NMR ($CDCl_3$) δ 1.20–1.65 (m, 6 H), 4.20–4.65 (m, 3 H), 7.33 (br s, 1 H). Anal. Calcd for $C_7H_{10}Cl_3NO_3$: C, 32.02; H, 3.85; N, 5.34. Found: C, 32.02; H, 3.88; N, 5.43.

Ethyl *N*-(trichloroacetyl)-2-aminobutanoate (5c): ethyl 2-bromobutanoate (**3c**); 72 h, petroleum ether and Et_2O (2:1). **5c**: 2.63 g, 95%; mp 45–47 °C; IR (Nujol) 3300, 1740, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85–1.50 (m, 6 H), 1.65–2.25 (m, 2 H), 4.10–4.70 (m, 3 H), 7.30 (br s, 1 H). Anal. Calcd for $C_8H_{12}Cl_3NO_3$: C, 34.74; H, 4.38; N, 5.07. Found: C, 34.79; H, 4.30; N, 5.03.

Ethyl *N*-(trichloroacetyl)-2-aminooctanoate (5d): ethyl 2-bromooctanoate (**3d**); 48 h; petroleum ether and Et_2O (12:1). **5d**: 2.86 g, 86%; n^{20}_D 1.4700; IR (neat) 3350, 1740, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.63–1.60 (m, 14 H), 1.70–2.20 (m, 2 H), 4.10–4.75 (m, 3 H), 7.25 (br s, 1 H). Anal. Calcd for $C_{14}H_{20}Cl_3NO_3$: C, 43.32; H, 6.07; N, 4.21. Found: C, 43.46; H, 6.18; N, 4.23.

Methyl *N*-(trichloroacetyl)-2-aminohexadecanoate (5e): methyl 2-bromohexadecanoate (**3e**); 160 h; petroleum ether and CH_2Cl_2 (4:1). **5e**: 2.67 g, 62%; mp 39 °C; IR (nujol) 3320, 1760, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.50–1.60 (m, 27 H), 1.65–2.25 (m, 2 H), 3.85 (s, 3 H), 4.30–4.60 (m, 1 H), 7.15 (br s, 1 H). Anal. Calcd for $C_{19}H_{34}Cl_3NO_3$: C, 52.96; H, 7.97; N, 3.25. Found: C, 52.88; H, 7.87; N, 3.25.

Methyl *N*-(trichloroacetyl)-2-amino-4-methylpentanoate (5f): methyl 2-bromo-4-methylpentanoate (**3f**); 18 d; petroleum ether and Et_2O (3:1). **5f**: 1.48 g, 51%; mp 64–65 °C; IR (Nujol) 3275, 1755, 1685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85–1.25 (m, 7 H), 1.60–2.00 (m, 2 H), 3.85 (s, 3 H), 4.40–4.85 (m, 1 H), 7.15 (br s, 1 H). Anal. Calcd for $C_9H_{13}Cl_3NO_3$: C, 37.20; H, 4.87; N, 4.82. Found: C, 36.98; H, 4.94; N, 4.88.

Ethyl *N*-(trichloroacetyl)-2-amino-3-phenylpropanoate (5j): ethyl 2-bromo-3-phenylpropanoate (**3j**); 40 h; petroleum ether and Et_2O (5:1). **5j**: 0.81 g, 24%; mp 61 °C; IR (Nujol) 3320, 1760, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31 (t, 3 H, J = 9 Hz), 3.20 (d, 2 H, J = 16 Hz), 4.20 (q, 2 H, J = 11 Hz), 4.60–4.95 (m, 1 H), 7.18 (m, 6 H). Anal. Calcd for $C_{13}H_{14}Cl_3NO_3$: C, 46.11; H, 4.18; N, 4.14. Found: C, 46.40; H, 4.24; N, 4.10. *trans*-Ethyl cinnamate (**7**): 0.55 g, 31%.

Methyl 1-(trichloroacetyl)-2-pyrrolidinecarboxylate (8): methyl 2,5-dibromopentanoate (**3k**); 24 h; petroleum ether and Et_2O (1:1). **8**: 2.06 g, 75%; n^{20}_D 1.5115; IR (neat) 1745, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.90–2.50 (m, 4 H), 3.80 (s, 3 H), 3.90–4.25 (m, 2 H), 4.40–4.65 (m, 1 H). Anal. Calcd for $C_8H_{10}Cl_3NO_3$: C, 35.00; H, 3.68; N, 5.10. Found: C, 35.02; H, 3.60; N, 5.07.

