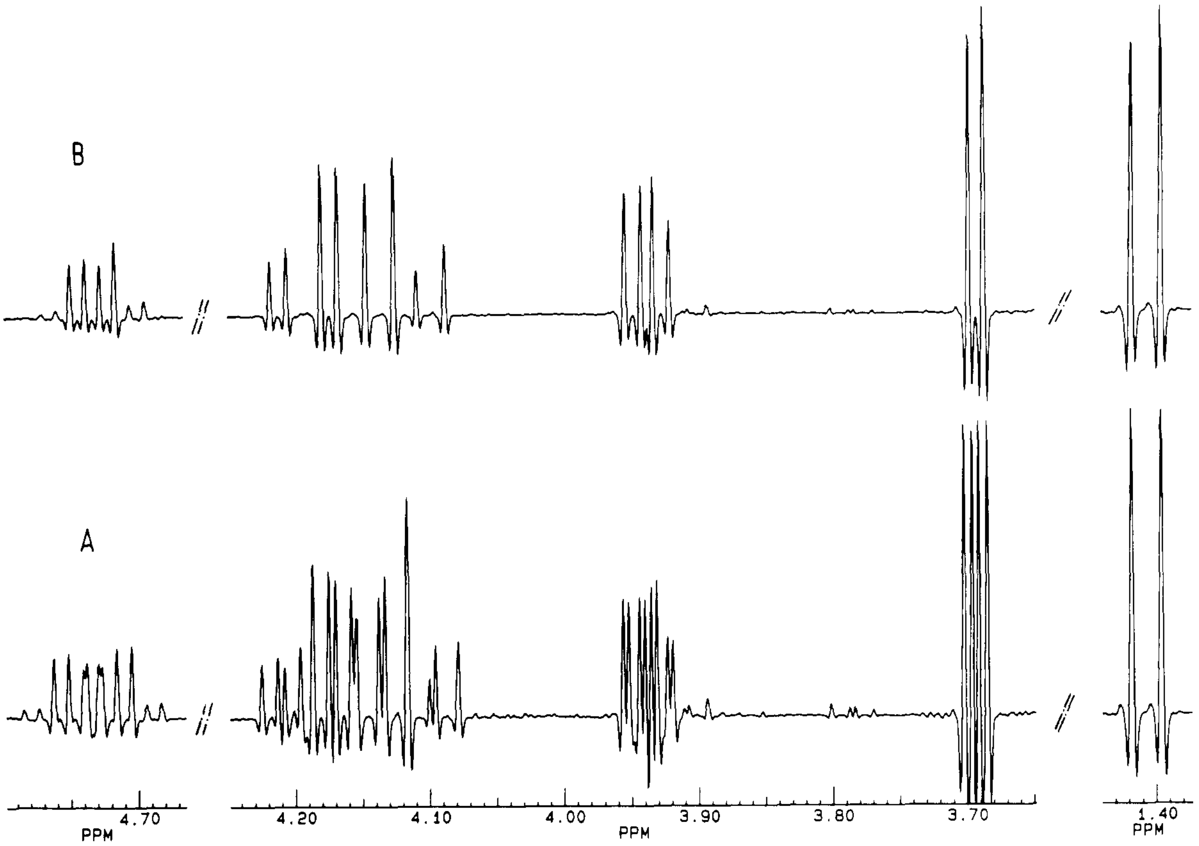

Figure 1. A. ^{1}H NMR spectrum of fully deprotected seryl threonyl phosphate **6**. B. ^{1}H{^{31}P} NMR spectrum of **6**.

Scheme I

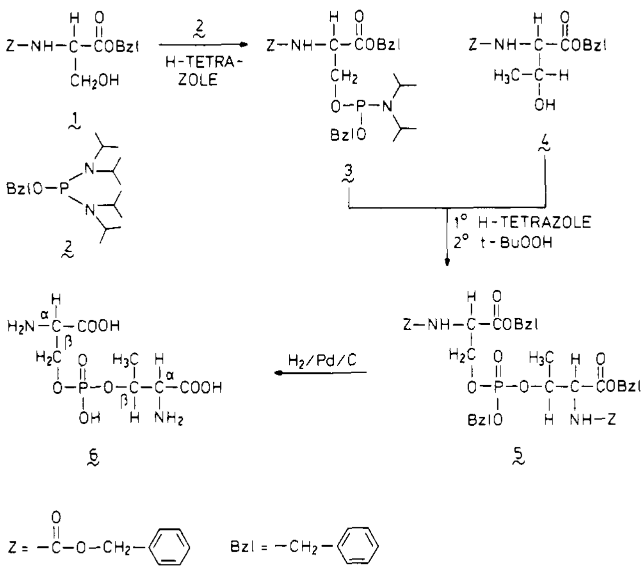

Table I. ^{1}H NMR Data of Compound **6** (Na$^+$ Salt, 0.16 mM in D$_2$O, pD 7.1)[15]

