

an f^3 electronic configuration) contains four broad features ($\nu_{1/2} \sim 100$ Hz) at 30 °C at δ 6.11, 2.23, -5.42, and -10.8 in approximate area ratio of 1.5:3:1:1 though at -70 °C all the resonances in the spectrum may be assigned based upon the crystallographic result.⁶ Most importantly, the $U_2(\mu\text{-Me})$ resonance at δ -284.7 (-70 °C) follows Curie law, and the extrapolated chemical shift at +30 °C is δ -185, in the region of uranium methyls.^{4b,7}

The crystal structure (Figure 1) contains one molecule each of $Li(tmed)_2$ (not shown in Figure 1 but see Supplementary Material) and $[Li(tmed)_2][\mu\text{-MeC}_5\text{H}_4]$, and two molecules of $[(\text{MeC}_5\text{H}_4)_3U]_2[\mu\text{-Me}]$. The $Li(tmed)$ fragments are not unusual in any way.⁸ In the bridging MeC_5H_4 fragment, the average Li-C distance of 2.31 ± 0.03 Å and the Li-ring centroid distance of 2.00 Å are in the range found in $[(\text{Me}_3\text{Si})_3\text{C}_5\text{H}_2]Li(tmed)^{9a}$ of 2.33 ± 0.03 Å and in $\text{Me}_3\text{SiC}_5\text{H}_4Li(tmed)^{9b}$ of 2.28 ± 0.01 Å. The Li-ring centroid-Li angle is 175°; the MeC_5H_4 group is the perpendicular bisector of the Li-Li vector, and the two $Li(tmed)$ fragments are oriented perpendicular to each other. The bonding in this inverted sandwich fragment may be viewed in the following way. Each lithium atom in the LiN_2^+ fragment can use a s- and two p-orbitals for four electrons in bonding to the tmed ligand. The empty sp^2 -hybridized orbital of σ -symmetry on each LiN_2^+ fragment can interact with the filled σ -symmetry orbital on the MeC_5H_4^- anion forming bonding, antibonding, and nonbonding combinations. The two electrons are located in the bonding molecular orbital; this description is the familiar one given for three-center two-electron bonding. The filled, π -symmetry orbitals on the MeC_5H_4^- fragment can act as π -donors toward the empty, unhybridized, orthogonal p-orbitals on each $Li(tmed)^+$ fragment, accounting for the perpendicular orientation of the two $Li(tmed)^+$ fragments. On the other hand, the perpendicular orientation minimizes the repulsion between the Me_2N groups across the MeC_5H_4 ring, and steric rather than electronic factors may be responsible for the observed geometry.

The other fascinating feature of the molecule is the geometry of the anion with the U-C(53)-U angle of 176.9 (11)° and U-C(53) distances of 2.71 (3) and 2.74 (2) Å. The hydrogen atoms on the bridging methyl groups were not located in the X-ray study^{6b} though the symmetry requires that the idealized geometry at carbon is apparently trigonal-bipyramidal, similar to that found for the benzyl group in tetrameric $\text{PhCH}_2\text{Na}(tmed)$,^{10a} a geometry that has fascinated theoreticians.¹⁰ The location of C(53) equidistant from the two uranium atoms could be due to disorder between two equivalent positions with unequal U-C distances. Unfortunately, all of the crystals fracture on cooling though efforts to obtain a better data set are continuing. The U-C(53) distance is long relative to $\text{Cp}_3\text{U}(n\text{-Bu})^{11}$ of 2.43 (2) Å and $[\text{Cp}_3\text{U}(n\text{-Bu})]^-$ of 2.56 (1) Å^{4c} as expected since linear bridge bonds are ca. 10% longer than terminal ones in $(\text{Me}_5\text{C}_5)_2\text{Lu}(\mu\text{-Me})\text{Lu}(\text{Me})(\text{C}_5\text{Me}_5)_2$.^{2c} The average U-C(cp) distance of 2.82 ± 0.04 Å and the ring centroid-U-ring centroid angle of 117° are identical with those found in $\text{Cp}_3\text{U}(n\text{-Bu})^{11}$ and $\text{Cp}_3\text{U}(n\text{-Bu})^-$.^{4c} It is difficult to describe the bonding in the anion, since the idealized C_{3v} symmetry $(\text{MeC}_5\text{H}_4)_3\text{U}$ fragment has many orbitals (s, p, d, f) of σ -symmetry, though the following description appears to be reasonable. The D_{3h} symmetry methyl anion is formed from s- and two p-orbitals giving a sp^2 -hybridized set that contains six

electrons for the C-H bonds and an unhybridized p-orbital with its two electrons that can be used in bonding with the σ -orbitals on the Lewis acid, $(\text{MeC}_5\text{H}_4)_3\text{U}$.

