), 4.92–4.94 (2 H, m, H-1 and H-2), 5.00 (1 H, t, *J* 9.7, H-4), 5.62 (1 H, [t], *J* 9.6, H-3), 6.91 (2 H, m, Ph), 7.93 (2 H, m, Ph); δ_C 17.3, 20.5, 20.8, 55.3, 55.4, 65.3, 69.7, 71.4, 74.2, 96.7, 128.5, 129.8, 133.5, 163.7, 165.1, 169.9, 170.1 (Found: C, 57.5; H, 6.0. $C_{19}H_{24}O_9$ requires C, 57.6; H, 6.1%).

Methyl 2,3-di-*O*-acetyl-6-*O*-*p*-methoxybenzoyl-4-deoxy-α-D-*xylo*-hexopyranoside 19

Mp 86–87 °C (from CH_2Cl_2–hexane); $[\alpha]_D^{22}$ +190.2 (*c* 1.1, $CHCl_3$); δ_H 1.67 (1 H, [q], *J* 12.0, H-4A), 2.02 (3 H, s, OMe), 2.09 (3 H, s, OMe), 2.25 (1 H, ddd, *J* 12.0, 5.3 and 2.2, H-4B), 3.37 (3 H, s, OMe), 3.86 (3 H, s, OMe), 4.20 (1 H, m, H-5), 4.32 (1 H, dd, *J* 11.7 and 3.9, H-6A), 4.34 (1 H, dd, *J* 11.7 and 5.8, H-6B), 4.89 (1 H, dd, *J* 10.2 and 3.6, H-2), 4.95 (1 H, d, *J* 3.6, H-1), 5.32 (1 H, ddd, *J* 12.0, 10.2 and 5.3, H-3), 7.91 (2 H, m, Ph), 7.97 (2 H, m, Ph); δ_C 20.9, 21.0, 32.9, 55.1, 55.4, 65.2, 65.6, 67.6, 71.8, 97.5, 113.7, 122.1, 131.7, 163.5, 165.9, 170.1, 170.5 (Found: C, 57.5; H, 6.1. $C_{19}H_{24}O_9$ requires C, 57.6; H, 6.1%).

Methyl 2,3-di-*O*-acetyl-4-*p*-methoxybenzoyl-6-deoxy-α-D-galactopyranoside 20

Mp 83–85 °C (from CH_2Cl_2–hexane); $[\alpha]_D^{22}$ +117.1 (*c* 0.4, $CHCl_3$); δ_H1.20 (3 H, d, *J* 6.6, Me-5), 1.93 (3 H, s, Ac), 2.08 (3 H, s, Ac), 3.42 (3 H, s, OMe), 3.87 (3 H, s, OMe), 4.23 (1 H, qd, *J* 6.7 and 2.3, H-5), 5.02 (1 H, d, *J* 3.6, H-1), 5.24 (1 H, dd, *J* 10.8 and 3.6, H-2), 5.45 (1 H, dd, *J* 10.8 and 3.4, H-3), 5.52 (1 H, m, H-4), 6.94 (2 H, m, Ph), 8.06 (2 H, m, Ph); δ_C 16.0, 20.7, 20.9, 55.4, 55.5, 64.5, 68.1, 68.4, 71.2, 97.2, 113.8, 121.7, 131.9, 163.7, 165.8, 170.1, 170.5 (Found: C, 57.5; H, 6.1. $C_{19}H_{24}O_9$ requires C, 57.6; H, 6.1%).

1,5-Anhydro-tetra-*O*-benzoyl-D-glucitol 27[43]

This compound was formed as a minor product of the redox rearrangement of the 1,2-benzylidene acetal **26** and was not isolated. It was identified in the product mixture by its ^{1}H NMR spectrum,[43] in particular from the presence of the characteristic pseudo-triplet at δ 3.53 (*J* 10.7) arising from the axial proton attached to C(1).

