4-[(1-Chloro-2-hydroxy-3-propanyl)thio]pyrimidine (16). Epichlorohydrin (1.9 mL, 24.5 mmol) was added to a mixture of 4-mercaptopyrimidine (2.5 g, 22.3 mmol) and sodium bicarbonate (1.99 g, 24.5 mmol) in ethanol (50 mL) and stirred at rt for 4 d. The mixture was worked up as described for **10** to give the product (1.02 g, 22%) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 3.41–3.69 (m, 4 H), 4.16–4.20 (m, 1 H), 4.9 (br s, 1 H, exchanges with D_2O), 7.29 (dd, J = 1.4, 5.5 Hz, 1 H), 8.39 (d, J = 5.5 Hz, 1 H), 8.91 (d, J = 1.4 Hz, 1 H). IR (neat): 3300, 1571, 1447 cm^{-1}. MS(CI): 205 (MH^+).

1-(Thietan-3-yl)-1*H*-pyrimidin-6-one (17) and -4(3*H*)-pyrimidone (18). Sodium methoxide (1.2 N, 4.1 mL, 4.9 mmol) was added to a solution of **16** (1.0 g, 4.9 mmol) in methanol (25 mL) at 0 °C. The resultant solution was stirred at rt for 16 h and worked up as described for **11** to give **17** as a colorless solid after flash chromatography using 5% methanol in methylene chloride as the eluant, 40 mg (5%), mp 48–50 °C. ^{1}H NMR ($CDCl_3$): δ 3.42–3.48 (m, 2 H), 3.55–3.61 (m, 2 H), 5.86–5.95 (m, 1 H), 6.70 (d of d, J = 1.1, 5.8 Hz, 1 H), 8.45 (d, J = 5.8 Hz, 1 H), 8.74 (s, 1 H); MS (CI): 169 (MH^+). Anal. Calcd for $C_7H_8N_2OS$: C, 49.98; H, 4.79; N, 16.65. Found: C, 50.26; H, 4.65; N, 16.43.

The pyrimidone **18** was eluted with 5–15% methanol in methylene chloride to give 208 mg (44%) as a colorless solid which was identical to an authentic sample (Aldrich).

2-[(1-Chloro-2-hydroxy-3-propanyl)thio]imidazole (19). Epichlorohydrin (3.66 mL, 46.8 mmol) was added to a mixture of 2-mercaptoimidazole (4.6 g, 45.9 mmol) and sodium bicarbonate (4.46 g, 52.4 mmol) in ethanol (100 mL) and stirred at rt for 16 h. The reaction mixture was worked up as described for **10** to give **19** as a colorless oil, 5.28 g (60%). ^{1}H NMR: δ 3.21–3.37 (m, 2 H), 3.65–3.68 (m, 2 H), 4.20–4.23 (m, 1 H), 5.3 (br s, 2 H), 7.02 (s, 2 H). MS (CI): 193 (MH^+). Anal. Calcd for $C_6H_9ClN_2OS$: C, 37.41; H, 4.71; N, 14.54. Found: C, 37.01; H, 4.83; N, 14.17.

3,4-Dihydro-3-hydroxy-2*H*-thiazino[3,2-*a*]imidazole (20). A solution of sodium methoxide (1.0 M, 12 mL, 12 mmol) was added to a solution of **19** (2.32 g, 12.0 mmol) in methanol and stirred at rt for 16 h. The mixture was worked up as described for **11** and purified by flash chromatography using 5% methanol in methylene chloride as the eluant to give **20** as a colorless solid, 1.47 g (78%), mp 202–205 °C. ^{1}H NMR ($CDCl_3$): δ 3.17–3.22 (m, 2 H), 3.95–4.00 (m, 1 H), 4.10–4.15 (m, 1 H), 4.20–4.30 (m, 1 H), 5.25 (br s, 1 H, exchanges with D_2O), 6.87 (d, J = 1.3 Hz, 1 H), 6.96 (d, J = 1.3 Hz, 1 H). MS (CI): 157 (MH^+). Anal. Calcd for $C_6H_8N_2OS$: C, 46.14; H, 5.16; N, 17.93. Found: C, 46.38; H, 5.02; N, 18.11.

2-[(1-Chloro-2-hydroxy-3-propanyl)thio]-1-methylimidazole (21). Epichlorohydrin (3.5 mL, 45.1 mmol) was added to a mixture of 2-mercapto-1-methylimidazole (5.0 g, 43.8 mmol) and sodium bicarbonate (4.1 g, 48.2 mmol) in ethanol (100 mL) and stirred at rt for 16 h. The mixture was worked up as described for **10** to give **21** 8.13 g (90%) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 3.31–3.36 (m, 2 H), 3.61 (s, 3 H), 3.64–3.68 (m, 2 H), 4.17–4.27 (m, 1 H), 6.87 (d, J = 1.4 Hz, 1 H), 6.94 (d, J = 1.4 Hz, 1 H), 7.76 (br s, 1 H, exchanges with D_2O). IR (neat): 1460 and 1280 cm^{-1}. MS (CI): 207 (MH^+). Anal. Calcd for $C_7H_{11}ClN_2OS$: C, 40.68; H, 5.36; N, 13.55. Found: C, 40.50; H, 5.17; N, 13.19.