The bridging cyclopentadienyl and methyl groups described in this note may be viewed as models for the bimolecular transition state in electrophilic substitution at unsaturated and saturated carbon centers.¹²

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Supplementary Material Available: A listing of positional parameters, thermal parameters, bond lengths and angles, distance restraints, least-squares planes, ORTEP view of the unit cell, and method of solution of X-ray data (14 pages). Ordering information is given on any current masthead page.

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Acyclic Tertiary and Quaternary Carbon Stereocontrol via New Aldol Equivalent Reactions of Optically Active (E)-Enol Ethers

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The development of enantioselective methodologies for acyclic multiple stereocontrol continues to represent an important challenge for synthetic chemists.¹ Optically active 2-ethenyl-1,3-dioxolanones, available in one step from acrolein or methacrolein and lactic acid, mandelic acid, or hexahydromandelic acid,² are of interest in this regard as a new class of enal equivalent for stereocontrolled synthesis. We have recently developed several new methodologies for the conversion of these materials into the corresponding (E)-enol ethers, including (Scheme I) (a) nickel- and palladium-catalyzed conjugate addition of organoborates,³ (b) Lewis acid-catalyzed addition of trimethylsilyl ketene acetals and thiophenols,⁴ and (c) nickel-mediated homoenolate coupling reactions with halocarbons.²

We now report that the optically active enol ethers so obtained undergo highly diastereoselective reactions with a variety of aliphatic and aromatic acetals to give the protected aldol products **1**, several of which have been reductively deprotected to afford the corresponding alcohols **2** (Scheme II, Table I).⁵⁻⁷

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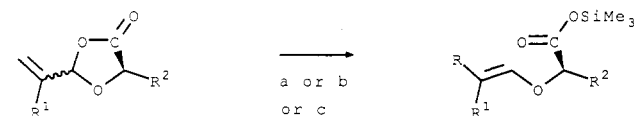
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Table I. Diastereoselective Aldol Equivalent Products

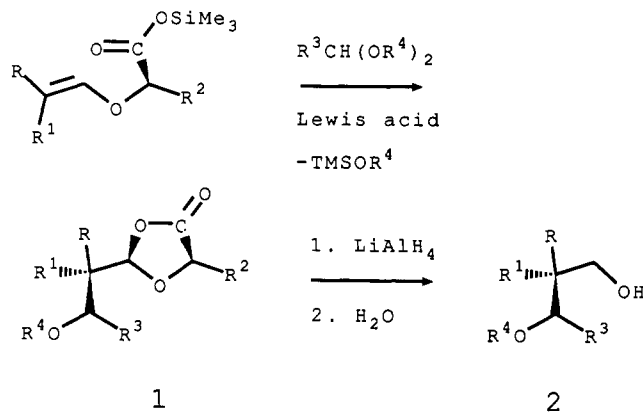
entry	R	R ¹	R ²	R ³	R ⁴	aldol products ^a		alcohols	
						% yield ^b	% ds 1 ^c	% ee 2 ^d	e/t 2 ^e
1	Bn ^f	H	Cy ^g	H	Bn	85	<i>h</i>	94	
2	Bn	H	Me	H	Bn	(94)	<i>h</i>	88 ⁱ	
3	Bn	H	Cy	Ph	Bn	(90)	95		
4	Bn	H	Cy	Ph	Me	72 (93)	94	92	99:1
5	Bn	H	Me	Ph	Me	(81)	90 ⁱ	85	97:3
6	Bn	H	Me	Ph	Me	(78)	85 ⁱ	68	95:5
7	Bn	H	Cy	PhCHO ^j	Me	84	87		7:93
8	<i>n</i> -Bu	H	Cy	Ph	Me	(93)	90 ^k		
9	Bn	H	Cy	Me	Me	80	<i>h</i>	60	90:10
10	Bn	H	Cy	Me	Me	(85)	≥75	74	90:10
11	Bn	H	Cy	<i>t</i> -Bu	Me	86 (89)	95	92	99:1
12	MeO ₂ CCMe ₂ CH ₂	Me	Me	Ph	Me	(75)	<i>h</i>	68 ⁱ	93:7
13	MeO ₂ CCMe ₂ CH ₂	Me	Cy	Ph	Me	(86)	≥90	90	97:3
14	PhSCH ₂	Me	Cy	Ph	Me	(79)	<i>h</i>	90	95:5