Tetra-*O*-benzoyl-2-deoxy-α-D-*arabino*-hexopyranose 28[44]

Mp 151–152 °C (from CH_2Cl_2–hexane) (lit.[44] 153–154 °C); $[\alpha]_D^{23}$ +53.1 (*c* 1.5, $CHCl_3$) {lit.[44] $[\alpha]_D^{22}$ +68.6 (*c* 3.2, $CHCl_3$)}; δ_H 2.29 (1 H, ddd, *J* 13.6, 11.5 and 3.6, H-2A), 2.72 (1 H, ddd, *J* 13.6, 5.1 and 1.1, H-2B), 4.45 (1 H, dd, *J* 12.1 and 4.5, H-6A), 4.51 (1 H, ddd, *J* 10.0, 4.5 and 2.6, H-5), 4.58 (1 H, dd, *J* 12.1 and 2.6, H-6B), 5.74 (1 H, [t], *J* 9.8, H-4), 5.85 (1 H, ddd, *J* 11.5, 9.7 and 5.1, H-3), 6.62 (1 H, dd, *J* 3.6 and 1.1, H-1), 7.36 (6 H, m, Ph), 7.50 (5 H, m, Ph), 7.63 (1 H, m, Ph), 7.95 (4 H, m, Ph), 8.00 (2 H, m, Ph), 8.15 (2 H, m, Ph); δ_C 34.5, 62.9, 69.5, 69.6, 70.8, 91.6, 128.3, 128.4(0), 128.4(2), 128.7, 129.0, 129.2(7), 129.3(2), 129.6(6), 129.7(0), 129.7(2), 129.8, 130.0, 133.0, 133.3, 133.4, 133.7, 164.5, 165.4, 165.9, 166.1.

1,5-Anhydro-tri-*O*-benzoyl-L-arabinitol 34

Mp 117–119 °C (from diethyl ether–hexane), $[\alpha]_D^{24}$ +217.2 (*c* 1.3, $CHCl_3$). The D-enantiomer[45] shows mp 120–121 °C, $[\alpha]_D^{22}$ −219 (*c* 0.11, $CHCl_3$). Compound **34** shows δ_H 3.68 (1 H, dd, *J* 11.8 and 7.6, H-1A), 3.92 (1 H, dd, *J* 12.5 and 2.2, H-5A), 4.17 (1 H, dd, *J* 12.5 and 4.3, H-5B), 4.33 (1 H, dd, *J* 11.8 and 4.1 H-1B), 5.65–5.75 (3 H, complex, H-2, -3 and -4), 7.30–7.65 (9 H, complex, Ph), 7.94 (2 H, m, Ph), 8.01 (2 H, m, Ph), 8.06 (2 H, m, Ph); δ_C 67.4, 67.6, 68.3, 68.9, 70.7, 128.4, 128.4(6), 128.4(7), 129.2, 129.5, 129.7(1), 129.7(8) (2 C), 129.8(3), 133.3(5), 133.3(6), 133.4(1), 165.4(7), 165.5(2), 165.6 (Found: C, 70.0; H, 4.8. $C_{27}H_{22}O_7$ requires C, 70.0; H, 5.0%).

Tri-*O*-benzoyl-2-deoxy-β-L-*threo*-pentopyranose 35

Mp 160–161 °C (from diethyl ether–hexane), $[\alpha]_D^{22}$ +193.1 (*c* 1.7, $CHCl_3$). The D-enantiomer[46] shows mp 159–161 °C, $[\alpha]_D^{22}$ −195 (*c* 1.0, $CHCl_3$). Compound **35** shows δ_H 2.36 (1 H, ddd, *J* 13.2, 5.0 and 1.8, H-2A), 2.65 (1 H, ddd, *J* 13.2, 11.8 and 2.6, H-2B), 4.16 (1 H, dd, *J* 13.2,and 3.0, H-5A), 4.32 (1 H, dd, *J* 13.2 and 1.4, H-5B), 5.68 (1 H, dd, *J* 3.0, and 1.4, H-4), 5.82 (1 H, ddd, *J* 11.8, 5.0 and 3.0, H-3), 6.66 (1 H, dd, *J* 2.6 and 1.8, H-1), 7.30–7.65 (9 H, complex, Ph), 7.94 (2 H, m, Ph), 8.12 (4 H, m, Ph); δ_C 30.3, 63.4, 66.3, 68.0, 92.5, 128.4, 128.5, 128.6, 129.4(8), 129.5(2), 129.7, 129.8 (2 C), 129.9, 133.3, 133.4, 133.6, 164.8, 165.6, 165.8 (Found: C, 69.8; H, 4.9. $C_{27}H_{22}O_7$ requires C, 70.0; H, 5.0%).