Methyl 1-(trichloroacetyl)-2-piperidinecarboxylate (9): methyl 1,6-dibromohexanoate (**3l**); 24 h; petroleum ether and Et_2O (2:1). **9**: 1.70 g, 59%; n^{20}_D 1.5120; IR (neat) 1740, 1675 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85–2.10 (m, 4 H), 2.20–2.50 (m, 3 H), 3.85 (s, 3 H), 4.35–4.65 (m, 2 H), 5.10–5.40 (m, 1 H). Anal. Calcd for $C_9H_{12}Cl_3NO_3$: C, 37.46; H, 4.20; N, 4.85. Found: C, 37.38; H, 4.22; N, 4.88.

Methyl *N*-(trichloroacetyl)-5-aminopentanoate (5m): methyl 5-bromopentanoate (**3m**); 20 d; petroleum ether and Et_2O (3:1). **5m**: 1.88 g, 68%; mp 23–25 °C; IR (neat) 3320, 1740, 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50–1.90 (m, 4 H), 2.25–2.50 (m, 3 H), 3.25–3.55 (m, 2 H), 4.75 (s, 3 H), 7.05 (br s, 1 H). Anal. Calcd for $C_8H_{12}Cl_3NO_3$: C, 34.74; H, 4.38; N, 5.07. Found: C, 34.66; H, 4.30; N, 5.12.

General Method for the Hydrolysis of *N*-(Trichloroacetyl)-2-amino Carboxylic Esters 5. Preparation of the Corresponding Amino Acids 6. A mixture of **5a–f,j,m** and **8,9** (5 mmol), aqueous 20% KOH (2.4 mL, 10 mmol), and MeOH (8.5 mL) was stirred overnight at rt. After the previously described workup,[1] amino acids **6d,e** and **10** were isolated as such, while products **6a–c,f,j,m** and **11** were obtained as hydrochlorides (Table I). Yields and physical data of the products of hydrolysis are reported.

Glycine hydrochloride (6a): 0.53 g, 95%; mp 180 °C dec (lit.[8] mp 185 °C dec).

Alanine hydrochloride (6b): 0.63 g, 100%. Free alanine **6b** was obtained from the hydrochloride via exchange with a basic polymeric resin and had mp 290 °C (lit.[8] mp 295 °C).

2-Aminobutanoic acid hydrochloride (6c): 0.66 g, 95%; mp 177 °C (lit.[8] mp 179–180 °C).

2-Aminooctanoic acid (6d): 0.73 g, 92%; mp 264 °C (lit.[8] mp 270 °C).

2-Aminohexadecanoic acid (6e): 1.22 g, 90%; mp 85 °C (lit.[8] mp 86–87 °C).

2-Amino-4-methylpentanoic acid hydrochloride (6f): 0.75 g, 90%. Free **6f**, obtained in the usual manner, had mp 288 °C (lit.[8] mp 293–295 °C).

2-Amino-3-phenylpropanoic acid hydrochloride (6j): 1.01 g, 100%. Free **6j** had mp 280 °C (lit.[8] mp 284–288 °C).

2-Pyrrolidinecarboxylic acid (10): 0.58 g, 100%; mp 200 °C (lit.[8] mp 203–205 °C).

2-Piperidinecarboxylic acid hydrochloride (11): 0.80 g, 97%; mp 255 °C (lit.[9] mp 259–261 °C).

5-Aminopentanoic acid hydrochloride (6m): 0.77 g, 100%; mp 93 °C (lit.[10] mp 92–94 °C).

