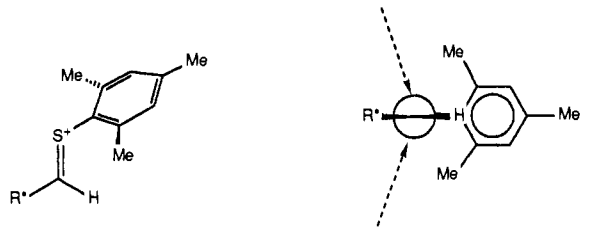
much more reactive dithioacetal that reacts in situ with the trimethylsilyl enol ether of pinacolone and $TiCl_4$ to give sulfide **11a** as the only detectable product (84% yield, diastereoselectivity >98:2). With allyltrimethylsilane, aldehyde **1a** affords sulfides **13a** and **14a** in a ratio of 97:3 (74% yield).

High diastereofacial selectivity is seen in the reactions of other α-chiral aldehydes with reagent **10** and the silyl enol ether of pinacolone. With 2-cyclohexylpropanal (**1b**) sulfide **11b** is again the only observed product (73% yield) and 2-methyl-3-phenylpropanal (**1c**) gives sulfides **11c** and **12c** in the surprisingly high ratio of 97:3 (80% yield). Even 2-methylbutanal (**1d**), in which the stereodifferentiating groups are methyl and ethyl, affords sulfides **11d** and **12d** in a ratio of 83:17 (70% yield)!

As in Lewis acid mediated additions to α-chiral aldehydes,[6b] allyltrimethylsilane is less selective than the silyl enol ether of pinacolone; with aldehydes **1b** and **1c**, allyltrimethylsilane provides sulfides **13b**/**14b** (94:6, 39% yield) and **13c**/**14c** (77:23, 77% yield).

The foregoing results are nicely accommodated by the previously enunciated theory.[2,4] The observed product ratios are consistent with reaction of the nucleophilic double bond with thionium ion **15**.[10] When Ar is phenyl, the lengths of the C=S and C-S bonds



15

probably allow the aryl group to be essentially coplanar with the thionium ion group, if the reasonable assumption is made that the thionium ion adopts the sterically less encumbered *E* configuration.[11] However, for the mesityl derivative, the aryl group is presumed to be tilted away from this plane. In this conformation, the ortho methyl groups present a significant barrier to attack on the mesityl side of the normal plane.

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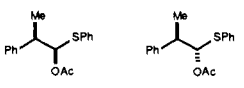
Supplementary Material Available: Experimental procedures and full characterization for all compounds reported in this communication (4 pages). Ordering information is given on any current masthead page.

(10) A referee has questioned the proposed thionium ion intermediate and suggested that the reaction may proceed by S_N2 displacement of one of the arylthio groups of the thioacetal. If this hypothesis were true, it would be coincidental that the stereochemical sense of the reaction is that predicted by the various models for diastereofacial preference in additions to carbonyl compounds (e.g., Cram, Felkin). However, the following experimental evidence argues strongly for the intermediacy of thionium ions. Diastereomeric α-acetoxy sulfides **16a** and **16b** were prepared and separated by chromatography. Treatment of each diastereomer with the silyl enol ether of pinacolone under the influence of $TiCl_4$ in CH_2Cl_2 at -78 °C gave sulfides **6** and **7** in the identical 4:1 ratio (87-90% yield), exactly as is observed in the reaction of **3** under the same conditions.



16a **16b**

(11) A referee has pointed out that alkyl sulfines prefer the *Z* configuration (see: inter alia, Block, E.; Penn, R. E.; Bazzi, A. A.; Cremer, D. *Tetrahedron Lett.* **1981**, 22, 29) and has suggested that this might be true as well for thionium ions derived from aldehydes, such as **15**. There is, of course, a great deal of steric difference between the oxygen of a sulfine and the mesityl group of a thionium ion, and we doubt that the extrapolation is valid. Indeed, the results of the present work may provide evidence that thionium ions, which have been little investigated, do form preferentially in the *E* configuration.