3,4-Dihydro-3-hydroxy-7-methyl-2*H*-thiazino[3,2-*a*]imidazolium Chloride (22). A solution of **21** (2.0 g, 9.67 mmol) in methylene chloride (40 mL) was stirred at rt for 2 weeks. The crystalline precipitate was collected by filtration and dried in vacuo to give **22** as a colorless solid, 0.197 g (10%): mp 178–180 °C; ^{1}H NMR (DMSO-d_6) δ 3.40–3.58 (m, 2 H), 3.66 (s, 3 H), 4.20 (m, 2 H), 4.53–4.54 (m, 1 H), 6.10–6.20 (d, J = 3.7 Hz, 1 H, exchanges with D_2O), 7.74 (s, 2 H). IR (KBr): 3207, 3067, 1570, 1475, 1435 cm^{-1}. Anal. Calcd for $C_7H_{11}ClN_2OS$: C, 40.68; H, 5.36; N, 13.55. Found: C, 40.63; H, 5.21; N, 13.44.

Alternatively, a solution of **21** (3.14 g, 15.2 mmol) in methanol (50 mL) was treated with 1 N sodium methoxide in methanol (15.2 mL, 15.2 mmol) and stirred at rt for 16 h. The mixture was neutralized with concentrated hydrochloric acid, the solvent was evaporated in vacuo, and the solid residue was triturated in methylene chloride. Filtration gave a colorless solid (3.82 g) which was a mixture of sodium chloride and 3,4-dihydro-3-hydroxy-7-methyl-2*H*-thiazino[3,2-*a*]imidazolium chloride.

2-[(1-Chloro-2-hydroxy-3-propanyl)thio]benzoxazole. Epichlorohydrin (2.7 mL, 34.7 mmol) was added to a mixture of 2-mercaptobenzoxazole (5.0 g, 33.1 mmol) and sodium bicarbonate (2.81 g, 33.1 mmol) in ethanol (100 mL) and stirred at rt for 24 h. The reaction was worked up as described for **10** to give the product as a colorless solid, 6.06 g (75%), mp 45–47 °C. ^{1}H NMR ($CDCl_3$): δ 3.46–3.63 (m, 2 H), 3.72 (d, J = 5.8 Hz, 2 H), 4.31–4.36 (m, 1 H), 4.85 (d, J = 4.8 Hz, 1 H, exchanges with D_2O), 7.24–7.33 (m, 2 H), 7.44–7.48 (m, 1 H), and 7.55–7.59 (m, 1 H). IR (KBr): 1500, 1454, 2140 cm^{-1}. MS (CI): 244 (MH^+). Anal. Calcd for $C_{10}H_{10}ClNO_2S$: C, 49.28; H, 4.14; N, 5.75. Found: C, 49.14; H, 4.21; N, 5.60.

2-Benzoxazolinone. A 1 N solution of sodium methoxide in methanol (13.2 mL, 13.2 mmol) was added to a solution of 2-[(1-chloro-2-hydroxy-3-propanyl)thio]benzoxazole (3.22 g, 13.2 mmol) in methanol (50 mL) at 0 °C and allowed to stir at rt for 16 h. The resultant mixture was neutralized with concentrated hydrochloric acid, and the solvent was evaporated in vacuo. The residue was dissolved in methylene chloride, and the inorganic materials were removed by filtration. The solution was dried over magnesium sulfate, and the solvent was evaporated to give the product as a colorless solid, 1.5 g (84%), mp 134–138 °C. ^{1}H NMR ($CDCl_3$): δ 7.08–7.26 (m, 4 H) and 8.2–8.9 (br s, 1 H, exchanges with D_2O). IR (KBr): 1778, 1736, 1481 cm^{-1}. MS (CI): 136 (MH^+). This material was identical to an authentic sample (Aldrich).