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Registry No. **2**, 594-65-0; **3a**, 105-36-2; **3b**, 41978-69-2; **3c**, 66025-42-1; **3d**, 138286-76-7; **3e**, 115401-57-5; **3f**, 70288-63-0; **3g**, 84984-05-4; **3h**, 600-00-0; **3i**, 2216-90-2; **3j**, 129592-91-2; **3k**, 138286-77-8; **3l**, 70288-66-3; **3m**, 5454-83-1; **5a**, 116963-47-4; **5b**, 138286-78-9; **5c**, 138286-79-0; **5d**, 138286-80-3; **5e**, 138286-81-4; **5f**, 138286-82-5; **5j**, 138286-83-6; **5m**, 138286-84-7; **6a**, 6000-43-7; **6b**, 25616-13-1; **6c**, 40522-79-0; **6d**, 644-90-6; **6e**, 98320-69-5; **6f**, 2508-63-6; **6j**, 27172-85-6; **6m**, 627-95-2; **7**, 4192-77-2; **8**, 138286-85-8; **9**, 138286-86-9; **10**, 609-36-9; **11**, 5107-10-8; $Me_2CHCH_2CH_2COOH$, 646-07-1; ε-caprolactone, 502-44-3.

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Lipase-Catalyzed Enantioselective Transesterification of *O*-Trityl 1,2-Diols. Practical Synthesis of (*R*)-Tritylglycidol

Mahn-Joo Kim* and Yoon Kyung Choi

Department of Chemistry and Center for Biofunctional Molecules, Pohang Institute of Science and Technology, P.O. Box 125, Pohang 790-600, Korea

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Glycidol and its derivatives are versatile C_3 synthons in organic synthesis.[1] Their optically active forms are especially useful in the asymmetric synthesis of β-blockers[2] and lipids.[3] Although several procedures[4] are currently available for their enantioselective synthesis (for example, Sharpless epoxidation of allylic alcohols[4b] and lipase-catalyzed hydrolysis of glycidyl esters[4c]), few of them provide high optical purity (>98% ee). We herein report a short efficient chemoenzymatic synthesis of optically pure (*R*)-tritylglycidol (**4**, >98% ee) whose optical purity results from lipase PS (LPS)-catalyzed enantioselective transesterification of an intermediate, 3-chloro-1-*O*-trityl-1,2-propanediol (**2a**).

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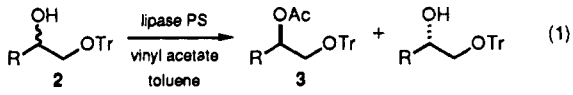
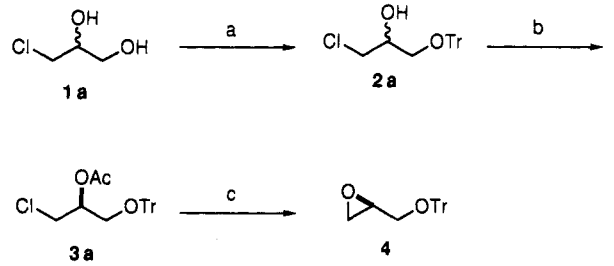
Table I. Lipase-Catalyzed Enantioselecttive Transesterifications of 2[a]



substrate R		product % yield[b]	product % ee[c]	product AC[d]	recovered substrate % yield[b]	recovered substrate % ee[e]	recovered substrate AC[d]
$ClCH_2$ (**2a**)	**3a**	43	>98	*S*[f]	54	72	*R*[f]
CH_3 (**2b**)	**3b**	37	>98	*R*	40	78	*S*
CH_3CH_2 (**2c**)	**3c**	43	>98	*R*	48	>98	*S*
$CH_3CH_2CH_2$ (**2d**)	**3d**	44	70	*R*	52	56	*S*

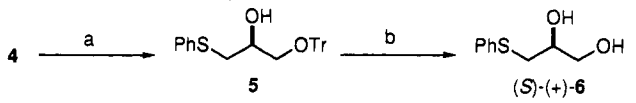
[a] Typical procedure: enzymes (lipase PS from *Pseudomonas* sp., 0.2 g) were added to an organic solution containing *O*-trityl 1,2-diol (**2**, 1 mmol), vinyl acetate (8 mmol), and toluene (10 mL). The resulting mixture was stirred at 25 °C for several days. The reaction was stopped when approximately 50% conversion was achieved. The reaction mixture, after removal of enzymes, was concentrated and subjected to chromatography to separate the acetylated productt **3** and the unreacted substrate. All products gave satisfactory analytical data. [b] Isolated; the theoretical maximum yield is 50%. [c] Determined by ^1H NMR spectroscopy in the presence of $Eu(hfc)_3$. [d] Absolute configuration. Based on the optical rotation of the recovered **2a**: $[\alpha]_D$ + 12.6 (*c* 2, $CHCl_3$); lit. −13.7 (*c* 10, $CHCl_3$) for (*R*)-**2a** (Baer, L.; Dike, A. J.; Buchnea, D. *Can. J. Biochem.* **1968**, *46*, 69–74). [e] Determined in the chemically-acetylated form by ^1H NMR spectroscopy in the presence of $Eu(hfc)_3$. [f] Confirmed by converting them chemically to (*S*)-(+)- and (*R*)-(−)-**6**, respectively. See text.

