Dithiol 1 was prepared by coupling of 3-methylpyridine to the bipyridine, conversion of the methyl groups to carboxyl and then amino, double diazotization, and reaction of the diazonium compound with potassium ethylxanthate. The resulting bis-dithiocarbonic acid was hydrolyzed and converted to the bis-thioacetate, and this was directly deprotected with NH3 to the dianion of the dithiol 1 and used in the next reaction. Reaction of the above dithiolate with &-cyclodextrin 6-iodide in DMF at 60-65 °C for 3 h afforded the cyclodextrin dimer 2 in 46% yield; it was isolated by reversed-phase chromatography and characterized by TLC, 'H NMR, and FAB-MS (M+ 1 = 2455). As expected, in water it is able to bind substrates having two appropriate hydrophobic groups. For instance, Trp-Trp 3, raised 10-fold when Zn2+ is also bound to the Cu2+ complex of dimer 2 and of 80-fold without the Cu2+. With simple β-cyclodextrin, the hydrolysis rate of 4 increased by a factor of only 30-fold, with and without Cu2+.

With Cu2+ the data for rate vs pH and vs catalyst concentration fit a mechanism in which the substrate binds to the Cu2+/2 catalyst, with &k = 7.0 × 10^−4 M⁻¹, and is attacked by hydroxide bound to copper, from a bound water with pKw = 7.15. Thus the observed acceleration relative to the simple hydroxide cleavage rate is at a maximum near pH 7. Ester 5 at 6.0 × 10⁻⁵ M shows a rate of hydrolysis with 1.0 × 10⁻⁴ M 2 and 2.0 × 10⁻⁴ M CuCl2 at pH 7.0 and 37 °C that is 220,000-fold faster than the rate of uncatalyzed hydrolysis. The kcat values are comparable in magnitude to those for the acylation step of one of the best catalytic antibodies by similar nitrophenyl esters.

The  nitrophenol and the corresponding carboxylic acid from 5 were both identified in approximately equal amounts by gas chromatography after isolation from the reaction catalyzed by Cu2+/2. Furthermore, with an excess of substrate 5, at least 50 turnovers were seen in the hydrolysis process. In our normal reactions the concentration of 5 is only 60% that needed (1.0 × 10⁻⁴ M) for solubility saturation, although in the turnover experiments it was 50 times higher and 5 was partially out of solution until the end of the hydrolysis reaction.

Thus, as hoped, stretching a substrate across a metal catalytic group has led to significant catalysis. We expect that the well-defined geometry in enzyme models using cyclodextrin dimers will lead to other advantages as well.

**Acknowledgment.** This work has been supported by grants from the NIH and the ONR.

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**Figure 1.**

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**Covalent Modification of Carbon Surfaces by Grafting of Functionalized Aryl Radicals Produced from Electrochemical Reduction of Diazonium Salts**

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Modification of carbon surfaces is of interest to several fields of material science and electrochemistry. Probably most important from the industrial point of view is the modification of the surface of carbon fibers to improve the mechanical properties of composites, particularly carbon–epoxy composites. Modification of electrode surfaces for catalytic or analytical purposes and biotechnological applications also currently attracts considerable attention. Most of the available methods for modifying carbon surfaces involve their oxidation, thus leading to the generation of superfluous carboxyl, quinonic, ketonic, or hydroxylic groups that are further reacted with the substance to be attached. The exact nature and number of oxygenated functional groups thus formed are difficult to ascertain and control, and corrosion of the carbon surface is often observed leading to large background.
For this purpose we have investigated a reductive, rather than an oxidative, strategy. It is based on the electrodeposition of diazonium salts, which leads to a very solid and noncorrosive covalent attachment of aryl groups onto the carbon surface. The versatility of the method is founded on the possibility of grafting a large variety of functionalized aryl groups, hence allowing the attachment of a broad spectrum of substances.

For example the 4-nitrophenyl group obtained from 1 could be reduced electrochemically (in 0.1 M KCl, irreversible 6e peak) to a 4-aminophenyl group (the CV and XPS signals of the nitro groups disappear and the XPS signal of the amino group appears). Such an amino group could also be obtained by hydrolysis of a 4-acetamidophenyl group. This 4-aminophenyl group could in turn be reacted with an epoxy function such as that of epichlorhydrin (the chlorine atom can be observed by XPS), demonstrating the possibility of generating covalent bonds between the carbon surface and epoxy resins. Preliminary experiments also indicated the viability of the attachment of enzymes along a similar strategy.

We assign the covalent attachment of the aryl groups to the binding of the aryl radical produced upon one-electron reduction of the diazonium salt to the carbon surface. Two factors favor such a reaction: (i) the diazonium salt is adsorbed prior to its reduction, and (ii) the aryl radical is not reduced at the very positive reduction potential of the diazonium salt (opposite to what is observed, for example, with aryl halides). As concerns the carbon surface, the covalent binding seems to involve at the same time edge defects and polycyclic aromatics, as shown by the attachment of aryl groups to the basal plane of HOPG.

As a result of the reductive strategy we used and of the strong bonding between the surface and the aryl groups, low residual currents (similar to those observed at a bare electrode) were obtained over a large window of potentials, the same as for the unmodified parent GC electrode.

Supercritical-Catalyzed Protium–Deuterium Exchange in Isobutane Competing with tert-Butyl Cation Formation

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That saturated hydrocarbons do react at room temperature and below with various superacidi media has been known since the late 1960s when Hogeveen and Olah and his group published their pioneering work. Both Hogeveen and Olah, in a HF-SbF₅-Freon...