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Registry No. 1a, 129205-12-5; **1b**, 129205-13-6; **1c**, 129205-14-7; **1d**, 143746-42-3; **2**, 129205-15-8; **3**, 50-44-2; **4**, 106-89-8; **5**, 129205-11-4; **6**, 143746-29-6; **7**, 129205-16-9; **9**, 143746-30-9; **10**, 143746-31-0; **11**, 143746-32-1; **12**, 143746-33-2; **13**, 143746-34-3; **14**, 143746-35-4; **15**, 143746-36-5; **16**, 143746-37-6; **17**, 143746-38-7; **18**, 4562-27-0; **19**, 143746-39-8; **20**, 34035-41-1; **21**, 143746-40-1; **22**, 143746-41-2; 9-methyl-6-mercaptopurine, 1006-20-8; 6-[(1-chloro-2-hydroxy-3-propanyl)thio]-9-methylpurine, 143746-43-4; 4-mercapto-1*H*-pyrazolo[3,4-*d*]pyrimidine, 5334-23-6; 4-[(1-chloro-2-hydroxy-3-propanyl)thio]-1*H*-pyrazolo[3,4-*d*]pyrimidine, 143746-44-5; 2-mercaptopyridine, 2637-34-5; 2-quinolinethiol, 2637-37-8; 4-mercaptopyrimidine, 1450-86-8; 2-mercaptoimidazole, 872-35-5; 2-mercapto-1-methylimidazole, 60-56-0; 2-mercaptobenzoxazole, 2382-96-9; 2-[(1-chloro-2-hydroxy-3-propanyl)thio]benzoxazole, 143746-45-6; 2-benzoxazolinone, 2637-37-8.

Diastereoselective Synthesis of Anti and Syn α,β-Dihydroxy Thioesters by Titanium Enolate Aldol Condensation

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The aldol condensation between α-alkoxy esters (or their synthetic equivalents) and aldehydes represents a versatile entry to the 1,2-diol unit. However, while syn configurated compounds are efficiently obtained by several of these processes,[1] precedents for highly stereocontrolled anti diol

(1) (a) Heathcock, C. H.; Pirrung, M. C.; Young, S. D.; Hagen, J. P.; Jarvi, E. T.; Badertscher, U.; Mark, H.-P.; Montgomery, S. H. *J. Am. Chem. Soc.* **1984**, *106*, 8161. (b) Takai, K.; Heathcock, C. H. *J. Org. Chem.* **1985**, *50*, 3247. (c) Gray, B. D.; White, J. D. *J. Chem. Soc., Chem. Commun.* **1985** 20. (d) Oesterle, T.; Simchen, G. *Justus Liebigs Ann. Chem.* **1987**, 693. (e) Evans, D. A.; Bender, S. L.; Morris, J. *J. Am. Chem. Soc.* **1988**, *110*, 2506. (f) Sugano, Y.; Naruto, S. *Chem. Pharm. Bull.* **1989**, *37*, 840. (g) Jones, T. K.; Mills, S. G.; Reamer, R. A.; Askin, D.; Desmond, R.; Volante, R. P.; Shinkai, I. *J. Am. Chem. Soc.* **1989**, *111*, 1157. (h) Mukaiyama, T.; Shiina, I.; Kobayashi, S. *Chem. Lett.* **1991**, 1901.

0022-3263/92/1957-6339$03.00/0

Scheme I

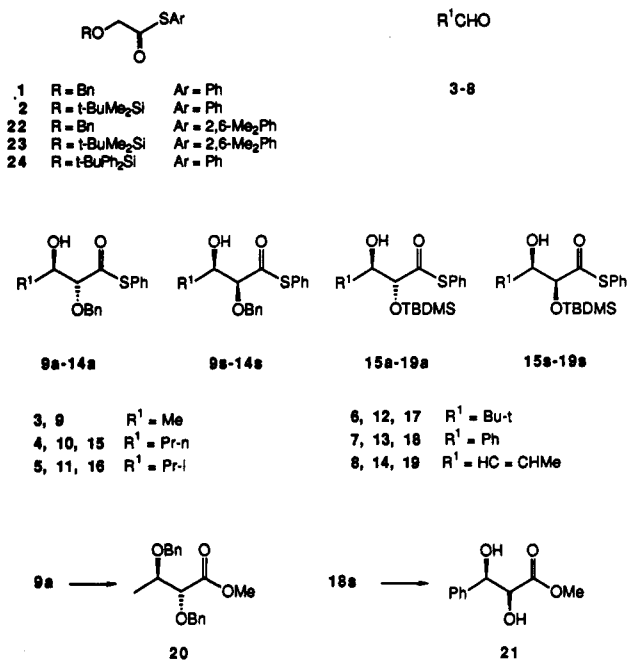

Table I. Stereoselective Aldol Condensation of Thioesters 1 and 2 with Aldehydes 3–8

thioester	aldehyde	product	% yield[a]	a:s ratio[b]
1	3	9	99	97:3
1	4	10	97	98:2[c]
2	4	15	99	16:84
1	5	11	95	98:2
2	5	16	98	10:90
1	6	12	81	98:2
2	6	17	87	17:83
1	7	13	99	92:8
2	7	18	99	12:88
1	8	14	95	98:2
2	8	19	97	28:72

[a] Isolated yields after flash chromatography. [b] As determined by 300-MHz ^{1}H NMR analysis of the crude products. [c] As determined by 75.4-MHz ^{13}C NMR analysis (see the Experimental Section).

