Table II. Methylchymotrypsin Catalyzed Peptide Synthesis[a]

no.	acyl donor	acyl acceptor	product	enzyme	rxn time (h)	yield (%)
1	Z-L-Phe-OCH_2CN	L-Leu-NH_2	Z-L-Phe-L-Leu-NH_2	MeCT[b]	0.7	88
2	Z-D-Phe-OCH_2CN	L-Leu-NH_2	Z-D-Phe-L-Leu-NH_2	MeCT	0.7	4
3	Z-L-Phe-OCH_2CN	L-Leu-NH_2	Z-L-Phe-L-Leu-NH_2	none	48	5
4	Z-L-Phe-OMe	L-Leu-NH_2	Z-L-Phe-L-Leu-NH_2	MeCT	48	41[c]
5	Z-L-Phe-OCH_2CN	D-Leu-NH_2	Z-L-Phe-D-Leu-NH_2	MeCT	0.5	18
6	Z-L-Phe-OCH_2CN	D-Leu-NH_2	Z-L-Phe-D-Leu-NH_2	α-CT	0.5	21
7	Z-L-Phe-OCH_2CN	L-Leu-OMe	Z-L-Phe-L-Leu-OMe	α-CT	0.5	2
8	Z-L-Phe-OCH_2CN	L-Leu-OMe	Z-L-Phe-L-Leu-OMe	MeCT	0.5	91
9	Z-L-Leu-OCH_2CN	L-Leu-NH_2	Z-L-Leu-L-Leu-NH_2	MeCT	3	77
10	Z-Y-G-G-F-OCH_2CN	L-Leu-NH_2	Z-Y-G-G-F-L-NH_2	α-CT	0.7	56[d]
11	Z-Y-G-G-F-OCH_2CN	L-Leu-NH_2	Z-Y-G-G-F-L-NH_2	MeCT	0.7	99[e]

[a] Reaction conditions unless otherwise indicated: 100 mM acyl donor, 200 mM acyl acceptor, 1–2 mg enzyme in 1 mL Tris HCl/DMSO (1:1), pH 8.8. Reactions monitored by HPLC, peaks identified by coelution with samples authenticated by NMR. Yields from reactions containing Tris were normalized for small amounts of Tris adduct formed. [b] In all reactions, MeCT was pretreated ith phenylmethylsulfonyl fluoride for 30 min to inhibit traces of native CT. [c] 41% of ester unreacted. [d] Reaction buffer: 0.1 M phosphate/dioxane (35%), pH 10. After 11 h, 21% Z-Tyr-OH (secondary hydrolysis product) was detected. Similar results were obtained in 35% acetonitrile, with a 66% yield of peptide and 3% yield of Z-Tyr-OH. [e] No hydrolysis product detected after 24 h.

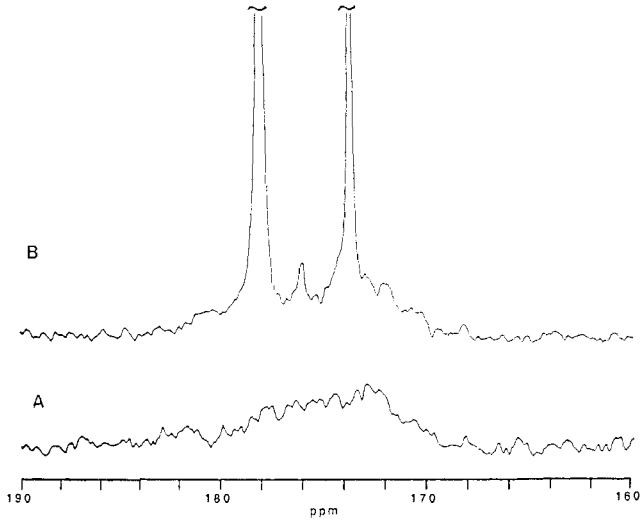

Figure 1. 75 MHz ^{13}C NMR spectrum of 1.6 mM MeCT in 0.1 phosphate/D_2O buffer, 50 mM NaCl, pH 4.4, 25 °C; (A) enzyme alone and (B) 24 h after the addition of 6 mM *N*-acetyl[1-13C]-L-Phe-OEt. Each spectrum represents 50000 scans (5 h) of accumulation.

