dithiothreitol (37 °C, pH 7.6). The DNA fragments were visualized by autoradiography of a high resolution denaturing gel, and the extent of DNA cleavage was quantitated by densitometry (Figure 3). Footprinting reactions revealed cleavage inhibition at the sequence 5'-AATTTTTTTTATTTAT-3'. The affinity cleaving reactions showed two cleavage patterns, asymmetric to the 3' side, flanking this same 16 bp stretch of A,T DNA.

According to the n + 1 rule,[7a] peptide (P4)₃E which contains 15 amide groups suitable for DNA recognition should bind 16 contiguous base pairs of A,T DNA (Figures 1 and 2). The correspondence of the cleavage loci for (P4)₃E·Fe(II) flanking the same 16 bp site as the cleavage inhibition patterns (footprinting) for (P4)₃E·In(III) is consistent with one major recognition mode for the peptide at that site. The asymmetry of the observed cleavage patterns to the 3' side confirms that the peptide is binding in the minor groove of right-handed DNA. The cleavage intensity flanking the 16 bp site is 2:1 which suggests two binding orientations that are not too different in energy. The observation of 16 base pair binding in the absence of obvious dimeric binding (11 base pairs) or monomeric (six base pairs) demonstrates that, at least for this 16 bp DNA sequence, β-alanine allows simultaneous binding of the three tetrapeptide subunits.

In summary, a peptide, 14 amino acid residues in length, has been constructed which is capable of binding 16 base pairs of contiguous A,T DNA in the minor groove. This demonstrates the feasibility of linking multiple DNA-binding subunits together to produce a synthetic scaffold amenable to further refinement that can bind a turn and a half of the DNA helix[17] in a sequence-specific fashion.

(17) Netropsin binds DNA in the B-form.[4] If the (P4)₃E:DNA complex is in the B-form (average 10.4 bp/turn), then this synthetic peptide binds a turn and one-half of the DNA helix.[17]

Catalytic Oxidative Cleavage of Vicinal Diols and Related Oxidations by Ruthenium Pyrochlore Oxides: New Catalysts for Low-Temperature Oxidations with Molecular Oxygen

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Oxidative cleavage of vicinal diols constitutes a key reaction encountered in the determination of carbohydrate structure[1] and in the metabolism of various polyhydroxylated substances.[2] Although stoichiometric high-valent oxidants are well-known reagents for glycol cleavage,[3] efficient nonenzymatic systems that

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Table I. Oxidation of 1,2-Cyclohexanediol, 1,6-Hexanediol, and Cyclohexanone by Ruthenium Pyrochlore Oxide Catalysts

A. Batch Autoclave Reactor Oxidations[a,b]

catalyst	substrate	T, °C	time, h	substrate conv,[c] %	sel,[d] %
Pb₂.₆₂Ru₁.₃₈O₆.₅	TCD	25	7.00	100.0	71.7
Pb₂.₆₂Ru₁.₃₈O₆.₅	CCD	25	4.00	98.5	74.6
Pb₂.₁₅Ru₁.₈₅O₆.₅	TCD	25	7.17	45.4	57.7
Pb₂.₀₀Ru₂.₀₀O₆.₅	TCD	35	1.00	11.0	0.0
Bi₂.₄₆Ru₁.₅₄O₇₋y	TCD	40	6.33	70.0	99.6
Pb₂.₆₃Ru₁.₃₇O₆.₅	HD	55	6.00	100.0	57.0
Pb₂.₆₂Ru₁.₃₈O₆.₅	CHO	30[e]	1.42[f]	100.0	68.9