synthesis by this route are scarce.[2,3]

We here report that both anti- and syn-configurated monoprotected α,β-dihydroxy thioesters can be obtained in good to high diastereoselectivity by the reaction of easily generated trichlorotitanium enolates[4,5] of differently O-protected aryl thioglycolates with aldehydes.[6]

Thioesters 1 and 2 (Scheme I) were readily prepared and enolized[4,5] by treatment with $TiCl_4$ and triethylamine (TEA) at −78 °C in CH_2Cl_2. Addition of 0.5 molar equiv of aldehydes 3–8 to the purple enolate solution at −78 °C resulted in the formation of aldols 9–19 as mixtures of diastereoisomers in excellent yields (Scheme I and Table I).[7] The anti (a):syn (s) ratios were determined on the crude materials by 300-MHz ^{1}H NMR spectroscopy and confirmed on the isolated products purified by flash chromatography. The configuration of 9a and 18s was established by chemical correlation. Compound 9a was converted ($Cu(OAc)_2$, MeOH, reflux;[8] benzyl bromide, Ag_2O, Et_2O, reflux; 50% overall yield) into the known[9] anti derivative 20. Compound 18s was transformed into syn diol 21 (obtained by osmylation of (*E*)-methyl cinnamate), by methanolysis (see above) followed by desilylation (HF, acetonitrile, rt; 58% overall yield). On the basis of chemical shift and coupling constant trend consideration,[10] as well as of common chromatographic behavior of the products,[11] the anti configuration was reasonably assigned to all major isomers of 9–14 and the syn one to the major isomers of 15–19.

As can be seen from the reported data, the use of benzyloxy thioester 1 led to the formation of anti monoprotected diols with high diastereoselectivity (a:s ratio >92:8) that is independent of the nature of the aldehyde R^1 residue. On the other hand, starting from thioester 2, which features a bulky oxygen protecting group (R = TBDMS), syn aldols were obtained with good stereocontrol (s:a ratios >83:17), with the only exception being the reaction of aldehyde 8. Ancillary experiments, carried out by reacting the differently substituted thioesters 22–24 with benzaldehyde, provided additional information.[12] A more bulky sulfur residue as in compound 22 decreased the anti stereoselectivity observed with benzyloxy thioester 1 (a:s ratio 63:37, 99% yield). On the contrary, an increase in the steric requirement of the sulfur or of the silyl group as in thioesters 23 and 24 did not result in any appreciable change in diastereoselection (s:a ratios 88:12 and 82:18 in 95% and 86% yield, respectively). It must be noted that the condensation of phenyl thioesters 1 and 2 with aldehydes almost perfectly parallels that of the silyl ketene acetals of the corresponding ethyl thioesters promoted by tin(II) triflate,[1h,2b] in both the sense and the extent of stereoselectivity.

The uncertainity about the nature of the trichlorotitanium enolates[4,5] clearly calls for caution in proposing models of stereoselection. We feel, however, that the opposite stereoselectivity can be explained by the reaction

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(3) For less stereoselective anti diol sinthesis, see: (a) D'Angelo, J.; Pages, O.; Maddaluno, J.; Dumas, F.; Revial, G. *Tetrahedron Lett.* **1983**, 5869. (b) Luengo, J. I.; Koreeda, M. *Tetrahedron Lett.* **1984**, 4881. (c) Evans, D. A.; Gage, J. R. Leighton, J. L.; Kim, A. S. *J. Org. Chem.* **1992**, *57*, 1961. (d) Nakahara, Y.; Shimizu, M.; Yoshida, H. *Tetrahedron Lett.* **1988**, 2325.

(4) (a) Evans, D. A.; Clark, J. S.; Metternich, R.; Novack, V. J.; Sheppard, G. S. *J. Am. Chem. Soc.* **1990**, *112*, 866. (b) Evans, D. A.; Urpi', F.; Somers, T. C.; Clark, J. S.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1990**, *112*, 8215. (c) Evans, D. A.; Rieger, D. L.; Bilodeau, M. T.; Urpi', F. *J. Am. Chem. Soc.* **1991**, *113*, 1047. (d) Evans, D. A.; Bilodeau, M. T.; Somers, T. C.; Clardy, J.; Kato, Y. *J. Org. Chem.* **1991**, *56*, 5750. For earlier references to this procedure for generating titanium enolates, see: Harrison, C. R. *Tetrhedron Lett.* **1987**, 4135. Brocchini, S. J.; Eberle, M. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5211.