actions are still general-base catalyzed, thus accounting for the increase of activities at higher pH.[11]

The catalytic competency of MeCT can be further demonstrated by nuclear magnetic resonance (NMR) spectroscopy. The MeCT catalyzed hydrolysis of *N*-acetyl[1-^{13}C]-L-phenylalanine ethyl ester was monitored by ^{13}C NMR under conditions expected to accumulate acyl–enzyme intermediate (Figure 1). In addition to resonances assignable to substrate ester (δ 173.8) and product acid (δ 178.2) is a third signal at δ 176.2 ppm which can be attributed to the acyl intermediate formed with serine 195 of the enzyme. The result is in agreement with the value of δ 176.5 observed for the acyl intermediate formed between *N*-CBZ-lysine *p*-nitrophenyl ester and trypsin at −21 °C.[12] In this case, the acyl enzyme is observable at *room temperature*. Additionally, based on the relative areas of the three signals, it is estimated that approximately 20% of the enzyme is present as the acyl intermediate.

Table II summarizes our initial investigations. MeCT efficiently catalyzes the coupling of phenylalanine and leucine at rates much higher than the direct chemical coupling of the activated ester and the nucleophile (reaction 1 versus 3). The reaction is stereospecific in that Z-D-Phe-OCH_2CN is not an effective acyl donor. The range of acyl acceptor specificity is very broad, including L- and D-amino acid derivatives. Higher nucleophile concentrations will give correspondingly higher yields. Interestingly, the differing reactivities of the esters allow for the use of the methyl ester as a *protecting* group for hydrophobic, L-nucleophiles, which is not possible with the native enzyme (reactions 8 and 9).

The acyl donor specificity is the same as that of the native enzyme but does not appear to be as broad as that for thiol-subtilisin. Aromatic and hydrophobic amino acids such as tyrosine, phenylalanine, leucine, and methionine are reactive, while less hydrophobic amino acid derivatives such as Z-Gly-OCH_2CN were not. The narrow specificity, however, is often desirable when an enzyme is used in fragment coupling.

As a model of fragment coupling, the synthesis of Z-Leu-enkephalinamide was undertaken. This peptide contains a chymotrypsin sensitive peptide bond (Tyr-Gly). Hydrolysis of this bond will be diagnostic of secondary hydrolysis by the catalyst. Indeed, upon extended incubation of the reaction containing α-CT, free Z-Tyr-OH was detected (4–20%, depending on cosolvent). No Z-Tyr-OH was detected with MeCT, even after 24 h.

In summary, this communication provides a simple chemical procedure for alteration of chymotrypsin to an amidase-free esterase useful for peptide synthesis. Other serine proteases could be modified similarly to have such new enzymatic activities. The histidine residue in the active site of serine proteases may be a target for site-directed mutagenesis in order to develop novel esterases. Application of this esterase as a catalyst for the condensation of large peptide fragments containing usual and unusual amino acids is in progress.

(10) At pH 7.8, the ratio of the first-order rate constants for acylation (k_2) to deacylation (k_3) is smaller for methylchymotrypsin than for the native enzyme (7 versus 27 for Ac-Tyr-OEt) (ref 8). Native chymotrypsin exhibits similar reactivities in high organic solvent and high pH (unpublished data).

