Supplementary Material Available: ORTEP drawings of the cation of $MeMg(15\text{-crown-5})^+Me_5Mg_2^-$ and tables for this salt of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters (5 pages); tables of observed and calculated structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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n-Pentenyl Glycosides Permit the Chemospecific Liberation of the Anomeric Center[1]

David R. Mootoo,* Vandana Date, and Bert Fraser-Reid*

Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University
Durham, North Carolina 27706

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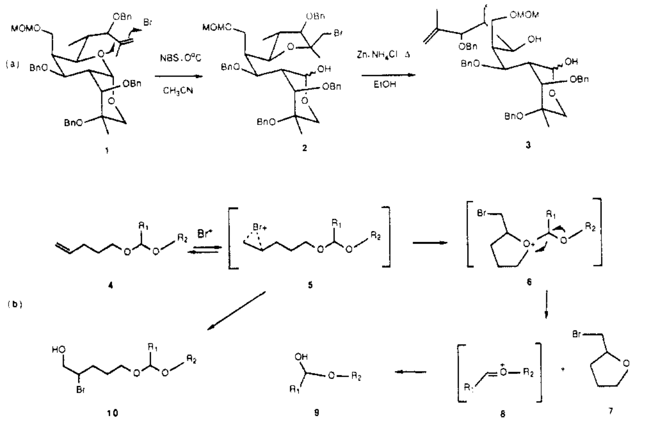
Synthetic manipulations of carbohydrate derivatives rely on efficient differential protecting group strategies, and excellent protocols have been developed which discriminate between various hydroxyl groups on the basis of their steric, electronic, or reactivity demands.[2] In this context, the anomeric center is particularly important, since it usually plays a key role in the syntheses, whether the sugar is used as a building block for oligosaccharides[3] or as a chiron[4] for natural products.[4,5] Therefore, a procedure for chemospecific liberation of the glycosidic oxygen would be advantageous, and in this manuscript, we describe such a reaction.

Our approach to this problem grew out of the serendipitous finding[6] that reaction of the dipyranoside **1** with NBS/CH_3CN/H_2O led not to the expected bromohydrin but to the bromomethyl tetrahydrofuran **2**[6] (Scheme Ia). We had failed in attempts to open the dipyranoside directly or indirectly (i.e., **1** → **3**) by use of protic or Lewis acid protocols. Hence, the ready formation of **2** was welcomed, particularly since reduction with zinc led readily to **3**.[6] With respect to the key step, a mechanistic rationale, summarized by the arrows in **1**, implied a unique case of "RO5 participation"[7] by the ring oxygen[8] in the opening of the putative cyclic bromonium ion.

The mechanistic proposition can be fleshed out by using the generalized structural element **4** (Scheme Ib). Thus, the process is driven by a cascade of ionic intermediates **5**, **6**, and **8**, which requires involvement of both oxygens. In effect, the overall transformation, **4** → **8**,[9] suggests a generalized protocol for "hydrolysis" of an acetal without the use of an acid, as is the customary requirement. The promise for sugar chemistry, therefore, was the possibility to cleave specifically the glycosidic oxygen under conditions that would leave a wide array of commonly used protecting groups unaffected.

Scheme I



Scheme II

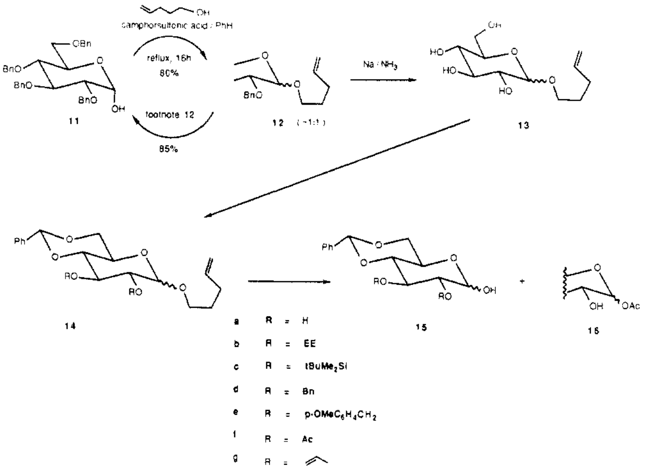


Table I. Deglycosidation of Protected *n*-Pentenyl α,β-D-Glucopyranosides with NBS[a]

entry	substrate	product	reaction time (h)	yield (%)
i	**12**	**11**	3	85
ii	**14a**	**15a**		complex mixture
iii	**14b**	**15b**	16	63
iv	**14c**	**15c**	7	90
v	**14d**	**15d**	6	70
vi	**14e**	**15e**	6	68
vii	**14f**	**15f**	36	62[b]
viii	**14g**	**15g**	9	72[b]

[a] For experimental conditions, see footnote 12. [b] These yields were not optimized. The reactions were stopped at ~50% completion, and the yields are based on recovered starting material.