1,5-Anhydro-tri-*O*-benzoyl-L-rhamnitol 38[47]

Mp 165–168 °C (from diethyl ether) (lit.[47] 169–170 °C); $[\alpha]_D^{22}$ +272.4 (*c* 1.0, $CHCl_3$) {lit.[47] $[\alpha]_D$ +279 (*c* 0.98, $CHCl_3$)}; δ_H 1.38 (3 H, d, *J* 6.2, Me-5), 3.77 (1 H, dd, *J* 9.5 and 6.2, H-5), 3.90 (1 H, dd, *J* 13.3 and 1.2, H-1A), 4.28 (1 H, dd, *J* 13.3 and 2.1, H-1B), 5.54 (1 H, dd, *J* 10.0 and 3.6, H-3), 5.68 (1 H, [t], *J* 10.0, H-4), 5.72 (1 H, m, H-2), 7.27 (2 H, m, Ph), 7.35–7.55 (6 H, complex, Ph), 7.60 (1 H, m, Ph), 7.84 (2 H, m, Ph), 7.97 (2 H, m, Ph), 8.10 (2 H, m, Ph); δ_C18.0, 68.1, 70.1, 71.9, 72.5, 75.4, 128.3, 128.4, 128.5, 129.1, 129.3, 129.7 (2 C), 129.9, 133.2, 133.3 (3 C), 165.7, 165.8, 165.8(4).

Tri-*O*-benzoyl-2-deoxy-β-L-*arabino*-hexopyranose 39

Foam, $[\alpha]_D^{22}$ +50.4 (*c* 1.01, $CHCl_3$); δ_H 1.38 (3 H, d, *J* 6.2, Me-5), 2.20 (1 H, [t]d, *J* 12.0 and 9.9, H-2A), 2.73 (1 H, ddd, *J* 12.0, 5.3 and 2.3, H-2B), 3.96 (1 H, dq, *J* 9.5 and 6.2, H-5), 5.33 (1 H, [t], *J* 9.4, H-4), 5.48 (1 H, ddd, *J* 10.4, 9.9 and 5.3, H-3), 6.20 (1 H, dd, *J* 9.9 and 2.3, H-1), 7.39 (4 H, m, Ph), 7.46 (2 H, m, Ph), 7.51 (2 H, m, Ph), 7.59 (1 H, m, Ph), 7.97 (4 H, m, Ph), 8.10 (2 H, m, Ph); δ_C17.8, 35.4, 71.1, 71.4, 73.9, 91.6, 128.4, 128.5 (2 C), 129.1, 129.3, 129.4, 129.7 (2 C), 130.0, 133.2, 133.3, 133.6, 164.5, 165.7 (2 C) (Found: C, 70.2; H, 4.9. $C_{27}H_{24}O_7$ requires C, 70.0; H, 5.0%).

Methyl 2,4-di-*O*-benzoyl-3-deoxy-β-L-*threo*-pentopyranoside 47

Syrup, $[\alpha]_D^{22}$ +152.6 (*c* 1.6, MeOH); δ_H 2.29 (1 H, m, H-3A), 2.43 (1 H, ddd, *J* 13.4, 12.2 and 3.3, H-3B), 3.48 (3 H, s, OMe), 3.82 (1 H, d[t], *J* 12.9 and 1.8, H-5A), 3.99 (1 H, dd, *J* 12.9 and 1.6, H-5B), 5.04 (1 H, d, *J* 3.3, H-1), 5.35 (1 H, m, H-2), 5.48 (1 H, ddd, *J* 12.2, 5.0 and 3.4, H-4), 7.36 (2 H, m, Ph), 7.45 (4 H, m, Ph), 8.07 (2 H, m, Ph), 8.12 (2 H, m, Ph); δ_C 28.5, 55.5, 60.6, 67.4, 69.6, 96.7, 128.3(6), 128.4(2), 129.7(6), 129.7(9), 129.8(1), 133.2, 166.2 (Found: C, 67.6; H, 5.9. $C_{20}H_{20}O_6$ requires C, 67.4; H, 5.7%).