(5) For the extension of this procedure to thioesters and α-thio- and α-halogeno-substituted esters, see: (a) Annunziata, R.; Cinquini, M.; Cozzi, F.; Cozzi, P. G.; Consolandi, E. *Tetrahedron* **1991**, *47*, 7897. (b) Cinquini, M.; Cozzi, F.; Cozzi, P. G.; Consolandi, E. *Tetrahedron* **1991**, *47*, 8767. (c) Annunziata, R.; Cinquini, M.; Cozzi, F.; Cozzi, P. G. *J. Org. Chem.* **1992**, *57*, 4155. The aldol condensation of trichlorotitanium enolates of *S*-aryl thiopropionate (see ref 5a) is syn stereoselective (s:a ratios up to 90:10).

(6) It must be noted that an alkoxy ester as methyl (benzyloxy)acetate is not enolized in these conditions. However, we found that 2-methoxyethyl propionate and 2-methoxyethyl (benzyloxy)acetate are easily enolized (unpublished results from these laboratories). Since recently the trichlorotitanium enolate of *N*-tosylnorephedrinepropionate has also been prepared (Xiang, Y.; Olivier, E.; Ouinet, N. *Tetrahedron Lett.* **1992**, 457), we think that chelation of titanium with the ester OR residue favors enolization of these nonactivated esters.

(7) A 1:1 enolate:aldehyde ratio gave slightly lower yields (75–90%) and identical stereoselections. The unreacted ester was recovered by chromatography.

(8) Green, C. L.; Houghton, R. P.; Phipps, D. A. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2623.

(9) Annunziata, R.; Cinquini, M.; Cozzi, F.; Fuchicello, A. *Tetrahedron* **1991**, *47*, 3853.

(10) For instance, the syn isomers generally feature smaller C*H*(OH)C*H*(OR) and larger C*H*OH *J* values. Furthermore, C*H*OH generally resonates at lower field in syn than in anti isomers.

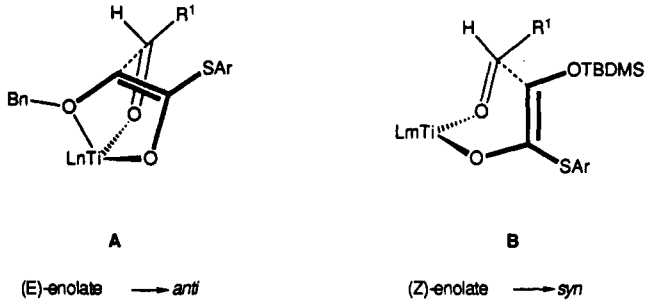
(11) In both series the syn isomers are always eluted first than the anti ones ($\Delta R_f > 0.1$).

(12) Chemical correlation of these products with compound 13 established their configuration.

of enolates of different configuration via transition structures of similar geometry. In the case of thioester 1, intramolecular chelation of Ti[13] between the carbonyl and the benzyloxy oxygens should provide the driving force for a highly stereoselective *E* enolate formation. On the other hand, the silyloxy group of 2 could prevent coordination[14] and the enolate should exist mainly in the *Z* configuration expected for a thioester-derived enolate.[15]

^{1}H NMR experiments supported this hypothesis. Indeed, by monitoring the enolate formation at −78 °C in CD_2Cl_2 solution,[5,16] a single enolate ($PhCH_2OCH$=C at δ 6.53 ppm) was observed in the case of 1, while two species in a 75:25 ratio were found for 2 (TBDMSOCH=C at δ 7.33 and 7.90 ppm, respectively).

On these bases, cyclic boat-like models[17] A and B can be used as working hypothesis to account for the stereochemical outcome. The lower stereocontrol observed in



the reaction of thioester 2 could arise from the less stereoselective enolate formation.

Experimental Section

***S*-Phenyl (phenylmethoxy)thioacetate (1) and *S*-2,6-dimethylphenyl (phenylmethoxy)thioacetate (22)** were prepared from (benzyloxy)acetyl chloride as described.[5a,b] Compound 1 was a colorless oil obtained in 95% yield by flash chromatography with a 85:15 hexanes–Et_2O mixture as eluant. ^{1}H NMR: δ 7.30–7.50 (m, 10 H), 4.75 (s, 2 H), 4.25 (s, 2 H). IR: 1690 cm^{-1}. Anal. Calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46. Found: C, 69.87; H, 5.37. Compound 22 was a thick oil obtained in 92% yield with a 90:10 hexanes–Et_2O mixture as eluant. ^{1}H NMR: δ 7.10–7.40 (m, 8 H), 4.75 (s, 2 H), 4.20 (s, 2 H). IR: 1690 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.33. Found: C, 71.18; H, 6.28.