B. Continuous Trickle Bed Reactor Oxidations[g]

catalyst	substrate	T, °C	contact time,[h] h	substrate conv,[c,i] %	sel,[d,i] %
Pb₂.₆₃Ru₁.₃₇O₆.₅	TCD	55	0.21	99.8	85.6
Bi₂.₃₉Ru₁.₆₁O₇₋y	TCD	55	0.21	99.7	86.8
Bi₂.₈₆Ru₁.₁₄O₇₋y	TCD	95	0.056	100.0	81.0
		95	0.021	65.2	74.2
Bi₂.₃₉Ru₁.₆₁O₇₋y	HD	95	0.062	100.0	91.3

[a] Performed in a 300-mL 316-stainless steel Autoclave Engineers reactor with 4.00 g of below 325 mesh powder, 100 mL of 0.517 M substrate in 1.5 N NaOH, 100 psi O₂ pressure, and an agitation rate of 1500 rpm. [b] Abbreviations: conv = conversion; sel = selectivity; TCD = *trans*-1,2-cyclohexanediol; CCD = *cis*-1,2-cyclohexanediol; HD = 1,6-hexanediol; CHO = cyclohexanone. [c] Analyses were made on 100-μL aliquots acidified with 100 μL of 1.5 N HCl. Samples were evaporated, taken up in 100 μL of pyridine containing xylitol as an internal standard, and then converted to the trimethylsilyl derivatives with ca. 0.3 mL of Regis RC-3 reagent (100 °C, 30 m). Portions of 0.2 μL were injected onto a methyl silicone capillary column in a gas chromatograph with FID that was programmed as follows: 100–250 °C at 8 °C/m with an 8-m hold at 250 °C. [d] Calculated selectivity to adipic acid product. Minor amounts of glutaric and succinic acids were observed (trimethylsilyl derivatives); all compounds were confirmed by GC/MS analysis. [e] Average temperature recorded throughout the oxidation. [f] Used 9.00 g (0.092 mol) CHO in 150 mL of 1.5 N NaOH. [g] Performed in 3.2-mm glass-lined tubing as a reactor containing 40–60 mesh (0.373–0.250 mm) catalyst particles packed between 0.12–0.18-mm glass beads with ca. 0.5 M substrate in 1.5 N NaOH, 100 psi O₂ pressure, and a downflow feed of liquid substrate and 30–45 cc/m O₂. [h] Contact time = volume of catalyst/volumetric substrate flow rate. [i] Average values for multiple samples taken at the conditions given; see Table IVS.[17]

function with molecular oxygen are relatively rare.[4,5] During evaluation of possible catalysts for the oxidative cleavage of various carbohydrates to yield ether polycarboxylates, reports appeared

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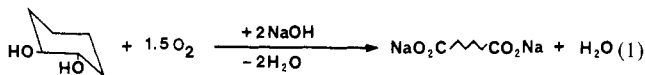(4) (a) Cobalt catalysts (>100 °C): De Vries, G.; Schors, A. *Tetrahedron Lett.* **1968**, 5689–5690. Zeidler, U.; Dohr, M.; Lepper, H. Ger. Offen. 2027924, 1970; *Chem. Abstr.* **1972**, *76*, 45736e. Schrever, G.; Schwarze, W.; Weigent, W. Ger. Offen. 2052815, 1972; *Chem. Abstr.* **1972**, *77*, 33963j. Camerman, P.; Hanotier, J. Fr. 2095160, 1972; *Chem. Abstr.* **1972**, *77*, 125991v. Zeidler, U. Ger. Offen. 2144117, 1973; *Chem. Abstr.* **1973**, *78*, 135664a. Zeidler, U.; Lepper, H. Ger. Offen. 2256888, 1974; *Chem. Abstr.* **1974**, *81*, 37251f. Zeidler, U. Ger. Offen. 2314454, 1974; *Chem. Abstr.* **1974**, *82*, 3811u. (b) Silver catalysts: Lamberti, V.; Kogan, S. L. U.S. Patent 3873614, 1975. (c) Review: Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981; Chapters 6 and 12. (d) Carbon anodes: Shono, T.; Matsumura, Y.; Hashimoto, T.; Hibino, K.; Hamaguchi, H.; Aoki, T. *J. Am. Chem. Soc.* **1975**, *97*, 2546–2548.
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Communications to the Editor