Methyl 2,3-di-*O*-benzoyl-4-deoxy-β-L-*threo*-pentopyranoside 48[48]

Mp 101–102 °C (from hexane–diethyl ether) (lit.[48a] mp 102–103 °C), $[\alpha]_D^{18}$ +207.1 (*c* 0.63, $CHCl_3$); δ_H 1.98 (1 H, [t]dd, *J* 12.0, 11.0 and 5.4, H-4A), 2.32 (1 H, ddd, *J* 11.0, 5.3 and 2.0, H-4B), 3.42 (3 H, s, OMe), 3.74 (1 H, ddd, *J* 12.0, 5.3 and 2.0, H-5A), 3.95 (1 H, [t]d, *J* 12.0 and 2.5, H-5B), 5.09 (1 H, d, *J* 3.6, H-1), 5.26 (1 H, dd, *J* 10.0 and 3.6, H-2), 5.69 (1 H, ddd, *J* 11.0, 10.0 and 5.3, H-2), 7.37 (4 H, m, Ph), 7.50 (2 H, m, Ph), 7.97 (2 H, m,

Ph), 8.01 (2 H, m, Ph); δ_C 31.2, 55.3, 57.3, 68.7, 72.8, 98.1, 128.3(2) (2 C), 128.3(4), 129.5, 129.6, 129.9, 133.0, 133.2, 165.8, 166.1.

Methyl 4-*O*-benzoyl-6-deoxy-α-D-glucopyranoside 53[49]

Syrup, $[\alpha]_D^{22}$ +135.3 (*c* 1.7, $CHCl_3$) {lit.[49] $[\alpha]_D$ 131 (*c* 1, $CHCl_3$)}. The ^1H NMR data was in accord with that in the literature.[47] The ^{13}C NMR spectrum showed δ_C 17.4, 55.5, 65.5, 72.9, 73.1, 76.4, 99.0, 128.4, 129.5, 129.8, 133.4, 165.4.

Methyl 4-*O*-benzoyl-2,3-di-*O*-toluene-*p*-sulfonyl-6-deoxy-α-D-glucopyranoside 54[50]

Foam, $[\alpha]_D^{22}$ −9.5 (*c* 1.6, $CHCl_3$) {lit.[50] $[\alpha]_D^{20}$ −9.9 (*c* 1.02, $CHCl_3$)}; δ_H 1.16 (3 H, d, *J* 6.3, Me-5), 2.24 (3 H, s, Ts-CH_3), 2.44 (3 H, s, Ts-CH_3), 3.39 (3 H, s, OMe), 3.95 (1 H, dq, *J* 9.6 and 6.3, H-5), 4.33 (1 H, dd, *J* 9.8 and 3.6, H-2), 4.95 (1 H, d, *J* 3.6, H-1), 5.02 (1 H, [t], *J* 9.7, H-4), 5.29 (1 H, [t], *J* 9.7, H-3), 7.04 (2 H, d, *J* 8.1, Ts-H), 7.26 (2 H, m, Ts-H), 7.41 (2 H, m, Ph), 7.52–7.68 (5 H, complex, Ph), 7.94 (2 H, m, Ph); δ_C 17.1, 21.6, 21.7, 55.8, 65.5, 73.3, 76.0, 76.8, 97.2, 127.6, 128.2, 128.3, 128.9, 129.4, 129.8, 130.0, 132.3, 133.3, 134.0, 144.4, 145.2, 165.0.

Methyl 2,3-anhydro-4-*O*-benzoyl-6-deoxy-α-D-allopyranoside 55[51]

Syrup, $[\alpha]_D^{26}$ +220.7 (*c* 1.2, CH_2Cl_2) {lit.[51] $[\alpha]_D^{20}$ +188.2 (*c* 1.3, CH_2Cl_2)}; δ_H1.22 (3 H, d, *J* 6.3, Me-5), 3.48 (3 H, s, OMe), 3.57 (1 H, dd, *J* 4.2 and 3.2, H-2), 3.61 (1 H, dd, *J* 4.2 and 1.6, H-3), 4.11 (1 H, dq, *J* 9.5 and 6.3, H-5), 4.90 (1 H, d, *J* 3.2, H-1), 5.05 (1 H, dd, *J* 9.5 and 1.6, H-4), 7.45 (2 H, m, Ph), 7.58 (1 H, m, Ph), 8.06 (2 H, m, Ph); δ_C17.4, 51.4, 54.8, 55.7, 62.3, 73.0, 94.6, 128.5, 129.5, 129.8, 133.4, 166.0.