Organometallic Synthesis of II-VI Semiconductors. 1. Formation and Decomposition of Bis(organotelluro)mercury and Bis(organotelluro)cadmium Compounds

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Compound semiconductors of the II-VI family are important optical materials. We recently reported that CdTe can be prepared by organometallic vapor phase epitaxy (OMVPE) by using dimethylditelluride.[1] As a comparison study we report some of the related chemistry of ditellurides.

It has been reported[2] that diphenylditelluride reacts with metallic mercury to give a product of stoichiometry $C_{12}H_{10}Te_2Hg$ (**1**). Details of the structure and reactivity of this class of compounds has not been forthcoming. We have found that the same material can be prepared from $HgCl_2$ and 2 equiv of PhTeLi.[3] The product is an amorphous powder which is soluble only in coordinating media. On the basis of these data we assign the structure of **1** to an oligomer of bis(phenyltelluro)mercury $[Hg(TePh)_2]_n$.[4] Further evidence for this assignment comes in the preparation[5] of the 4-methylphenyl analogue **2**. When solubilized in benzene by tributylphosphine, **2** shows only one tolyl-CH_3 resonance in the proton NMR. The simplest connectivity consistent with these observations is $Hg(TeC_6H_4CH_3)_2$.

The thermal behavior of these compounds is interesting. They are thermochromic (red at room temperature, bright yellow at -78 °C), and at higher temperatures they decompose to give HgTe and diaryltellurium. Thus when **1** is sealed under vacuum and heated at 120 °C for 24 h, HgTe and Ph_2Te are isolated in 93% and 83%, respectively. This is a very mild route to polycrystalline HgTe.

Similar behavior is seen in solution. When a solution of **2** in C_6D_6/PEt_3 is heated to reflux, resonances due to bis(4-methylphenyl)tellurium appear in the proton NMR spectrum, and HgTe precipitates. Resonances due to bis(4-methylphenyl)ditelluride also appear, showing that the reaction of ditellurides with Hg is reversible. This is verified in a larger scale reaction. When a sample of **2** in toluene/PEt_3 is heated to reflux 24 h, HgTe and Hg precipitate,[6] and GC analysis of the solution show the organic mono- and ditelluride in a 10:1 ratio in a combined yield of >90%.

Our study of bis(organotelluro)mercurials is summarized in eq 1.

$$(RTe)_2 + Hg \rightleftharpoons Hg(TeR)_2 \rightarrow HgCl_2 + 2RTeLi \quad (1)$$
$$\downarrow \Delta$$
$$HgTe + TeR_2$$

Cadmium telluride can be prepared in an entirely analogous fashion. Bis(4-methyophenyltelluro)cadmium (**3**) is prepared by treating $CdCl_2$ with (4-methylphenyl)(trimethylsilyl)tellurium.[7]

(1) Kisker, D. W.; Steigerwald, M. L.; Kometani, T. Y.; Jeffers, K. S. *Appl. Phys. Lett.* **1987**, *50*, 1681-3.
(2) Okamoto, Y.; Yano, T. *J. Organomet. Chem.* **1971**, *29*, 99-103. (b) Dance, N. S.; Jones, C. H. W. *J. Organomet. Chem.* **1978**, *152*, 175-85.
(3) A solution of 0.55 equiv of $HgCl_2$ was added at room temperature to a solution of PhTeLi in THF. Upon completion of addition the mixture was stirred 30 min. Filtration and washing (pentane) gave the crude red-orange product. This was purified by extraction with toluene/PMe_3 (10/1 by volume). The dried product was identical with material prepared as per ref 2a. Yield: 49%.
(4) Dance, I. G. *Polyhedron* **1986**, *5*, 1037-1104.
(5) This material can be prepared either as in ref 2a or ref 3: ^1H NMR (C_6D_6 with a small amount PBu_3) δ 2.05 (S, $-CH_3$), 6.74 (d, J = 7.9 Hz), and 8.10 (d, J = 7.9 Hz), AB quartet due to aromatic protons. Anal. Calcd for $C_{12}H_{10}Te_2Hg$: C, 26.35; H, 2.21; Te, 40.00; Hg, 31.44. Found (Schwartzkopf): C, 25.63; H, 2.22; Te, 40.73; Hg, 32.40.
(6) HgTe is identified by X-ray powder diffraction. Elemental mercury is identified visually and by DSC.