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Photoelectrochemical Evolution of Elemental Fluorine at TiO_2 Electrodes in Anhydrous Hydrogen Fluoride Solutions

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Received December 29, 1987

Although elemental fluorine has been known for more than 100 years,[3] it is still produced by Moissan's original method, electrolysis of anhydrous HF/alkali fluoride solutions. Only one convenient alternative route for preparing fluorine has been reported to date.[4] Several oxide and oxyfluoride semiconductors have valence band

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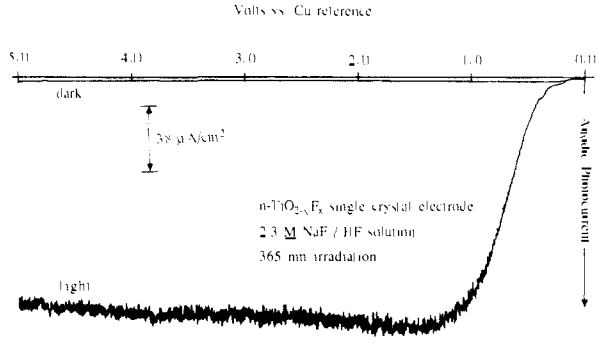

Figure 1. *i–V* curves for electrolysis of anhydrous HF/2.3 M NaF at a $TiO_{2-x}F_x$ electrode in the dark and under 365-nm illumination. Potentials are referred to a Cu wire pseudoreference (see text). Incident light intensity (corrected for absorbance by the Teflon FEP cell) is 0.82 mW/cm². Scan rate 20 mV/s.

edges that are positive of the F^-, F_2 standard potential,[5] and holes photogenerated in the valence band of these materials should, in principle, be capable of oxidizing F^- to F_2. In aqueous fluoride-containing solutions other processes such as water oxidation and photoanodic corrosion compete effectively with F^- oxidation, and no fluorine is formed.[6] Even in nonaqueous solutions these wide bandgap semiconductors photocorrode, unless sufficient reductant is present to compete for photogenerated holes.[7] In anhydrous solutions containing sufficient quantities of fluoride ion is is reasonable to expect that fluorine might be generated photoelectrochemically at a semiconductor surface which is somehow stabilized against photocorrosion. We report here that elemental fluorine is evolved at n-type TiO_2 electrodes in anhydrous HF/NaF solutions. Using bandgap illumination (365 nm) gaseous F_2 is produced with a sizable photovoltage and high power conversion and current efficiencies. While electrode photocorrosion occurs to some extent in all these experiments, it may be minimized greatly by using fluorine-doped TiO_2 electrodes.

Figure 1 shows typical *i–V* curves obtained[8] from a $TiO_{2-x}F_x$ ($x \approx 0.001$) electrode in HF/2.3 M NaF solution. In this medium hydrogen evolution occurs at a Pt electrode at −0.35 V vs a Cu wire reference electrode; from the free energy of formation of liquid HF we then calculate the formal potential of the F^-, F_2 couple, E_{F^-,F_2}, to be +2.47 V vs Cu. The onset of photocurrent in Figure 1, at +0.25 V, corresponds to an open circuit photovoltage of 2.2 V. This unusually high photovoltage derives from the large difference (ca. 2.7 V) between the $TiO_{2-x}F_x$ flatband potential and the F^-, F_2 formal potential. Implied is an absence of midgap surface states which could limit the photovoltage via Fermi level pinning.[9] The power conversion efficiency[10] measured at the maximum power point (+1.0 V vs Cu) is 22 ± 3% and the quantum efficiency measured at E_{F^-,F_2} is 55 ± 8%. The photogenerated fluorine was identified by its volatility at −196 °C, infrared inactivity, mass spectrum,[11] and chemical interaction with mercury and KI.

By holding the potential of the illuminated electrode at +2.0 V and integrating the current, it was possible to assess accurately the current efficiency for photoelectrochemical fluorine production. After photoelectrolysis under white (150 W mercury vapor lamp) light for a fixed period of time at current densities 0.5 to 1.0 mA/cm², the photogenerated fluorine was passed through a cold trap held at −88 °C and into a trap containing excess KI. The I_3^- produced was titrated with aqueous $Na_2S_2O_3$. *n*-TiO_{2-x} electrodes prepared by heating TiO_2 in air to 900 °C and subsequent hydrogen reduction at 400–500 °C initially gave *i–V* curves similar to those shown in Figure 1 and current efficiencies in the range 87–91 ± 1%. However, after several hours of illumination these electrodes showed poorer performance with increasing (dark) background currents, decreasing photocurrent, and decreasing current efficiency for fluorine production. After 4–5 h, no more fluorine was produced and the electrode surface was visibly etched. On the other hand, $TiO_{2-x}F_x$ electrodes showed excellent current efficiency (99–100% after 4–5 h), relatively stable photocurrent, and low background current. Visible etching of these electrodes took place only slowly, over a period of 1–2 days of continuous photoelectrolysis.