J. Am. Chem. Soc., Vol. 109, No. 24, 1987 7567

on a new class of high surface area ternary ruthenium oxides that are effective in electrochemical oxygen reduction and electrocatalytic oxidation of organic substrates including vicinal diols.[6] These findings combined with studies of oxoruthenium complex catalyzed oxidations[7-10] prompted investigation of these ternary ruthenium oxides for the aerobic oxidative cleavage of the carbohydrate model compound *trans*-1,2-cyclohexanediol (TCD). The results described herein provide the first example of a mixed metal oxide catalyst system that functions in the absence of a coreductant with molecular oxygen for the oxidative cleavage of vicinal diols.

The ruthenium pyrochlore oxides have been known for many years,[11,12] but high surface area compounds were first described in 1978.[13] This high surface area synthesis[14] has been used to prepare a series of ruthenium pyrochlore oxides with the general formula $A_{2+x}Ru_{2-x}O_{7-y}$ (A = Pb, Bi; $0 < x < 1$; $0 < y \leq 0.5$). X-ray powder diffraction measurements established[15] the A and B site stoichiometries. Thermogravimetric data on $Pb_{2.62}Ru_{1.38}O_{7-y}$ gave an oxygen stoichiometry number of 6.40, a value in agreement with a recent neutron powder diffraction study of $Pb_2Ru_2O_{6.5}$.[16] BET N_2 surface areas for the series ranged from 44 to 165 m^2/g and average pore diameters varied from 70 to 256 Å.[17]

Preliminary autoclave reactor experiments at 25 to 55 °C under 30 psi O_2 pressure with an aqueous solution of TCD and a powdered sample of $Pb_{2.62}Ru_{1.38}O_{6.5}$ established that at a pH above 13 (KOH or NaOH), conversion of TCD to adipate is detected upon analysis[17] of the reactor solution. Subsequent experiments were in a reactor equipped with an O_2 gas reservoir and pressure transducer to monitor O_2 consumption. These results are shown in Table IA. For the first entry in the table a relatively constant O_2 uptake (0.072 mol O_2 consumed, 92% of theoretical) was observed suggesting the overall reaction stoichiometry depicted in eq 1. Closely similar results were obtained for the cis isomer

$$\text{HO—} \bigcirc \text{—OH} \quad + \quad 1.5\,O_2 \quad \xrightarrow[-2H_2O]{+2\,NaOH} \quad NaO_2C \sim\!\!\sim\!\!\sim CO_2Na \quad + \quad H_2O \quad (1)$$

(CCD) of TCD although the reaction proceeded at a faster rate. Catalysts with a low Pb/Ru ratio (i.e., $Pb_{2.15}Ru_{1.85}O_{6.5}$) or low surface area ($Pb_2Ru_2O_{6.5}$, <1 m^2/g) were both less active and selective. In contrast, a high surface area $Bi_{2.46}Ru_{1.54}O_{7-y}$ catalyst displayed excellent product selectivity. As shown in Table I, primary alcohols (1,6-hexanediol, HD) and cyclic ketones (cyclohexanone, CHO) are also converted to carboxyl-containing products (adipate in both cases) under similar reaction conditions with these ruthenium pyrochlore oxide catalysts. These oxidations with molecular oxygen appear to follow the same trends in relative functional group reactivity (ketone = 1,2-diol > primary alcohol) as those observed when these oxides function as anodic electrocatalysts.[6] Common surface intermediates may account for these similar trends in reactivity.