unit	δ values (ppm)	coupling constants (Hz)
		Seryl
Hα	3.95	$J_{H\alpha,P} = 1.2$, $J_{H\alpha,H\beta(a)} = 6.3$, $J_{H\alpha,H\beta(b)} = 3.6$
Hβ(a)	4.14	$J_{H\beta(a),P} = 5.0$, $J_{H\beta(a),H\beta(b)} = 11.3$
Hβ(b)	4.22	$J_{H\beta(b),P} = 5.1$
		Threonyl
Hα	3.70	$J_{H\alpha,P} = 1.9$, $J_{H\alpha,H\beta} = 3.3$
Hβ	4.74	$J_{H\beta,P} = 7.4$, $J_{H\beta,CH_3} = 6.6$
CH$_3$	1.42	

the rate of the elimination reaction.

In conclusion, the NMR data and virtually inertness of compound **6** toward base do not a priori exclude the presence of an unusual phosphodiester bond in *Azotobacter* flavodoxin; the assignment of the individual peaks, however, may be subject to further investigation. To this end, we are at present actively engaged in preparing model compounds which contain, apart from an intermolecular or intramolecular phosphodiester linkage, also peptide bonds.

Acknowledgment. We thank Prof. Dr. D. E. Edmondson for his critical remarks and helpful discussions.

Alkoxyl Radicals in 1,5-Hydrogen Shifts for Site-Specific, Stereocontrolled Alkylation of Carbohydrates[1]

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Two areas of continued interest in our laboratory in developing the organic chemistry of carbohydrates are concerned with enhancing stereoselectivity at (normally) "off-template" sites[4] and with the application of radical processes for mild transforma-

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(2) Holder of Research Fellowship from the Consejo Superior de Investigaciones Cientificas of Spain.

(3) Research Associate from the Universidad de Santiago de Compostela (Spain); acknowledges a fellowship from the Ministerio de Educacion y Ciencia (Spain).

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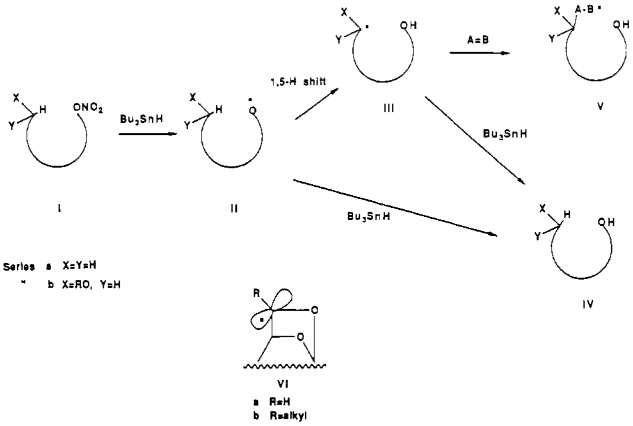
Scheme I

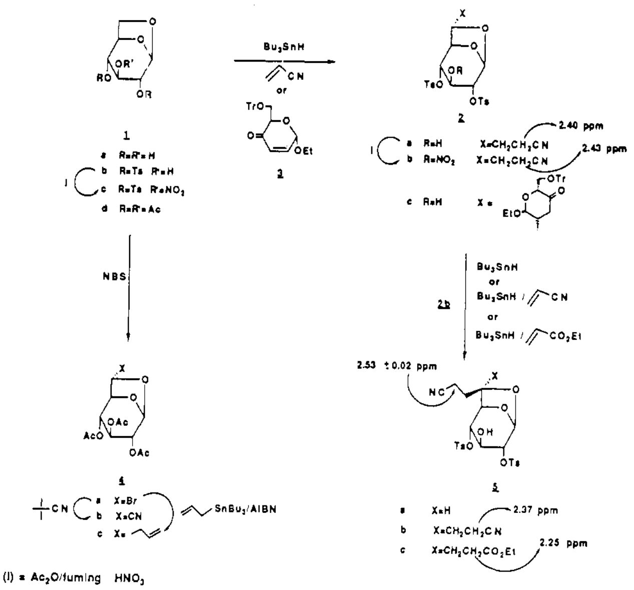


tions.[5-7] Thus far, the latter studies have focused primarily on ring-forming[5,6] and conjugate addition processes that exploit the nucleophilic character of carbon-centered radicals.[6,7] However, in view of the wealth of hydroxyl groups in sugars, the use of oxygen-centered radicals for eliciting specific functionalization in carbohydrates seemed worthy of investigation. Our efforts in this direction were prompted by recent studies in our laboratory that showed that alkoxy radicals could be conveniently generated by reaction of nitrate esters with tri-*n*-butyltin hydride,[8] I → II (Scheme I), thereby providing an operationally simple alternative to the well-known photochemical decomposition originated by Barton and co-workers[9,10] and modified by Binkley.[11]