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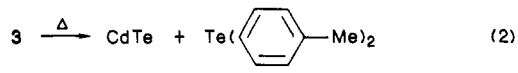
The yellow solid shows solubility similar to, and a proton NMR essentially identical with, the corresponding mercury complex. Pyrolysis of **3** in the solid state (200 °C, 16 h) gives CdTe and bis(4-methylphenyl)tellurium in 98% and 82% yields, respectively (after purification) (eq 2).



(2)

Owing to the drastic differences in reaction conditions, the relevance of the present work to thin-film growth by OMVPE with use of ditelluride source compounds is not clear, although one point is noteworthy. In the OMVPE reactor we found[1] that the ditelluride itself is stable, in the absence of the cadmium source, under conditions which, when cadmium is present, CdTe is produced. This implies that the cadmium source (or its decomposition products) reacts with the ditelluride. One mechanism which would explain this is that the cadmium source decomposes to give cadmium atoms which subsequently react with the ditelluride to give a complex such as **3** which decomposes to give CdTe.

(7) A slight excess of (4-methylphenyl)(trimethylsilyl)tellurium was added to $CdCl_2$, suspended in THF, and the mixture was stirred at room temperature 14 h. The yellow solid was isolated, washed with pentane, and extracted with toluene/PMe_3. Evaporation gave **3** as a bright yellow solid: yield 32%; ^1H NMR (C_6D_6 with PEt_3) δ 2.02 (s, $-CH_3$), 6.75 (d, J = 6.6 Hz), 8.14 (d, J = 6.6 Hz), AB quartet due to aromatic protons. Anal. Calcd for $C_{14}H_{14}Te_2Cd$: C, 30.58; H, 2.57. Found: C, 30.24, H, 3.29.

The Catalytic Base of Enolase Is a Sulfhydryl Group

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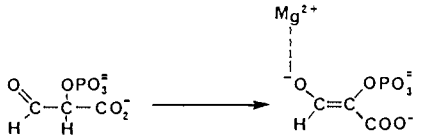
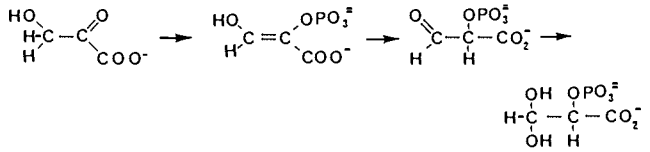
We have made use of the partial chemistry undergone by the competitive inhibitor, D-tartronate semialdehyde phosphate (D-TSP), in the presence of enolase, to investigate the acid–base catalyst of enolase responsible for proton removal from D-TSP and presumably from the substrate, D-2-phosphoglyceric acid (D-2PGA). From the differential inhibition of D-2-proteo-TSP (D-TSPH) and D-2-deuterio-TSP (D-TSPD) we conclude that the base responsible for this process is a sulfhydryl group of a cysteine residue.

It has been known for some time that enolase catalyzes the enolization of D-TSP.[1,2] The C-2 proton is removed by an enzymic base, facilitating formation of the enzyme:Mg:enolate complex.



The nature of this base, however, has remained unknown despite extensive studies on enolases from various sources. We have been able to compare the inhibition of yeast and muscle enolase by D-TSPH and D-TSPD under conditions where isotopic discrimination can be detected in the form of a deuterium isotope effect on the inhibition constant, ^DK_i.

TSP was prepared by reacting β-hydroxypyruvate and MgATP with pyruvate kinase at pH 9.[3] The stereochemistry of this TSP has been found to be racemic;[4] that is, the phosphorylated enol is the actual product of the pyruvate kinase reaction. This tautomerizes in solution to the aldehyde form, which, in turn, hydrates to >95%.[5] TSPD was synthesized by carrying out the pyruvate kinase reaction in D_2O rather than H_2O.