It is interesting that fluorine doping stabilizes *n*-TiO_2 against photocorrosion, and that non-fluorinated *n*-TiO_{2-x} prepared by hydrogen reduction, which photocorrodes readily, produces any fluorine at all. It is known[6] that fluoride ions enhance the photocorrosion of TiO_2 via reactions 1 and 2 in aqueous solution; the standard potentials of these reactions are estimated to be +1.42

$$TiO_2 + 2h^+ = TiO^{2+} + \tfrac{1}{2}O_2 \quad (1)$$

$$TiO_2 + 4F^- + 2h^+ = TiOF_4^{2-} + \tfrac{1}{2}O_2 \quad (2)$$

and +1.15 V vs NHE, respectively,[12,13] far negative of the potential of reaction 3 which is responsible for fluorine production. While the standard potentials of (1) and (2) refer to pH 0 aqueous

$$2F^- + 2h^+ = F_2 \quad (3)$$

solutions, it is reasonable to expect that in HF/NaF the analogous reactions will also be appreciably negative of (3). We conclude therefore that (3) is favored for kinetic reasons. Photocorrosion via (1) and/or (2) occurs more readily at TiO_{2-x}, which contains anion vacancies, than at $TiO_{2-x}F_x$, which has a relatively perfect anion lattice. SEM photographs of etched *n*-TiO_{2-x} crystals show tetragonal etch pits; XPS and AES spectra show the presence of only Ti and O on the surface, indicating that soluble species are formed in the etching process. These observations are consistent with photocorrosion via (1) and/or (2). Remarkably, (3) is competitive with these processes in anhydrous HF/NaF. It is possible that similar stabilization may be found in other anhydrous solvents; investigation of the photoelectrochemical behavior of these

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(9) Complex admittance analysis of the *n*-TiO_2/aqueous electrolyte interface (Nagasubramanian, G.; Wheeler, B. L.; Bard, A. J. *J. Electrochem. Soc.* **1983**, *130*, 1680) indicates an insufficient density of mid-gap surface states for Fermi level pinning. A similar analysis in anhydrous HF/NaF is presently contemplated.
(10) Defined as $[(E_{F^-,F_2} - V)(i_{photo})/\text{incident power}] \times 100$; the incident power is corrected for absorbance of the Teflon FEP cell at 365 nm.
(11) Electron impact spectra were recorded on a Finnigan 4023 mass spectrometer with a gas inlet probe. The gaseous product from 8 h of photoelectrolysis at a $TiO_{2-x}F_x$ electrode was passed through a cold trap to remove HF and collected in a stainless steel can. The positive ion mass spectrum was dominated by the F_2 parent ion peak at m/z 38 and a smaller fragment peak at m/z 19; small background peaks at m/z 32, 28, and 44, attributed to air leaks in the inlet probe, were also observed.
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electrodes, and of other oxyfluoride semiconductors, in fluoride-containing solvents is currently in progress.

Acknowledgment. We thank Dr. Michael Schmerling for carrying out the SEM work and Dr. Sohail Akhter and Jeffrey Cook for the XPS and AES spectra. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. XPS instrumentation was supported by a National Science Foundation grant (DMR 8418086) to the University of Texas Materials Research Group. Q.-C.M. thanks the NSF-Sponsored Summer Research Program in Solid State Chemistry for support of her stay at UT Austin.