Accordingly, the perbenzylated *n*-pentenyl glycoside **12**[10] was prepared by Fischer glycosidation of **11**[11] (Scheme II).

(1) Reaction either the α or β anomer of **12** with NBS in wet acetonitrile[12] regenerated **11** cleanly in 85% yield (Table I, entry i).

In order to examine a more discriminating substrate, the benzylidene derivative **14a** was prepared via **13** and converted into various diprotected derivatives, **14b** → **14g**.[10]

(2) Reaction of **14a** itself did not give high yields of **15a**, owing to complex side reactions.

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[1] This work is supported by a grant from the National Science Foundation (CHE 8703916).

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[3] See, for example: Sinay, P. *Pure Appl. Chem.* **1987**, *59*, 445. Sadozai, K. K.; Ito, Y.; Nukada, T.; Ogawa, *Carbohyd. Res.* **1986**, *150*, 91. Paulsen, H.; Lorentzen, J. P. *Carbohyd. Res.* **1986**, *150*, 63. Fugedi, P.; Binberg, W.; Garegg, P. J.; Pilotti, A *Carbohyd. Res.* **1987**, *147*, 297. Lemieux, R. U.; Bundle, D. R.; Baker, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 4076. Nashed, M. A.; Anderson, L. *Carbohydr. Res.* **1983**, *114*, 43.

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[8] Mootoo, D. R.; Fraser-Reid, B. *J. Chem. Soc., Chem. Commun.* **1986**, 1570.

[9] At the present time, the formation of bromomethyltetrahydrofuran **7** is only postulated. A search for the compound is underway.

[10] All new compounds were characterized by 300 MHz ^1H NMR and by HRMS and/or elemental analysis.

[11] Schmidt, O. T.; Auer, T.; Schmadel, H. *Chem. Ber.* **1960**, *93*, 556.

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(3) The result with **14b** (Table I, entry iii) indicates that of the three acetals (benzylic, α-ethoxyethyl, and glycosidic) present in the molecule, only the last was removed during brominolysis. By contrast, upon treatment of **14b** with mild acid, the last was the only acetal to survive—as expected.

(4) Pursuant to the survival of the acid labile protecting groups, the result with the silyl ether **14c** (entry iv) should be noted.

In general, the results with **14b** → **14g** reveal that under the deglycosidation conditions, the benzylidene ring does not undergo the well-known Hanessian–Hullar[13,14] reaction with NBS, a procedure widely used to cleave a benzylidene acetal while leaving a glycosidic center intact The formation of **15b** → **15g** allows that pattern of chemoselectivity to be reversed.

(5) In view of the reactions in entry i, survival of the *O*-benzyl ethers in entry v (**14d** → **15d**) is not surprising. However, the oxidative conditions proved to be so mild that even the activated methoxybenzyl ether survived (**14e** → **15e**) to a substantial degree (entry vi).

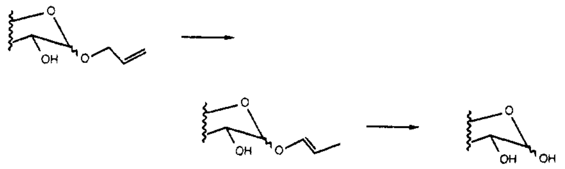
(6) The results with the diacetate **14f** (entry vii) were complicated by acetyl migration to give **16**. (In this context, it should be noted that silyl migration[15] was not observed with **15c**.)

An obvious question relates to the formation of bromohydrins **10** from intermediate **5** (Scheme Ib). Such substances were indeed encountered, particularly when the proportion of water in the solvent was higher than prescribed.[12] Indeed, there is enough adventitious water in "dry" acetonitrile to accomplish the hydrolysis step but at an appreciably slower rate.

The foregoing observation had seminal overtones, since it implied that double bonds, which do not lead to intermediates such as **6**, would not compete significantly for NBS. This postulate was tested by use of allyl protecting groups.[16]

(7) Indeed, the result in entry viii shows that substantive glycosidic cleavage can be achieved in the presence of *O*-allyl ethers.

The specificity of the deglycosidation is particularly noteworthy in light of the result in (7). Thus, while it is true that an allyl protecting group can also be removed from the glycosidic center under nonacidic conditions,[16] the process is not chemoselective, being operational for other allyloxy groups. The same holds true for the cleavage of benzyl glycosides.[17]



(ref 16)

The apparent driving force of the ready formation of the oxonium ion species **6** is of added interest in view of the timely report from the laboratories of Liotta and Maryanoff on the reversibility of bromonium ion catalyzed RO5 participation.[18] That aspect as well as other mechanistic details is currently being probed and will be reported in due course.[19]

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(12) *N*-Bromosuccinimide (2.5 equiv) was added to a solution of the pentenyl glycosides in 1% aqueous acetonitrile (20 mL/mmol of glycoside). The progress of the reaction was monitored by TLC and quenched by addition of 10% aqueous sodium thiosulfate solution. Most of the solvent was removed in vacuo, and the residue was diluted with water and extracted with ether. The ethereal extract was dried (Na_2SO_4), filtered, and evaporated in vacuo. Column chromatography of the resulting residue afforded the respective pyranose.