^a Conditions: 1.41 mmol enol ether/1.84 mmol acetal/6 mL CH₂Cl₂/−78 °C with 0.141 mmol TMSOTf for 6 h (entries 3–9, 11) or 0.028 mmol Ph₃CSbCl₆ for 120 h (entries 1 and 2) or 0.070 mmol Ph₃CSbCl₆ for 12 h (entries 12, 13, and 14) or 1.41 mmol enol ether/5.52 mmol acetal/3 mL of Et₂O/0.282 mmol TMSOTf/−78 °C/21 h (entry 10), followed by cannulation into aqueous NaHCO₃. ^b Isolated yield of purified product, isolated crude yield in parentheses. ^c Major diastereomer of 1 as a percentage of total aldol product.^{6,7} ^d Enantiomeric excess of 2 (entries 1 and 2) or the erythro diastereomer thereof (entries 4–6, 9–14).^{6,7} ^e Erythro/threo ratio. ^f Bn = benzyl. ^g Cy = cyclohexyl. ^h Not accurately determined. ⁱ Starting material and product enantiomeric to those depicted. ^j Benzaldehyde reaction. ^k Starting enol ether *E/Z* ratio 21:1.

Scheme I^a

^a (a) (R¹ = H, Me; R = CH₂Ph) (i) NaBPh₄, 0.1 mol % [(^π-C₃H₅)PdCl]₂, (ii) TMSCl; (R¹ = H, Me; R = CH₃) (i) NaHB(OMe)₃, 10 mol % Ni(1,5-COD)₂, (ii) TMSCl; (b) (R¹ = H, Me; R = CH₂CH₂CO₂Me) (TMSO)(MeO)CCMe₂, 10 mol % TMSOTf; (R¹ = H, Me; R = CH₂SPh) PhSTMS, 10 mol % TMSOTf; (c) (one-pot) (R¹ = H, Me; R = CH₂RO) (i) Ni(1,5-COD)₂, (ii) TMSCl, (iii) R³X/hν.

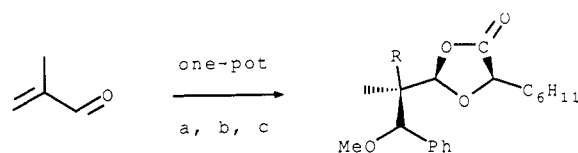
Scheme II



The aldol reactions are erythro-diastereoselective and give rise to cis 2,5-disubstituted dioxolanones, corresponding to net *syn-periplanar* addition of the acetal-derived electrophile and ester oxygen nucleophile across the enol ether double bond.⁷ Inter-

(6) Diastereomer ratios were determined by 400 MHz ¹H NMR. Enantiomeric excesses were determined by Eu(hfc)₃ shift experiments (Eu(hfc)₃ = tris[3-[(heptafluoropropyl)hydroxymethylene]-*d*-camphorato]europium-(III)).

(7) (a) The stereochemistry of the aldol products has been securely established by (1) X-ray crystallography (entries 5 and 12), (2) conversion to known, optically active compounds (entries 2 and 8), (3) preparation of *O*-methyl mandelate ester derivatives^{7b} (entry 7), (4) NOE experiments to assign dioxolanone cis/trans isomerism (entry 1), and (5) preparation of cyclic acetonides and other derivatives to assign erythro/threo diastereoisomerism (entries 4 and 7). Details of the proofs of relative and absolute stereochemistry are provided as Supplementary Material. (b) Belletire, J. L.; Godleski, S.; McDougal, P. G.; Balkovec, J. M.; Baldwin, J. J.; Christy, M. E.; Ponticello, G. S.; Varga, S. L.; Springer, J. P.; Trost, B. M. *J. Org. Chem.* **1986**, *51*, 2370.