Intramolecular Hydrosilation of α-Hydroxy Enol Ethers: A New Highly Stereoselective Route to Polyhydroxylated Molecules[1]

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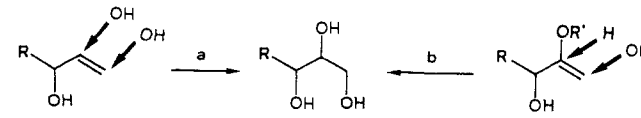
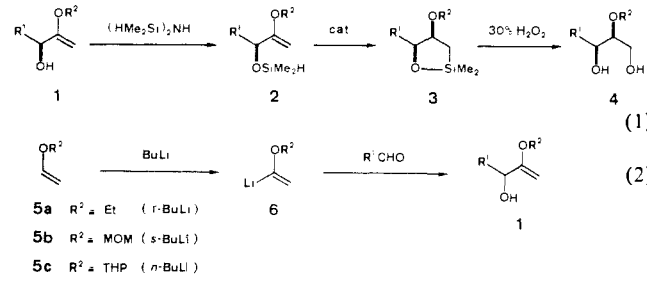
Received November 30, 1987

Stereoselective chemical synthesis of carbohydrates constitutes a large and challenging field in modern synthetic organic chemistry.[2] Among a wide variety of methodologies for stereoselective construction of polyoxygenated skeletons,[3] that being the most straightforward is the stereoselective introduction of two oxygen functionalities to the carbon–carbon double bonds (Scheme I, route a), as represented by the Sharpless epoxidation[4] or osmium tetroxide oxidation of allyl alcohols.[3h,5] An alternative route may be achieved by anti-Markownikoff hydration of enol ether counterparts (Scheme I, route b), but such an approach has so far been rarely studied.[6]

Scheme I



We report herein our initial results of stereoselective polyol synthesis via the latter process. Thus, a new route to 2,3-*threo*-1,2,3-triols **4** can be realized by intramolecular hydrosilation[7] of 2-alkoxy-1-alken-3-ols **1**, followed by oxidative cleavage of the carbon–silicon bond,[8] as shown in eq 1. Since the starting materials **1** are readily available from aldehydes and vinyl ethers **5a–c** (eq 2),[9] the new method should find a wide application.



Representative results are listed in Table I. A typical experimental procedure is given for the preparation of **4b** from **1b**. A mixture of **1b** (465 mg, 2.4 mmol), $(HMe_2Si)_2NH$ (2.4 mmol), and ammonium chloride (ca. 3 mg) was allowed to stand at room temperature overnight to ensure silylation of the hydroxy group in **1b**. The excess disilazane was removed in vacuo. To the remaining oil was added a toluene solution of $[Pt\{[(CH_2{=}CH)Me_2Si]_2O\}_2]$[10] (0.25 M, 48 μL; 0.5 mol%), and the mixture was stirred at room temperature for 0.5 h. GLC analysis showed the completion of hydrosilation. The platinum species were removed by stirring the mixture with EDTA·2Na (480 mg) and hexane (10 mL) overnight and subsequent filtration. The filtrate was stripped off the solvent and treated with 15% KOH (1.0 mL) and 30% H_2O_2 (1.62 mL, 14.4 mmol) in a 1:1 mixed solvent of MeOH/THF (ca. 14 mL) at room temperature. The oxidative cleavage was completed in 2 h, as monitored by TLC. The usual anhydrous workup[8c] followed by column chromatography gave 360 mg (71% yield) of **4b** (silica gel; hexane/EtOAc, 1:1, R_f 0.23). The acetonide of **4b** (2,2-dimethoxypropane, CSA catalyst, room temperature, 1 h; 93%) was isomerically pure by GLC and 400 MHz NMR analysis.[11]

Since the most commonly used catalyst, $H_2PtCl_6{\cdot}6H_2O$ in *i*-PrOH or in THF, was not suitable for the hydrosilation of acid-sensitive enol ethers,[12] we examined several neutral catalysts and found the platinum(0)/vinylsiloxane[10] to be most effective.

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