behavior indicated by $\phi^{\ddagger} = 0.30$ for proton transfer from phenylacetylene to hydroxide ion. Phenylacetylene, moreover, changes from its pseudoacid behavior toward hydroxide ion, where ΔpK is only 4, to normal acid behavior toward the considerably weaker bases used in constructing its unit-slope Brønsted plot, where $\Delta pK = 10-14$. Differences in reaction energetics would thus appear to play a decisive role in determining normal acid and pseudoacid behavior.

This, however, cannot be the sole determining factor in the present case, for $|\Delta pK|$ is the same for cyanoacetylene plus hydroxide ion as for chloroform plus hydroxide ion, and yet isotope effects indicate the former to be a pseudo, and the latter a normal, acid–base system. Moreover, the value of ΔpK for phenylacetylene plus hydroxide ion is the same as that for cyanoacetylene plus formate ion, but the isotope effect in the latter system is twice as strong as that in the former.

It is not clear why cyanoacetylene should be so much more inclined to act as a pseudoacid: proton transfer from its C–H bond leaves behind a basic electron pair localized on a single atom, just as in the case of chloroform and the monoacetylenes. A difference which could be significant, however, is the presence of two conjugated triple bonds in cyanoacetylene, and in the diacetylenes as well: this provides a highly polarizable π-electron system through which an appreciable shift of negative charge could be induced upon formation of the acetylide ion, and this change in charge distribution would require reorganization of solvent molecules which might slow proton transfer sufficiently to convert normal acid behavior into pseudoacid behavior.

Acknowledgment. We are grateful to Professor James R. Keeffe for valuable discussion and to the Natural Sciences and Engineering Research Council of Canada and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.

High Diastereofacial Selectivity in Nucleophilic Additions to Chiral Thionium Ions[1]

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In a recent publication,[2] we presented computational evidence in favor of a theory of diastereofacial selectivity in additions to α-chiral carbonyl compounds. The calculations show that nucleophiles will tend to attack the carbonyl group in a compound RCOR* along a trajectory that is displaced from the normal plane (the plane perpendicular to the R–C–R* plane and containing the C=O bond) in the direction of the sterically less demanding R and R* (Figure 1). If R* is a stereocenter, the diastereofacial preference of the chiral carbonyl compound should then be related to steric bulk on the same side of the normal plane as R, as is observed in reduction of chiral ketones PhCH(Me)COR (R = Me, Et, *i*-Pr, and *t*-Bu)[3] and in the Lewis acid mediated additions of silyl enol ethers and silyl ketene acetals to chiral aldehydes.[4] Similar ideas have been advanced by Liotta, Burgess, and Eberhardt[5] and by Nguyên Trong Anh and Bui Tho Thanh.[6] In this communication, we present further experimental results that are consistent with this theory.

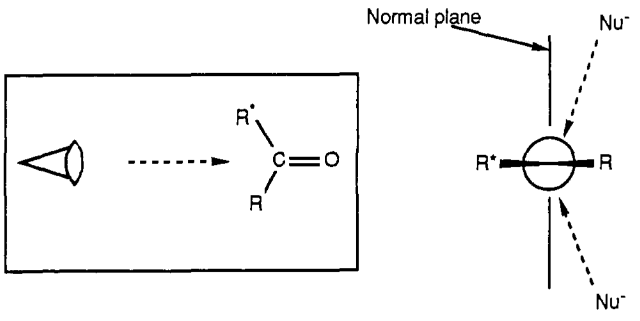
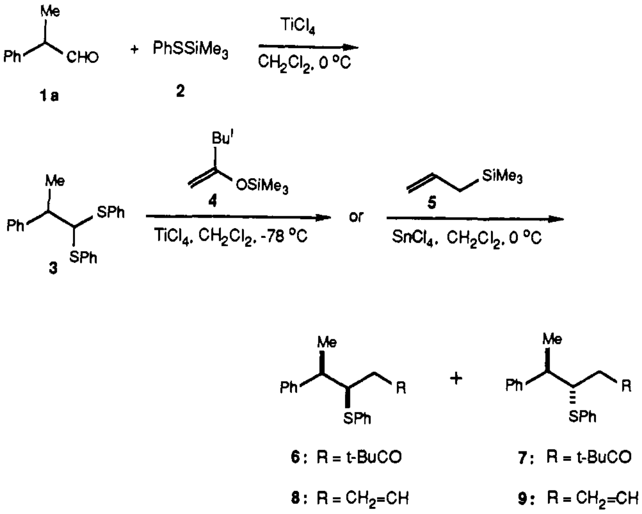
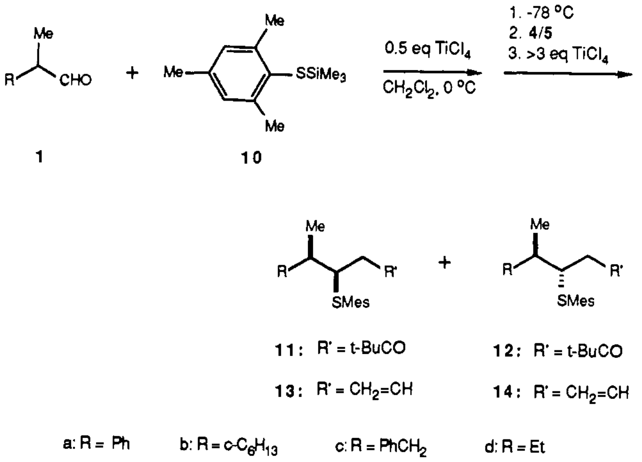


