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 ¹H 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
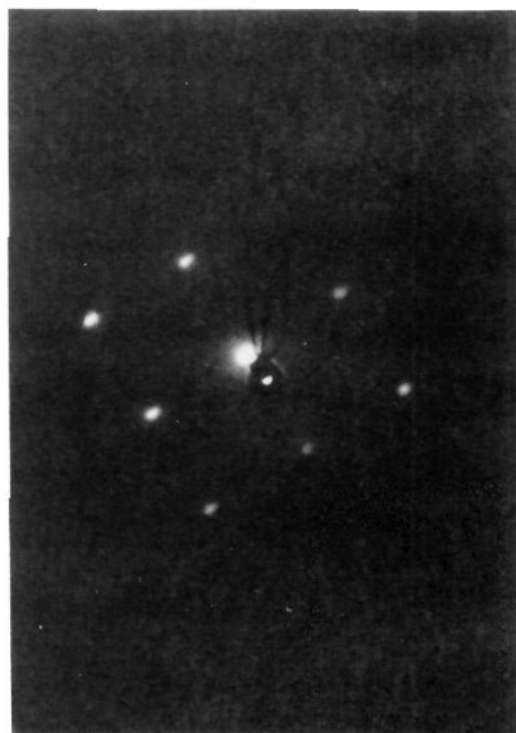

Figure 1. LEED photograph of Cu(100)($\sqrt{2}\times\sqrt{2}$)R45°–Cl, after immersion in 1 mM HCl, 51 eV.
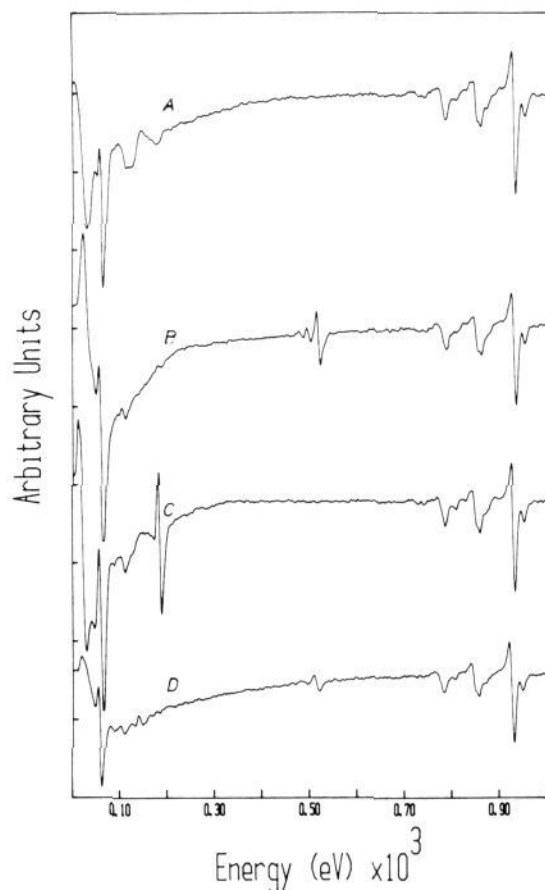

Figure 2. Auger spectra: 1 mm² beam size, 0.1 nA beam current, 3000 V, and 5 min scans. (A) Clean copper surface; (B) oxidized copper surface, O₂ at 1 atm for 5 min; (C) after immersion in 1 mM HCl; and (D) after immersion in 1 mM H₂SO₄.

of Ar⁺ ion bombardment; the second was accomplished by air-oxidation of the Cu surface.

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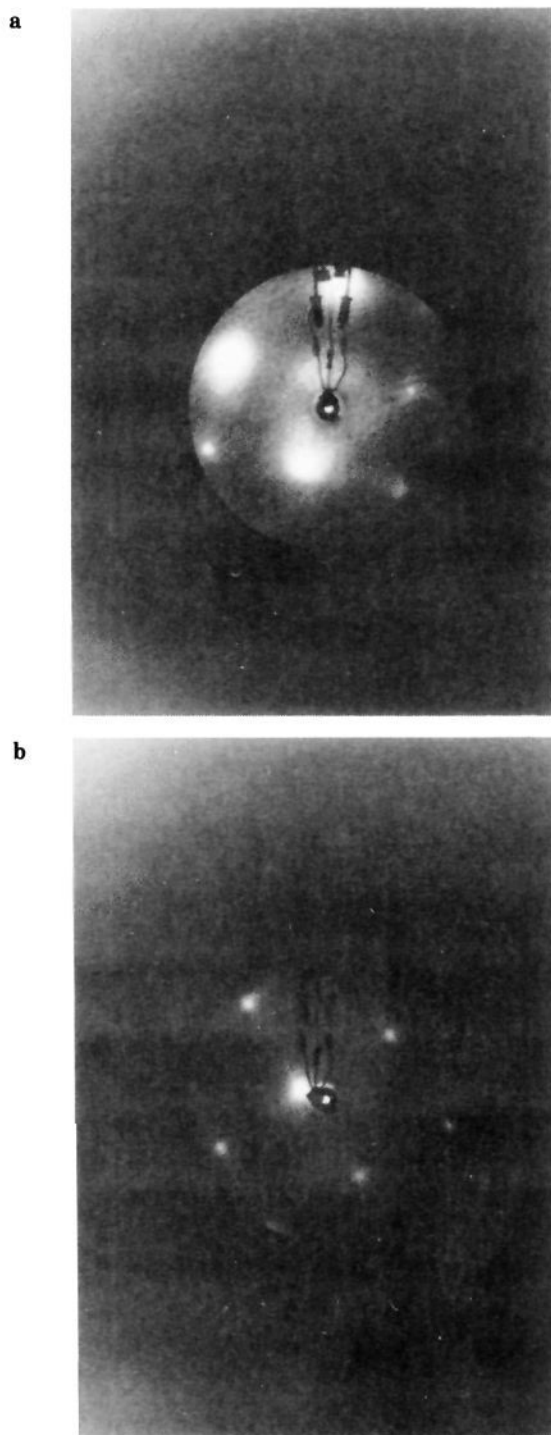
a