The inhibition constants for D-TSPH and D-TSPD were determined at 25 °C and pH 7.4. Initial velocities were obtained by varying the concentration of D-2PGA (added last to initiate the reaction) at various fixed concentrations of each inhibitor. The concentration of free Mg^{2+} was maintained at 8.5 mM. A pyruvate kinase and lactate dehydrogenase coupled assay was used to monitor the enolase reaction. The phosphoenolpyruvate (PEP) is converted into pyruvate, which is subsequently reduced to lactate with the concomitant oxidation of NADH ($\Delta\epsilon = -6220\ M^{-1}$). The stock concentrations of D-TSPH and D-TSPD were accurately determined by reduction of the aldehyde to the corresponding alcohol (D-2PGA) with $NaBH_4$.[6] End-point assays for D-2PGA, and thus D-TSP, were carried out with use of the same coupled assay described above.

From six independent experiments, in which the D-TSPH and D-TSPD were each resynthesized and recalibrated, the K_i values shown in Table I were obtained. The ratio of the K_i values, ^DK_i, is also shown for each experiment. The weighted average of these ratios is 0.41 ± 0.02. Since these K_i values are dissociation constants, the value of 0.41 represents the equilibrium isotope effect for the two-step process of binding and enolization of D-TSP. Further, this value suggests that the fractionation factor[7] for the proton transferred from C-2 of D-TSP to the enzymic base has decreased drastically, from 1.19 when on D-TSP (the value for the C-2 proton of D-2PGA[8] and assumed to be the same for the C-2 proton of D-TSP) to ~0.4 when on the enzymic base. The only reasonable functional group with a fractionation factor so

Table I. Michaelis and Inhibition Constants for Yeast and Muscle Enolase[a]

enolase source	D-TSPH $K_{D\text{-}2PGA}$, μM	D-TSPH K_i, μM	D-TSPD $K_{D\text{-}2PGA}$, μM	D-TSPD K_i, μM	^DK_i = K_i(D-TSPH)/K_i(D-TSPD)
yeast	13.5 ±0.9	0.46 ±0.04	12.1 ±0.7	1.02 ±0.08	0.45 ±0.05
yeast[b]	3.9 ±0.4	0.23 ±0.02	4.9 ±0.5	0.50 ±0.07	0.46 ±0.08
yeast	12.8 ±0.06	0.48 ±0.02	12.2 ±0.07	1.36 ±0.09	0.35 ±0.03
muscle	4.3 ±0.7	0.10 ±0.01	4.4 ±0.6	0.25 ±0.03	0.40 ±0.06
muscle	5.8 ±0.5	0.13 ±0.01	5.3 ±0.7	0.24 ±0.03	0.54 ±0.08
muscle	4.7 ±0.4	0.14 ±0.01	4.6 ±0.4	0.31 ±0.03	0.45 ±0.05

[a] Values for these constants were obtained by fitting the initial velocities to the equation for competitive inhibition ($v = VA/[K_{D\text{-}2PGA}(1 + I/K_i) + A]$ where v, V, A and I are the initial velocity, maximum velocity, D-2PGA concentration, and D-TSPH or D-TSPD concentration, respectively) by using a Fortran program[11] and microcomputer. [b] Despite the fact that these values are significantly lower than the other yeast enolase values, ^DK_i is in excellent agreement with the other ^DK_i values. The ratio of K_i/K_m is the value most accurately determined in these experiments, and these values are in better agreement with the other K_i/K_m ratios for yeast enolase.

(5) Stubbe, J.; Abeles, R. H. *Biochemistry* **1980**, *19*, 5505.

(6) The pyruvate kinase reaction mixture was passed through an ultrafiltration apparatus to remove enzyme. The TSP was used without further purification, as the coupled assays also contained K^+, Mg^{2+}, and ADP at levels similar to those in the TSP solution. There was no remaining β-hydroxypyruvate by lactate dehydrogenase assay.

(7) The fractionation factor of a hydrogen is the equilibrium constant for exchange with deuterium in one-half of a solvent water molecule. Thus a fractionation factor less than unity implies depletion of deuterium in the group relative to water.

(8) Cleland, W. W. *Methods Enzymol.* **1980**, *64*, 108.

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