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(19) An invention disclosure has been filed for the process described in this communication.

Synthesis and Reactivity of a Stable Nitrile Imine

Ghislaine Sicard, Antoine Baceiredo, and Guy Bertrand*

Laboratoire des Organométalliques, U.A. 477
Université Paul Sabatier, 118, route de
Narbonne, 31062 Toulouse Cédex, France

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Nitrile imines, first prepared by Huisgen et al.,[1] have been widely used in organic synthesis and in regioselective 1,3-dipolar cycloadditions.[2] Up to now, they have only been observed by IR and UV in 85 K matrix[3a–c] or by mass[3c] and real time photoelectron spectroscopy[4] in the gas phase. Hydrolysis of alkali metal salts of diazomethane A,A′ (R = H), at −15 °C, with a concentrated weakly acidic buffer solution, leads to a colorless diazomethane isomer, which was originally considered to possess the nitrile imine structure B (R = E = H),[5] but which is now identified as the amino isocyanide C.[6] However, one can imagine that substituted salts of type A or A′ are suitable candidates for an electrophilic addition leading to B or B′ (Scheme I), and here we wish to report that, by using this hypothesis, we have been able to synthesize the first stable nitrile imine.

We have already shown that the reaction of the lithium salt of bis(diisopropylamino)phosphinodiazomethane (**1a**), with an acyl chloride, led to the formation of 1,3,4-oxadiazole **2a**, in addition to the expected diazoketone **3**.[7] Interestingly, the thiophosphine analogue **1b** quantitatively affords the five-membered ring heterocycle **2b**.[8] In order to rationalize the formation of products **2**, one can postulate a 1,5-electrocyclization[9] of the first-formed carbonylnitrile imine **4** (Scheme II). In other words, N-acylation strongly competes with C-acylation in the case of phosphorus-substituted diazo lithium salts.

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(8) All new compounds afforded satisfactory elemental analysis. Selected spectroscopic data are the following. **2b**: ^{31}P NMR (C_6D_6) +45.5 ppm; ^{1}H NMR (C_6D_6) 1.55 (d, *J*(HH) = 6 Hz, 12 H, $CHCH_3$), 1.58 (s, 9 H, CCH_3), 1.70 (d, *J*(HH) = 6 Hz, 12 H, $CHCH_3$), 3.90 (d of sept, *J*(PH) = 17.8 Hz, *J*(HH) = 6 Hz, 4 H, CH); mass spectrum *m/e* 388 (M^+). **5a**: ^{31}P NMR ($CDCl_3$) +60.6 ppm; IR (C_6H_6) 2020 cm^{-1}. **5b**: ^{31}P NMR ($CDCl_3$) +68.8 ppm; IR (C_6H_6) 2040 cm^{-1}. **6a**.[11] **6b**: ^{31}P NMR (C_6D_6) +65.7 ppm; IR (C_6H_6) 2050 cm^{-1}. **7b**: ^{31}P NMR ($CDCl_3$) +68.5 ppm; IR (C_6H_6) 2020 cm^{-1}. **14**: ^{31}P NMR ($CDCl_3$) +75.0, +57.9, *J*(PP) = 3.6 Hz; ^{13}C NMR ($CDCl_3$) 42.13 (dd, *J*(PC) = 26.4 and 4.5 Hz, CH_2), 51.9 (s, CH_3O), 61.7 (dd, *J*(PC) = 27.1 and 5.3 Hz, CHring), 144.2 (d, *J*(PC) = 151.6 Hz, C=N), 173.4 (s, C=O); IR (KBr) 1740 cm^{-1} (CO), mass spectrum *m/e* 620 (M^+). **15**: ^{31}P NMR ($CDCl_3$) +95.8, +59.5, *J*(PP) = 4.34 Hz; ^{13}C NMR ($CDCl_3$) 51.6 (s, CH_3O), 120.8 (d, *J*(PC) = 27.2 Hz, =CH), 136.9 (t-like, *J*(PC) = 10.56 Hz, =C), 152.6 (dd, *J*(PC) = 148.7 and 3.0 Hz, C=N), 162.2 (s, CO); IR ($CDCl_3$) 1730 (CO), 1590 (C=N) cm^{-1}; mass spectrum *m/e* 618 (M^+).

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