Since higher selectivities were obtained at lower substrate/catalyst ratios, several sets of experiments were conducted with various $A_{2+x}Ru_{2-x}O_{7-y}$ catalysts in a continuous trickle bed reactor.[17,18] Representative results at relatively short contact times and high temperatures (55–95 °C) are displayed in Table IB. These conditions afford efficient conversion of the aldehyde intermediates[19-21] to the carboxylate products. A $Bi_{2.39}Ru_{1.61}O_{7-y}$ catalyst run for more than 180 h gave no evidence of deactivation, leaching by the alkaline solution (ICP/AES analysis) or change in the bulk structure (XRD).[22]

The strongly basic reaction conditions in conjunction with the low ionization potential of the diol oxygen lone pairs[4d] suggest formation of a coordinated diol intermediate. The redox–active surface B sites represent probable points for the initial substrate binding. Image analysis techniques on a 300 keV TEM micrograph of a 100-Å $Pb_{2.62}Ru_{1.38}O_{6.5}$ particle show expansion of oxide lattice periodicities in a 25-Å surface region suggesting Pb^{IV} enrichment at the surface, and such a species is known to effect diol cleavage.[3] Alternatively, surface oxoruthenium groups must also be considered as sites for diol binding. Oxoruthenium(IV) complexes are known to exchange with primary and secondary alcohol groups to yield reduced ruthenium(III)–alkoxide species.[23] Reduced ruthenium species are unstable in alkaline solutions[24] under O_2 pressure that results in a high open circuit potential.[6c] While details of the O_2 interaction with the reduced oxide catalyst are unknown, electrochemical studies have proposed both inner[22] and outer[25] sphere mechanisms for O_2 activation by reduced ruthenium sites on the electrode surface.

In summary, vicinal diols are oxidized catalytically by ruthenium pyrochlore oxides under O_2 pressure at low temperatures. Product selectivities in these multielectron liquid phase oxidations rival those reported with electrochemical techniques.[4d,9c] Further studies are needed to ascertain the molecular events occurring at the gas–liquid–solid interfaces in this novel catalyst system.

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Scheme I

## Direct Conversion of 2,3-Dihydrofurans to Silylsiloxyalkynes and Bis(silyl)ketenes

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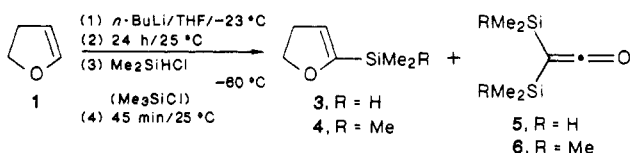Ames, Iowa 50011*

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The recent independent reports by Stang[1] and Kowalski[2] on the first silylations of ynolate anions on oxygen prompt us to disclose our preliminary results on the generation and trapping of ynolate dianions directly generated from the readily available precursor, 2,3-dihydrofuran (**1**).

Metalation of 2,3-dihydrofuran (**1**) to produce α-lithiodihydrofuran (**2**) is a well-established reaction, and the carbanion structure has been studied by ^{13}C NMR.[3] Boeckman[4] has used
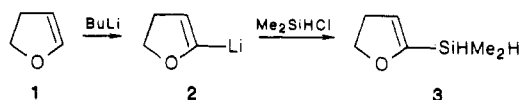
this carbanion to react with a variety of electrophiles, while Sebastian[3] reports that **2** is conveniently prepared at ambient temperatures with *n*-BuLi in hexane and a catalytic amount of TMEDA. We desired a sample of 5-(dimethylsilyl)-2,3-dihydrofuran (**3**) for flash pyrolytic studies[5] and found that its preparation was reported by Lukevics[6] to be achieved in 50% yield by metalation of **1** with *n*-BuLi/THF at –30 °C and quenching with Me₂HSiCl at –45 °C.

Thus, we were surprised to find that upon deprotonation of **1** with *n*-BuLi in THF (–23 °C, 24 h at 25 °C), quenching with Me₂HSiCl (–60 °C, 45 min at 25 °C), and vacuum distillation, the product **3**[7] was severely contaminated with bis(dimethyl-

silyl)ketene (**5**).[7] The yield of **5** was 28% or 56% based on the limiting reagent, *n*-BuLi. The same procedure, substituting Me₃SiCl for Me₂HSiCl, afforded bis(trimethylsilyl)ketene (**6**)[7] [21% (42%) yield] which was readily separable from the accompanying **4**.