***S*-Phenyl [[(1,1-dimethylethyl)dimethylsilyl]oxy]thioacetate (2), *S*-2,6-dimethylphenyl [[(1,1-dimethylethyl)dimethylsilyl]oxy]thioacetate (23), and *S*-phenyl [[(1,1-dimethylethyl)diphenylsilyl]oxy]thioacetate (24)** were prepared from methyl glycolate in two steps involving silylation and Me_3Al-promoted thioesterification as described.[18] Compound 2 was a colorless oil obtained in 83% yield with a 90:10 hexanes–Et_2O mixture as eluant. ^{1}H NMR: δ 7.45 (bs, 5 H), 4.40 (s, 2 H), 1.05 (s, 9 H), 0.20 (s, 6 H). IR: 1690 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O_2SSi$: C, 59.53; H, 7.85. Found: C, 59.70; H, 7.97. Compound 23 was an oil obtained in 75% yield with a 95:5 hexanes–Et_2O mixture as eluant. ^{1}H NMR: δ 7.10–7.25 (m, 3 H), 4.35 (s, 2 H), 2.30 (s, 6 H), 0.95 (s, 9 H), 0.20 (s, 6 H). IR: 1695 cm^{-1}. Anal. Calcd for $C_{16}H_{26}O_2SSi$: C, 61.89; H, 8.44. Found: C, 61.77; H, 8.57. Compound 24 was a thick oil obtained in 69% yield with a 95:5 hexanes–Et_2O mixture as eluant. ^{1}H NMR: δ 7.20–7.80 (m, 15 H), 4.35 (s, 2 H), 1.00 (s, 9 H). IR: 1690 cm^{-1}. Anal. Calcd for $C_{24}H_{26}O_2SSi$: C, 70.89; H, 6.44. Found: C, 70.80; H, 6.49.

***S*-Phenyl 3-Hydroxy-2-(phenylmethoxy)thiobutanoate (9).** To a stirred solution of thioester 1 (1 mmol, 258 mg) in dry CH_2Cl_2 (10 mL) cooled at −78 °C was added dropwise a 1 M solution of $TiCl_4$ in CH_2Cl_2 (1 mL). After 2 min, TEA (1 mmol, 0.140 mL) was added dropwise. After 30 min of stirring at −78 °C, freshly distilled acetaldehyde 3 (0.5 mmol, 0.028 mL) was added, and stirring was continued for 4 h at −78 °C. The reaction was quenched by addition of saturated $NaHCO_3$, and the resulting slurry was filtered through Celite. The organic phase was extracted twice with CH_2Cl_2, and the combined organic extracts were dried and concentrated in vacuo. After NMR determination of the isomer ratio, the product was purified by flash chromatography with a 50:50 hexanes–Et_2O mixture as eluant. The 97:3 **9a:9s** mixture was a solid, mp 43 °C. Selected ^{1}H NMR data for **9a**: δ 4.11 (CHOH), 4.03 (CHOR), $J_{2,3}$ = 5.0 Hz, J_{CH-OH} = 6.0 Hz. For **9s**: 4.09 (CHOH), 3.91 (CHOR), $J_{2,3}$ = 5, 5 Hz. IR: 3470, 1702 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00. Found: C, 67.41; H, 6.06. By the same procedure aldols **10–19** were prepared. For each compound physical properties of the diastereoisomeric mixture and hexanes–Et_2O eluting mixture for flash chromatography are indicated in brackets after the compound name. Yields and diastereoisomeric ratios are collected in Table I. IR data and elemental analyses were obtained on diastereoisomeric mixtures. Selected ^{1}H NMR data are given for both isomers when possible and are reported in the following order: CHOH (ppm), CHOR (ppm); $J_{2,3}$ (Hz), J_{CH-OH} (Hz).

***S*-Phenyl 3-Hydroxy-2-(phenylmethoxy)thiohexanoate (10)** (oil, 50:50). A single isomer was detected by ^{1}H NMR: 4.08, 3.97, 4.7, 5.6. Two products were observed by 75.4-MHz ^{13}C NMR. Selected data for **10a**: 200.50, 87.75, 34.14. For **10s**: 200.90, 87.10, 34.96. IR: 3480, 1705 cm^{-1}. Anal. Calcd for $C_{19}H_{22}O_3S$: C, 69.06; H, 6.71. Found: C, 68.92; H, 6.83.

***S*-Phenyl 3-Hydroxy-4-methyl-2-(phenylmethoxy)thiopentanoate (11)** (oil, 50:50). ^{1}H NMR data for **11a**: 3.72, 4.09, 6.0, 5.0. For **11s**: 3.58, 4.12, 4.0, 7.8. IR: 3475, 1700 cm^{-1}. Anal. Calcd for $C_{19}H_{22}O_3S$: C, 69.06; H, 6.71. Found: C, 68.94; H, 6.77.

***S*-Phenyl 4,4-Dimethyl-3-hydroxy-2-(phenylmethoxy)-thiopentate (12)** (80–81 °C, 55:45). ^{1}H NMR data for **12a**: 3.67, 4.10, 6.0, 7.0. A single isomer was also detected by ^{13}C NMR: 200.80, 86.53, 78.75, 73.37, 35.26, 26.11. IR: 3480, 1700 cm^{-1}. Anal. Calcd for $C_{20}H_{24}O_3S$: C, 69.73; H, 7.02. Found: C, 69.84; H, 7.09.