Figure 1. Proposed trajectory of attack of a nucleophile Nu⁻ on carbonyl compound R*COR, where R* is larger than R.

2-Phenylpropanal (**1a**) reacts with the trimethylsilyl derivative of thiophenol **2**[7] under the influence of $TiCl_4$ to provide the dithioacetal **3**. Treatment of this derivative with the trimethylsilyl enol ether of pinacolone **4** in the presence of several equivalents of $TiCl_4$ in CH_2Cl_2 at −78 °C affords sulfides **6** and **7** in a ratio of 4:1 (77% yield); when the nucleophilic alkene is allyltrimethylsilane (**5**) and the reaction is carried out in the presence of $SnCl_4$ in CH_2Cl_2 at 0 °C, sulfides **8** and **9** are obtained in a ratio of 3:1 (56% yield).[8]



In contrast, treatment of aldehyde **1a** with the corresponding trimethylsilyl derivative of 2,4,6-trimethylthiophenol **10**[9] gives a



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[1] Part 41 in the series "Acyclic Stereoselection". For part 40, see: Lodge, E. P.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 3353.

[2] Lodge, E. P.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 2819.

[3] Chérest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199.

[4] Heathcock, C. H.; Flippin, L. A. *J. Am. Chem. Soc.* **1983**, *105*, 1667.

[5] Liotta, C. L.; Burgess, E. M.; Eberhardt, W. H. *J. Am. Chem. Soc.* **1984**, *106*, 4849.

[6] Anh, N. T.; and Thanh, B. T. *Nouv. J. Chim.* **1986**, *10*, 681.

[7] Glass, R. S. *J. Organomet. Chem.* **1973**, *61*, 83.

[8] Relative stereochemistry for pairs **6**/**7** and **8**/**9** was assigned on the basis of ^1H NMR spectroscopy, by using the chemical shifts of the methyl and *tert*-butyl signals in the case of **6**/**7** and the methyl signals in the case of **8**/**9**; see: (a) Heathcock, C. H.; Lampe, J. *J. Org. Chem.* **1983**, *48*, 4330. (b) Heathcock, C. H.; Kiyooka, S.; Blumenkopf, T. A. *Ibid.* **1984**, *49*, 4214.

[9] Jutzi, P.; König, E.; Huttner, G.; Frank, A.; Schubert, U. *Chem. Ber.* **1978**, *111*, 606.

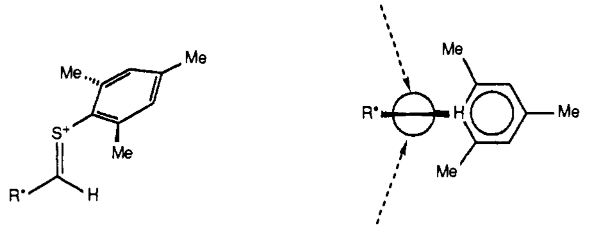
0002-7863/87/1509-7199$01.50/0

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 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.



15

Acknowledgment. This research was supported by research grants from the United States Public Health Service (AI-15027 and GM-30759).

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.

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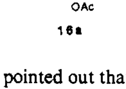
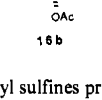
[10] A referee has questioned the proposed thionium ion intermediate and suggested that the reaction may proceed by S_N2 displacement of one of the arylthio groups of the thioacetal. If this hypothesis were true, it would be coincidental that the stereochemical sense of the reaction is that predicted 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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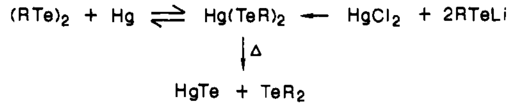
Compound semiconductors of the II–VI family are important optical materials. We recently reported that CdTe can be prepared by organometallic vapor phase epitaxy (OMVPE) by using dimethylditelluride.[1] As a comparison study we report some of the related chemistry of ditellurides.

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.



$$\begin{array}{c} (RTe)_2 + Hg \rightleftharpoons Hg(TeR)_2 \leftarrow HgCl_2 + 2RTeLi \\ \downarrow \Delta \\ HgTe + TeR_2 \end{array} \qquad (1)$$

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]

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[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: ^{1}H 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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