A variety of experimental modifications were employed in attempts to maximize the yield of ketene from **1**. TMEDA had
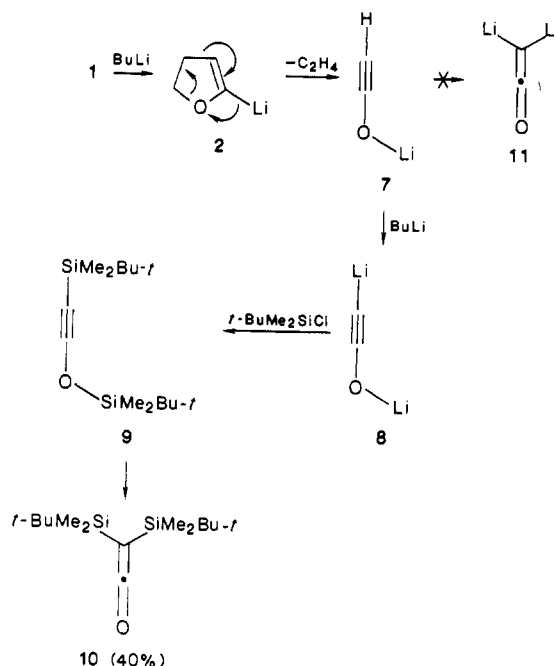
no effect on the ratios of ketene and dihydrofuran products, and changing the solvent to Et₂O and quenching with Me₃SiCl produced *only* **4** (51%). Metalation with 1 equiv each of *n*-BuLi and potassium *tert*-butoxide in a solution of THF and hexane (4:3) at –23 °C produced only **4** upon quenching with Me₃SiCl at –23 °C, while allowing the reaction to warm to room temperature resulted in the destruction of even this product. Reaction of **1** with *n*-BuLi/*t*-BuOK in only hexane at –23 °C and then 1 h at 25 °C afforded, upon addition of Me₃SiCl, both **4** and **6** (17% and 13%). Two equivalents of BuLi are obviously required for the production of ketenes **5** or **6**, but because BuLi will react with THF under these conditions both equivalents cannot be added simultaneously. Maximum yields to date have been obtained by reacting **1** with a single equivalent of *n*-BuLi for 24 h, addition of a second equivalent, and stirring for an additional 10 h at room temperature. Quenching this mixture with Me₃SiCl produced **4** in 33% yield and **6** in 38% yield.

Formation of ketenes **5** and **6** obviously involves loss of ethylene, and this might occur by decomposition of **2** (Scheme I)[9] to afford lithium alkynolate **7**. Alternatively, elimination may occur from a dimetalated dihydrofuran and our data to date do not allow for other than speculation. The nature of the products make it tempting to invoke the intermediacy of dilithioketene (**11**) which is then silylated. However, we find (following the observations of Kowalski[2]) that if 1 h or less after quenching with *tert*-butyldimethylsilyl chloride the reaction mixture is diluted with pentane, followed by washing with aqueous bicarbonate, IR analysis reveals *only* siloxyacetylene **9** (2185 cm⁻¹)[7] and no ketene **10** (2075 cm⁻¹).[11] If the reaction mixture is allowed to stand for 8 h before pentane/aqueous NaHCO₃ workup, the IR showed both acetylenic and ketene stretches (ca. 1:1). After 20 h, the ratio is ca. 1:3, and if the pentane/NaHCO₃ workup is not employed for 36 h after quenching with *t*-BuMe₂SiCl, only the ketene stretch at 2075 cm⁻¹ is present. However, a dried pentane solution of the reaction products worked up with pentane/aqueous NaHCO₃

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