***S*-Phenyl 3-Hydroxy-3-phenyl-2-(phenylmethoxy)thiopropanoate (13)** (77–80 °C, 50:50). ^{1}H NMR data for **13a**: 4.99, 4.21, 6.5, 3.5. For **13s**: 5.11, 4.23, 3.2, 6.0. IR: 3485, 1705 cm^{-1}. Anal. Calcd for $C_{22}H_{20}O_3S$: C, 72.50; H, 5.53. Found: C, 72.38; H. 5.47.

***(E)*-*S*-Phenyl 3-Hydroxy-2-(phenylmethoxy)thiohex-4-enoate (14)** (oil, 50:50). ^{1}H NMR data for **14a**: 4.39, 4.15, 4.7, 7.0. For **14s**: 4.37, 3.99, 4.8, undet. IR: 3470, 1704 cm^{-1}. Anal. Calcd for $C_{19}H_{20}O_3S$: C, 69.48; H, 6.14. Found: C, 69.61; H, 6.07.

***S*-Phenyl 2-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-3-hydroxythiohexanoate (15)** (oil, 80:20). ^{1}H NMR data for **15s**: 3.77, 4.24, 3.9, 9.0. For **15a**: 3.84, 4.17, 4.0, 4.7. IR: 3480, 1700 cm^{-1}. Anal. Calcd for $C_{18}H_{30}O_3SSi$: C, 60.97; H, 8.53. Found: C, 61.09; H, 8.49.

***S*-Phenyl 2-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-3-hydroxy-4-methylthiopentanoate (16)** (46–47 °C, 80:20). ^{1}H NMR data for **16s**: 3.46, 4.37, 3.0, 7.5. For **16a**: 3.49, 4.39, 4.0, 4.2. IR: 3480, 1705 cm^{-1}. Anal. Calcd for $C_{18}H_{30}O_3SSi$: C, 60.97; H, 8.53. Found: C, 61.08; H, 8.58.

***S*-Phenyl 2-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-4,4-dimethyl-3-hydroxythiopentanoate (17)** (54–57 °C, 80:20). ^{1}H NMR data for **17s**: 3.45, 4.47, 2.3, 5.5. For **17a**: 3.60, 4.43, 4.0, undet. IR: 3480, 1705 cm^{-1}. Anal. Calcd for $C_{19}H_{32}O_3SSi$: C, 61.91; H, 8.75. Found: C, 62.00; H, 8.64.

***S*-Phenyl 2-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-3-hydroxy-3-phenylthiopropanoate (18)** (71–73 °C, 80:20). ^{1}H NMR data for **18s**: 5.06, 4.42, 3.0, 9.0. For **18a**: 4.87, 4.37, 6.3, 3.5. IR: 3475, 1703 cm^{-1}. Anal. Calcd for $C_{21}H_{28}O_3SSi$: C, 64.91; H, 7.27. Found: C, 64.79; H, 7.36.

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(16) A detailed NMR study of the complexation/enolization process of these and related thioesters[5] will be reported in the future.

(17) Cyclic models involving coordination of the aldehyde oxygen to the Lewis acidic titanium species should be favored in a noncoordinating solvent as dichloromethane. Boat-like transition states have been previously proposed for the aldol reaction of trichlorotitanium enolates: Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* **1983**, *24*, 3343. The possibility that these enolates can exist as aggregate in solution and/or as "ate" complexes has also been suggested (see refs 4 and 13).

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(*E*)-*S*-Phenyl 2-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-3-hydroxythiohex-4-enoate (19) (oil, 80:20). ^{1}H NMR data for **19s**: 4.31, 4.26, 3.3, 9.0. For **19a**: 4.31, 4.31, 4.5, undet. IR: 3480, 1707 cm^{-1}. Anal. Calcd for $C_{18}H_{28}O_3SSi$: C, 61.32; H, 8.00. Found: C, 61.23; H, 8.07.

Synthesis of Methyl 2,3-Bis(phenylmethoxy)butanoate 20 from 9a. Compound **9a** was converted (87% yield) into the corresponding methylester by treatment with $Cu(OAc)_2$ in refluxing methanol as described.[8] Benzylation with benzyl bromide in the presence of Ag_2O in refluxing Et_2O afforded **20**[9] in 58% yield after flash chromatography with a 80:20 hexanes–Et_2O mixture as eluant.

Synthesis of Methyl 2,3-Dihydroxy-3-phenylpropanoate from 18s. Compound **18s** was converted (60% yield) into the corresponding methylester as described above.[8] Desilylation with a few drops of 40% aqueous HF in acetonitrile at rt afforded compound **21** in 97% yield. The crude product was shown to be identical by ^{1}H NMR to the diol prepared by osmylation of (*E*)-methyl cinnamate.