Scheme III^a

^a (a) (R)-(TMSO)CyCHCO₂TMS/TMSOTf; (b) (TMSO)(Me)-CCMe₂/TMSOTf; (c) PhCH(OMe)₂/Ph₃CSbCl₆.

estingly, benzaldehyde also reacts but gives the corresponding threo diastereomer (entry 7).⁸

With regard to the diastereoselectivities, the following points are noted. (1) The highest diastereoselectivities are obtained with a bulky cyclohexyl substituent at the primary chiral center (R² = Cy); however, synthetically useful diastereoselectivities are possible even with the lactic acid derivatives (e.g., entry 5, R² = Me, 85% ee). (2) Enantiomeric excesses ≥90% are observed with acetals derived from formaldehyde, benzaldehyde, and pivalaldehyde (entries 1, 4, and 11), while the product of the acetaldehyde dimethyl acetal reaction exhibits a more modest enantiomeric excess (entry 10, 74% ee). (3) The aldol products 1 are generally subject to enrichment to diastereomeric purity, either via a single crystallization (entries 3, 5, 12, and 13) or by column chromatography (remaining entries). (4) Perhaps most notably, the diastereoselectivities are remarkably insensitive to changes in substitution at the enol ether carbon (cf. entries 4, 8, 13, and 14) thus allowing for acyclic quaternary carbon stereocontrol,⁹ even when the enol ether substituents are of comparable steric bulk (e.g., entry 14, R = CH₂SPh, R¹ = Me, 90% ee, e/t = 95:5).

In the case of those enol ethers generated by Lewis acid-catalyzed conjugate addition (cf. Scheme I) one-pot acetalization¹⁰/conjugate addition/aldol equivalent reaction sequences are

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also possible (e.g., Scheme III, R = CH₂CMe₂CO₂Me, 72% yield, diastereoselectivities as per Table I, entry 13) and promise to provide exceptionally convenient access to protected, optically active aldol products.

Experiments designed to further probe the scope, mechanism, and synthetic utility of this new approach to diastereoselective enol functionalization are in progress.

Acknowledgment. We are grateful to the National Institutes of Health (Grant GM40546) and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We also thank Professor A.G.M. Barrett for helpful discussions.

Supplementary Material Available: Spectroscopic and analytical data for all new compounds and crystallographic details for the aldol products of entries 5 and 12, including ORTEP diagrams, tables of atomic coordinates, thermal parameters, bond angles, and bond lengths (32 pages). Ordering information is given on any current masthead page.

Synthesis of 10,10-Difluorothromboxane A₂, a Potent and Chemically Stable Thromboxane Agonist[†]

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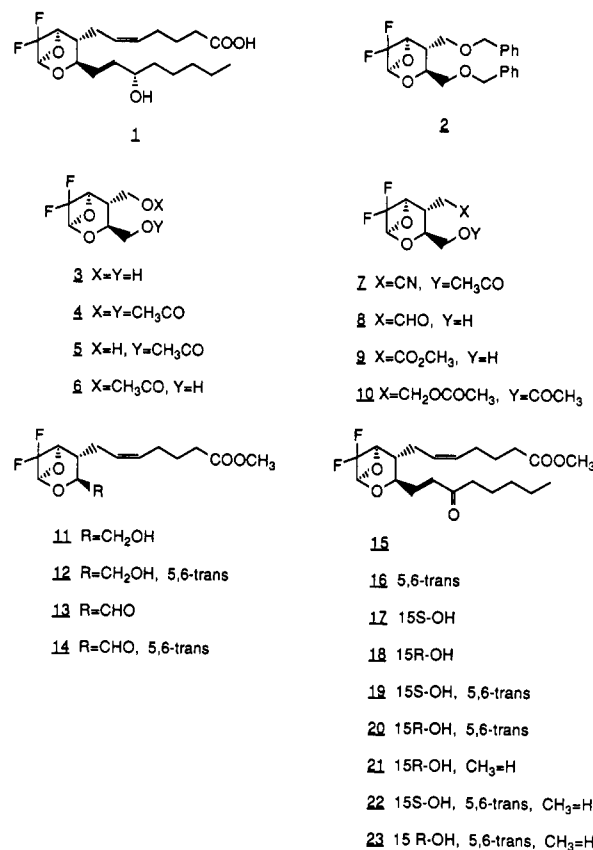
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Thromboxane A₂,¹ a member of the eicosanoid family, exerts powerful contractile effects on vascular and bronchial tissues and causes aggregation of blood platelets. Its unique oxetane acetal structure suffers facile hydrolytic cleavage even at pH 7.4 (*t*_{1/2} = 30 s) by a general acid catalyzed reaction.² As a result there has been much interest in synthesizing stable analogues of this important substance in order to mimic its biological properties, inhibit its biosynthesis, or serve as receptor antagonists.³ A common feature of all these reports is that stabilization of the molecule is achieved by replacement of one or both of the acetalic oxygens by carbon or sulfur. It is the purpose of this paper to describe the first TXA₂ mimic, (+)-10,10-difluoro-TXA₂, in which the acetalic structure of TXA₂ is retained, and stabilization of the molecule is achieved solely by the electronic influence of two neighboring fluorine atoms.