The ease of 1,5-hydrogen transfer to such alkoxy radicals,[12] IIa → IIIa, is the basis of the original Barton reaction for functionalizing a remote angular methyl group.[10] In the case where the oxygen radical is generated by tri-*n*-butyltin hydride, the intramolecular process, II → III, must compete with intermolecular reaction with tri-*n*-butyltin hydride, II → IV. Our hope for the success of the postulated process for the ethers Ib (vis-à-vis Ia) was based on three factors. The first is that hydrogen abstractions IIb → IIIb should be facile because of the α-oxygen.[10] The second and third factors relate to the dual characteristics of the α-oxygenated radical IIIb. Thus, the stability of IIIB (vis-à-vis IIIa) should be enhanced by the stabilizing effect of the n electrons of the OR group.[13] Second, and on the other hand, radical IIIb is more nucleophilic[14] than its carbon counterpart IIIa and should therefore be readily trapped by a suitable electrophile, AB, to give adduct V. In this paper, we describe recent studies on the use of suitably stationed alkoxy radicals for specific functionalization of normally "off-template" centers of sugars.

Our starting material for these studies was readily available levoglucosan[15] (**1a**, Scheme II), which was smoothly converted into the test substrate by partial sulfonation to give **1b**,[16] followed by nitration[8,11] to give **1c** in 72% and 82% yields, respectively. Reaction of **1c** with tri-*n*-butyltin hydride in the presence of acrylonitrile led to **2a** in 78% yield, based on recovery of **1b**. Similarly, reaction of **1c** in the presence of the α-enone **3**[17] afforded a 38% yield of adduct **2c**.

Scheme II



The structures of **2a** and **2c** could be assigned on the basis of ample precedent.[18] Ferrier has shown that the triacetyl derivative **1d** reacts with *N*-bromosuccinimide to give the exo bromide **4a** exclusively.[19] The work of Ohrui has shown similar exo preference.[20] On the basis of Giese's work, radicals at the anomeric center, as in VI (Scheme I), are expected to be planar π-radicals[21] and because of steric factors, reaction from the exo face should be preferred, leading to products **2a**, **2c**, or **4a**. Indeed, we have found that bromide **4a** reacts with *tert*-butyl isocyanide[22] and with $CH_2{=}CHCH_2SnBu_3$[23] to give exo-substituted compounds **4b** and **4c**, respectively.

The exo facial selectivity of the planar radical VI could be exploited. Thus, when the nitrated propionitrile **2b** was treated with tri-*n*-butyltin hydride, the epimer **5a** was obtained in 67% yield based on 18% recovery of **2a**.

The ratio ~3:1 of **5a** and **2a** shows that C3 alkoxy radicals undergo 1,5-H shifts to a greater extent than intermolecular reaction with tri-*n*-butyltin hydride. These results raised the possibility that further functionalization at C6 of **1** could be effected. Thus, on this basis, it was reasonable to assume that

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(15) Levoglucosan (1,6-anhydro-β-D-glucopyranose) is commercially available from Hoechst, Frankfurt, West Germany. However, instructions for a ready, large-scale preparation from D-glucose are available from the authors upon request.

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secondary radicals (e.g., VIb) would also be alkylated preferentially from the exo face. Indeed, when the foregoing reaction of nitrate ester **2b** was conducted in the presence of acrylonitrile, the principal product was the bisnitrile **5b** along with some **5a** (26%) and recovered **2a** (14%).

Comparison of the ^{1}H NMR spectra of the C6 epimers **2a** and **5a** was instructive because it revealed characteristic differences in the chemical shifts for the α-methylenes of the exo- and endo-oriented cyanoethyl residues, as indicated in Scheme II. These differences were preserved in the bisnitrile **5b** and aided in assignment of the adduct **5c**, obtained as the only disubstituted product from reaction with ethyl acrylate. Thus, the resonance at 2.52 ppm in **5c** is consistent with the (expected) endo orientation of the cyanoethyl residue.

The use of these alkylated derivatives in ring-forming and other reactions of pyranoses is being investigated and will be reported in due course.