Methyl 4-*O*-benzoyl-2,6-dideoxy-α-D-*erythro*-hexopyranosyl-3-ulose 56[52]

Mp 100–103 °C (from CH_2Cl_2–hexane) (lit.[52] 103.5–104.5 °C), $[\alpha]_D^{22}$ +188.1 (*c* 1.9, $CHCl_3$); δ_H 1.43 (3 H, d, *J* 6.1, Me-5), 2.67 (1 H, d, *J* 14.4, H-2), 2.90 (1 H, dd, *J* 14.4 and 4.4, H-2), 3.40 (3 H, s, OCH_3), 4.27 (1 H, dq, *J* 10.0 and 6.1, H-5), 5.13 (1 H, d, *J* 4.4, H-1), 5.18 (1 H, d, *J* 10.0, H-4), 7.46 (2 H, m, Ph), 7.59 (1 H, m, Ph), 8.08 (2 H, m, Ph); δ_C 18.7, 46.4, 55.0, 67.8, 78.8, 99.5, 128.4, 129.2, 129.9, 133.4, 165.3, 198.0.

3,6-Di-*O*-benzoyl-1,2-*O*-isopropylidene-5-deoxy-α-D-*xylo*-hexofuranose 58[7,10*b*]

Oil, $[\alpha]_D^{24}$ −27.5 (*c* 5.0, $CHCl_3$) {lit.[7] $[\alpha]_D^{23}$ −27.0 (*c* 7.80, $CHCl_3$)}; δ_H 1.31 (3 H, s, Me-5), 1.52 (3 H, s, Me), 2.17 (2 H, [q], *J* 6.5, H-5), 4.40 (1 H, dt, *J* 11.2 and 7.0, H-6A), 4.52 (1 H, dt, *J* 11.1 and 5.9, H-6B), 4.57 (1 H, td, *J* 6.7 and 2.8, H-4), 4.65 (1 H, d, *J* 3.8, H-2), 5.41 (1 H, d, *J* 2.8, H-3), 5.97 (1 H, d, *J* 3.8, H-1), 7.37 (2 H, m, Ph), 7.43 (2 H, m, Ph), 7.51 (1 H, m, Ph), 7.57 (1 H, m, Ph), 7.95 (2 H, m, Ph), 8.00 (2 H, m, Ph); δ_C 26.2, 26.6, 27.8, 61.9, 76.5, 77.5, 83.7, 104.5, 112.0, 128.3, 128.5, 129.2, 129.5, 129.7, 130.0, 132.9, 133.5, 165.3, 166.3.

3,5-Di-*O*-benzoyl-1,2-*O*-isopropylidene-6-deoxy-α-D-gluco-furanose 59[53]

Because of the small amount of this product formed in the rearrangement, it was not possible to obtain it completely free of **58**. However, the NMR data were entirely consistent with its structure; δ_H 1.32 (3 H, s, Me), 1.53 (3 H, d, *J* 6.2, Me-5), 1.59 (3 H, s, Me), 4.49 (1 H, dd, *J* 8.8 and 3.0, H-4), 4.64 (1 H, d, *J* 3.7, H-2), 5.44 (1 H, dq, *J* 8.8 and 6.2, H-5), 5.52 (1 H, d, *J* 3.0, H-3), 5.99 (1 H, d, *J* 3.7, H-1), 7.34 (2 H, m, Ph), 7.39 (2 H, m, Ph), 7.48 (1 H, m, Ph), 7.53 (1 H, m, Ph), 7.86 (2 H, m, Ph), 7.92 (2 H, m, Ph); δ_C 18.2, 26.2, 26.7, 67.9, 76.1, 81.2, 83.5, 105.0, 112.3, 128.2, 128.4, 129.1, 129.5, 129.7, 129.9, 132.9, 133.4, 165.2, 165.3.