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Photoinduced Electron-Transfer Reactions of 1-Substituted 2,3-Diphenylaziridines with 9,10-Dicyanoanthracene and Chloranil

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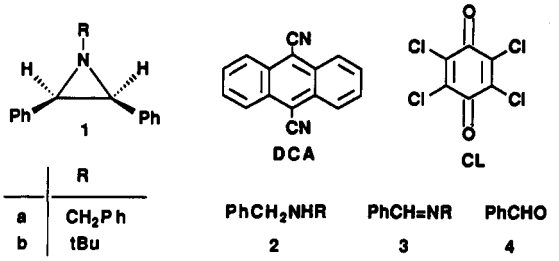
Introduction

An electron donor can be converted to the corresponding cation radical through a single electron transfer (SET) to an excited state of an electron acceptor. Back-electron transfer (BET) from the anion radical of the acceptor to the cation radical leads to unproductive decay, but rapid bond cleavage can compete with this energy-wasting process.[1] Aziridines are reactive substrates under photoinduced SET conditions since their cation radicals can undergo facile bond cleavage driven by the relief of the ring strain. Previous studies have demonstrated that 1,3-dipolar cycloaddition is involved in SET photoreactions of certain aryl-substituted aziridines with electron acceptors in the presences of dipolarophiles.[2] In these cases, cycloadducts are produced through dipolar additions between the dipolarophile and the ring-opened intermediates that have escaped from the geminate ion radical pairs. Interestingly, little information is available on the behavior of aziridine cation radicals in ion radical pairs.[3] In this paper, we report the results of a study of the photoreactions of 1-substituted 2,3-diphenylaziridines (**1**) with electron acceptors 9,10-dicyanoanthracene (DCA) and chloranil (CL).[4]



Results

The DCA-sensitized photoreactions of cis 1-substituted 2,3-diphenylaziridines **1** were conducted in methylene chloride (entries 1–6 in Table I). To prevent decomposition of the initial products, irradiation was discontinued at 44–67% conversion of **1**. ^{1}H NMR analysis of the reaction mixture obtained from the irradiation of *cis*-1-benzyl-2,3-diphenylaziridine (**1a**) demonstrated that dibenzylamine (**2a**) and benzaldehyde (**4**) were the major products along with a small amount of benzalbenzylamine (**3a**). When *cis*-1-*tert*-butyl-2,3-diphenylaziridine (**1b**) was subjected to the similar reaction conditions, benzyl-*tert*-butylamine (**2b**), benzal-*tert*-butylamine (**3b**), and **4** were formed. The yield of **4** was nearly the same whether the reaction was conducted under a N_2 or an O_2 atmosphere (entries 1 and 2). This result suggests that the oxygen in **4** does not come from molecular oxygen. Since **2** and **4** appear to be formed through a formal hydrolysis of **1**, a trace amount of H_2O in photolysis solutions must be responsible. Indeed, the yields of **2** increased when H_2O was added to the photolysis solutions (entries 3 and 6). Similarly, the yield of **2a** increased when MeOH was present (entry 4).

These observations suggest that the addition of a nucleophilic species to intermediates in these processes is involved in product formation. To test whether a nucleophile was involved, DCA-sensitized photoreactions of **1a** in methylene chloride were conducted in the presence of D_2O or MeOD. Under these conditions, we expected that one hydrogen at the benzylic position of **2a** would be substituted by deuterium. Indeed, dibenzylamine obtained from the acidic extraction of the reaction mixtures was found (^{1}H NMR analysis) to be nearly quantitatively monodeuterated at the benzylic position (see Experimental Section).

The product distributions from photoreactions in MeCN were different from those in methylene chloride, and the yields were relatively low (entry 7 in Table I). While H_2O had little influence on the product yields (entry 8), MeOH significantly increased the yields of **2a** and **4** (entry 9). Moreover, **2a** was not detected when $LiClO_4$ was present in the photolysis solution (entry 10). The absence of **2a** is not due to decomposition, since more than 87% of **2a** was recovered when DCA-sensitized photoreactions of **2a** were performed under similar conditions.

In contrast, when a methylene chloride solution of **1a** (0.043 M) and CL (0.044 M) was irradiated for 60 min, tetrachlorohydroquinone (CLH_2) was formed in 82% based on consumed **1a**. Products **3a** (82%) and **4** (74%) were also detected by ^{1}H NMR analysis of the photolysate at 81% conversion of **1a**. Thus, photoreactions of **1a** with CL lead to consumption of the acceptor. Results from studies of the photoreactions of **1a** and CL (ca. 0.5 equiv) under various conditions are notable in that **2a** is not formed under any of the reaction conditions used (Table II). In both methylene chloride and acetonitrile, H_2O and MeOH had little effect on the yield of **3a** (entries 2, 3, 5, and 6), and appreciable amounts of the dimethyl acetal

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