We recently described the synthesis of two model compounds possessing the 2,6-dioxo[3.1.1]bicycloheptane system present in TXA₂, in which the 7-hydrogens are replaced by fluorine.⁴ The bimolecular rate constant of hydrolysis for one of these, compound **2**, was found to be $2.4 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ compared to $5.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for TXA₂, an astonishing 10⁸-fold decrease in rate. This finding permitted the prognosis that **2** and related compounds possessing this fluorinated ring system would be sufficiently stable to serve



as intermediates for the synthesis of **1**. The use of **2** itself presented two major problems: (1) the two substituents on the ring are identical and (2) the compound is racemic. In spite of this we chose to proceed with **2** in the hope that the diacetate **4** derived from **2** could be converted in a regio- and enantioselective manner to the monoacetate **5** or **6** by selective enzymatic hydrolysis with either porcine liver esterase (PLE) or pancreatic lipase (PPL). These enzymes have been used extensively for the preparation of chiral synthons from prochiral substrates.⁵ However, this approach has only rarely been employed with racemic substrates.⁶

Catalytic hydrogenation of (±)-**2** with 10% Pd on carbon in isopropyl alcohol gave the racemic diol **3**, mp 112–112.5 °C, in 86% yield after recrystallization from ethyl acetate/hexane. The diacetate (±)-**4**, mp 41 °C, prepared with acetic anhydride and pyridine, was reacted with PLE at 25–26 °C for 10 min. Workup with ethyl acetate and chromatographic separation gave pure monoacetate (+)-**5**, 24.5% (49% of theory), [α]_D²⁵ = +49.7° (*c* 2.15 in CHCl₃), partially resolved monoacetate **6**, 9%, [α]_D²⁵ = +13°, and partially resolved diol **3**, 64%, [α]_D²⁵ = –12.6° (70% ee). Enantiomerically pure diol (+)-**3**, [α]_D²⁵ = +18.1° (*c* 0.36, CH₃OH/CHCl₃, 1:4), and diacetate (+)-**4**, [α]_D²⁵ = +37.5° (*c* 0.33, CHCl₃), were prepared from (+)-**5**. This result indicates that of the eight possible rates of sequential deacetylation available to the racemic substrate the rate of hydrolysis of (+)-**5** is sufficiently slow to permit complete kinetic resolution of that regioisomer. Reexposure of (+)-**5** to PLE for 10 min yielded material of unchanged specific rotation indicating that this process indeed yields (+)-**5** in 100% ee. Comparison of the ¹H and ¹⁹F NMR spectra of the (–)-MTPA esters of (+)-**5** and partially resolved **5** showed no evidence for the presence of (–)-**5** in the former. The absolute configuration of the dextrorotatory series of products **3** to **6** was shown to be that of TXA₂ by comparison of the diacetate (+)-**10** derived from (+)-**5** with that prepared from (2*R*,3*S*)-2,3-oxido-5-(*tert*-butyldimethylsilyloxy)pentan-1-ol.^{7,8} With (+)-**5** in hand the completion of the synthesis of the

[†] Dedicated to the memory of Tom Kaiser.

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