Methyl 3,4-di-*O*-benzoyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside 61[54]

Mp 92–93 °C (from diethyl ether–pentane) (lit.[54*a*] 93–94 °C, lit.[54*c*] 80–83 °C), $[\alpha]_D^{22}$ 0.0 (*c* 1.0, $CHCl_3$) {lit.[54*a*] $[\alpha]_D$ −0.5 (*c* 1.0, $CHCl_3$), lit.[53*c*] $[\alpha]_D$ 0 (*c* 0.9, $CHCl_3$)}; δ_H 1.28 (3 H, d, *J* 6.3, Me-5), 1.96 (1 H, ddd, *J* 12.5, 11.5 and 3.5, H-2A), 2.50 (1 H, ddd, *J* 12.5, 5.5 and 1.0, H-2B), 3.41 (3 H, s, OMe), 4.09 (1 H, dq, *J* 9.6 and 6.3, H-5), 4.87 (1 H, d, *J* 3.5, H-1), 5.24 (1 H, [t], *J* 9.6, H-4), 5.64 (1 H, ddd, *J* 11.5, 9.6 and 5.5, H-3), 7.36 (4 H, m, Ph), 7.49 (2 H, m, Ph), 7.93 (2 H, m, Ph), 7.99 (2 H, m, Ph); δ_C 17.7, 35.4, 54.9, 65.9, 69.9, 74.9, 98.0, 128.3, 128.4, 129.5, 129.6, 129.7, 129.8, 133.0, 133.2, 165.7, 165.8.

Methyl 2,4-di-*O*-benzoyl-3,6-dideoxy-α-D-*arabino*-hexopyranoside 62[55]

Syrup, $[\alpha]_D^{22}$ −22.7 (*c* 2.5, $CHCl_3$) {lit.[55*a*] $[\alpha]_D$ −22.9 (*c* 2.4, $CHCl_3$) and lit.[55*b*] $[\alpha]_D$ −53.0 (*c* 1.6, $CHCl_3$}; δ_H 1.32 (3 H, d, *J* 6.3, Me-5), 2.20 (1 H, ddd, *J* 14.0, 11.4 and 3.4, H-3A), 2.42 (1 H, d[t], *J* 14.0, and 4.0, H-3B), 3.48 (3 H, s, OMe), 4.07 (1 H, dq, *J* 9.7 and 6.3, H-5), 4.74 (1 H, br s, H-1), 5.16–5.24 (2 H, complex, H-2 and H-4), 7.46 (4 H, m, Ph), 7.57 (2 H, m, Ph), 8.03 (2 H, m, Ph), 8.12 (2 H, m, Ph); δ_C 17.7, 29.6, 55.0, 66.0, 70.3, 70.5, 97.4, 128.4(2 C), 129.6, 129.8, 129.9, 133.0, 133.2, 133.3, 165.6, 165.7.

2,2′,3,3′,4,4′-Hexa-*O*-benzoyl-6,6′-dideoxy-α,α-trehalose 67

Mp 222–224 °C (from CH_2Cl_2–diethyl ether–hexane), $[\alpha]_D^{22}$ +245.5 (*c* 1.1, $CHCl_3$); δ_H 0.76 (6 H, d, J 6.2, Me-5 and -5′), 4.06 (2 H, dq, *J* 9.8 and 6.2, H-5 and -5′), 5.25 (2 H, [t], *J* 9.8, H-4 and -4′), 5.37 (1 H, dd, *J* 10.0 and 3.9, H-2 and -2′), 5.62 (2 H, d, J 3.9, H-1 and 1′), 6.17 (2 H, [t], *J* 9.9, H-3 and -3′), 7.25–7.47 (12 H, complex, Ph), 7.84 (6 H, m, Ph), 7.91 (6 H, m, Ph), 8.12 (6 H, m, Ph); δ_C 16.5, 66.4, 70.3, 71.9, 73.5, 92.9, 128.2(9), 128.3(1), 128.6, 128.8, 129.1, 129.3, 129.7, 129.8, 129.9, 133.1, 133.3, 133.5, 165.3, 165.5, 165.6 (Found: C, 69.2; H, 5.1. $C_{54}H_{46}O_{15}$ requires C, 69.4; H, 5.0%).

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