b

Figure 3. (A) LEED photograph for ion-bombarded Cu(100), no anneal, 76 eV. (B) LEED photograph for ion-bombarded crystal immersed in 1 mM HCl for 5 min, 33 eV.

An initially clean and ordered Cu(100) single crystal electrode surface was exposed to 1 atm of high-purity oxygen gas for 5 min. No distinct LEED spots were visible, in the resulting pattern, at any energy. These results indicate complete destruction of the crystalline order on the initially prepared (100) surface. The Auger electron (AES) spectrum of this oxidized surface is shown in Figure 2B. Formation of multiple layers of copper oxide, about 2 nm thick, is indicated by the oxygen Auger transition, 510 eV. Bombardment of the Cu(100) surface with energetic Ar^+ ions, without subsequent annealing, also results in disruption of the initially ordered single crystal surface, evidenced by the LEED pattern shown in Figure 3A; LEED spots are present, but they

are diffuse and considerably enlarged in comparison with the clean and annealed surface pattern.

Immersion of the oxidized surface into 1 mM HCl resulted in the same rest potential as that for the reduced surface, after 2 min. The LEED pattern following immersion in the dilute HCl solution, and emersion into vacuum is shown in Figure 1. Clearly, exposure of the oxide-coated Cu(100) surface to dilute HCl brought about the reappearance of sharp LEED spots. The LEED pattern shown in Figure 1 is characteristic of a Cu(100)($\sqrt{2} \times \sqrt{2}$)R45° structure; the AES spectrum is shown in Figure 2C. These LEED and AES results are identical with those observed when a clean, ordered Cu(100) surface is immersed directly in dilute HCl.[4] These results are irrefutable evidence that the single crystallinity of the Cu(100) surface is restored when an amorphous or disordered oxidized surface is immersed in dilute HCl solution. The AES spectrum in Figure 2C shows chlorine but no oxygen.

Immersion of the oxidized surface in a 1 mM H_2SO_4 solution also resulted in reordering of the Cu(100) surface as evidenced by formation of a Cu(100)(2×2) LEED pattern;[4] Figure 2D indicates that 1/4 coverage sulfate is responsible for the (2×2) pattern. Clearly, restoration of long-range order on an oxidized surface is not limited to HCl.

Figure 3B is a photograph of the LEED pattern observed when an ion-bombarded, unannealed, Cu(100) surface, Figure 3A, was immersed in 1 mM HCl and electrochemically oxidized. It can be seen that the diffuse intensity was substantially reduced, and a Cu(100)($\sqrt{2} \times \sqrt{2}$)R45° pattern was formed. 100 monolayers of Cu were oxidatively removed prior to formation of the ordered surface, Figure 3B. It is probable that electropolishing baths other than 1 mM HCl would lead to more facile restoration of crystalline order on the Cu electrode surface, and further studies are being pursued in this regard.

Data for the HCl-treated, ion-bombarded Cu surface, reported here, represent the first observations of electropolishing at the atomic level. It is clear that disordered single crystal surfaces may be restored in situ by electrolytic dissolution in mild acid solutions.

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Zinc and Copper Carbenoids as Efficient and Selective a^1/d^1 Multicoupling Reagents. 1

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The high-covalent character and the consequent low reactivity of the carbon–zinc bond allow the synthesis of highly functionalized organozinc compounds RZnX. These organometallics can be converted to the corresponding copper derivatives RCu(CN)ZnX which react efficiently with various electrophiles.[1] Of special interest are functionalized organozinc halides in which the functional group can interact with the carbon–zinc bond leading to new reactivity patterns. Zinc carbenoids of type **1** belong to this category of reagents. They may be precursors of the carbene **2** and as such have found several synthetic applications.[2] Due

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