Supplementary Material Available: Experimental details for preparation of the products as well as the new procedure for large-scale preparation of levoglucosan (8 pages). Ordering information is given on any current masthead page.

In Situ Restoration of Atomically Well-Ordered Copper Single Crystal Electrode Surfaces

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The importance of single crystals in fundamental studies of surface electrochemistry cannot be overemphasized.[1] Investigations aimed at correlating orientation with electrochemical reactivity require single crystal electrodes. In such studies it is necessary to establish that the surface structure is ordered and uniform.[2] The preparation of single crystal electrode surfaces involves orienting and metallographic polishing, followed by removal of the residual selvage layer. The selvage is usually removed by ion bombardment followed by annealing in ultrahigh vacuum (UHV) to restore atomic smoothness. Surface orientation and order are then examined by low-energy electron diffraction (LEED). In favorable cases, it is possible to remove the selvage by chemical and/or electrochemical etching. However, in the absence of LEED verification, the surface structure and order can only be assumed.

It is desirable to avoid the transfer of electrodes to and from a UHV analysis chamber for each experiment. It is thus critical to develop methodology which allows, in situ, the formation or restoration of atomically well-ordered electrode surfaces. In this brief communication, we describe a novel method which permits the formation or restoration of well-ordered surface structures of copper single crystal electrodes whose surfaces had been disordered either by oxidation or by ion bombardment.

The experimental procedures employed in this study have been described in detail elsewhere.[3] Surface structural and compositional analysis made use of a UHV surface analysis instrument to which an antechamber had been interfaced that permitted electrochemical experiments to be performed at ambient pressures without exposure to air. Crystalline damage or disorder of the Cu(100) surface was accomplished in two ways. The first consisted of Ar$^+$ ion bombardment; the second was accomplished by air-oxidation of the Cu surface.

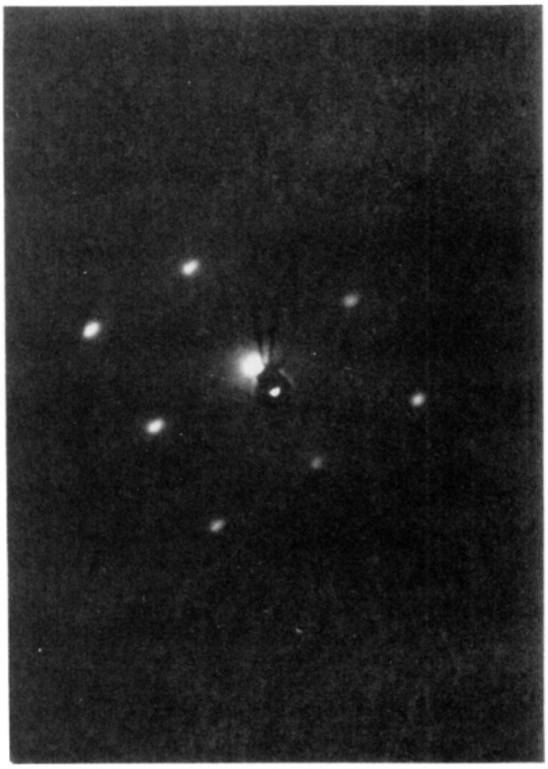

Figure 1. LEED photograph of Cu(100)($\sqrt{2}\times\sqrt{2}$)R45°–Cl, after immersion in 1 mM HCl, 51 eV.

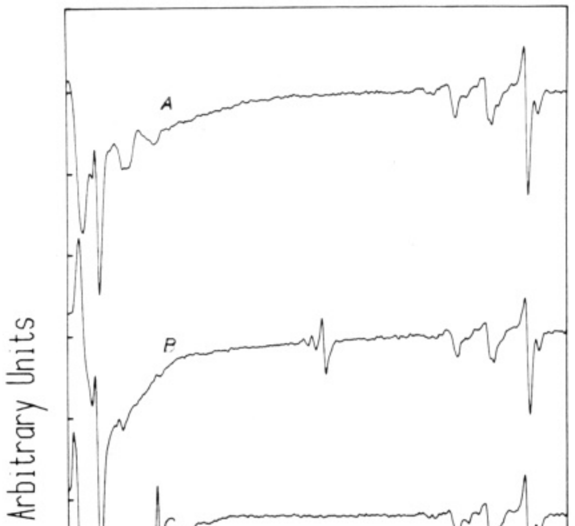

Figure 2. Auger spectra: 1 mm^2 beam size, 0.1 nA beam current, 3000 V, and 5 min scans. (A) Clean copper surface; (B) oxidized copper surface, O_2 at 1 atm for 5 min; (C) after immersion in 1 mM HCl; and (D) after immersion in 1 mM H_2SO_4.

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