Scheme I[a]



[a] (a) Ph_3CCl, Et_3N, DMAP, 85%; (b) lipase PS, vinyl acetate, toluene, 43%; (c) KOH, EtOH, 83%.

Scheme II[a]



[a] (a) PhSNa, PhSH, 89%; (b) TsOH, MeOH, 92%.

The synthesis of **4** started from 3-chloro-1,2-propanediol (**1a**), which was first converted by treatment with trityl chloride, Et_3N, and DMAP[5] to monoprotected diol **2a** (Scheme I). The tritylated diol was then subjected to LPS-catalyzed transesterification in the presence of vinyl acetate in toluene to yield the acetylated product **3a** (*S*, >98% ee, 43%) and the unreacted **2a** (*R*, 72% ee, 54%). The acetylated product was finally treated with alcoholic alkaline to give the desired product (*R*)-**4**. The overall yield was 61% based on an enantiomer of **1a**, and the optical purity, measured by ^1H NMR spectroscopy in the presence of $Eu(hfc)_3$, was >98% ee. The *R* absolute configuration was confirmed by its conversion to (*S*)-(+)-**6**[6] (Scheme II).

Thus we have achieved a practical synthesis of (*R*)-**4**. It is short and straightforward. It uses readily available enzymes and chemicals and provides the highest optical purity. It can be upscaled to multigrams without major difficulty. The trityl derivative of glycidol has some advantages over other derivatives: (1) it is solid and can be shelf-stored for long term; (2) its trityl group is stable under the conditions for useful chemical transformations such as ring-opening by Grignard reagents or basic nucleophiles; and (3) it can be deprotected under mild conditions after the transformations are complete.

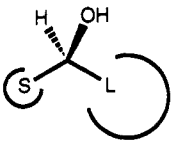


Figure 1. For secondary alcohols, the enantiomer shown reacts faster with LPS than the other enantiomer.

The high enantioselectivity observed in the LPS-catalyzed transesterification of **2a** encouraged us to test other trityl 1,2-diols as the LPS substrates. Three trityl 1,2-diols (**2b–d**) were prepared from the corresponding diols (**1b–d**) by the same procedure as above and subjected to the LPS-catalyzed transesterification. The results are described in Table I together with those from the LPS-catalyzed transesterification of **2a**. All the acetylated products (**3b–d**) have the *R* configuration and high optical purities (>98% ee) except **3d** (70% ee). The recovered substrates have the *S* configuration and optical purities ranging from 56 to >98% ee. These results constitute the first successful kinetic resolution of monoprotected simple 1,2-diols.

The stereochemical preference and enantioselectivity of LPS toward **2** can be interpreted using a simple rule[7] proposed recently: *For secondary alcohols, LPS transforms preferentially the enantiomer shown in Figure 1, and its enantioselectivity is high when the substituents at the stereocenter differ significantly in size.* In our case, the (trityloxy)methyl group is significantly larger than Me, Et, or chloromethyl, and the resulting steric difference seems to direct the specificity of LPS toward such high level. This interpretation implies that the trityl group serves as a useful steric auxiliary for high enantioselection. It is noteworthy that the enantioselectivity of LPS is significantly reduced when the smaller substituent changes from ethyl (**2c**) to propyl (**2d**) (Table I). This result indicates that the maximum size of smaller substituent should be limited to a two-carbon unit for high enantioselection. We conclude based on these observations that proper modification of substrate structure must be considered as a good strategy for enhancing the enantioselectivity of LPS-catalyzed reaction.

In summary, this paper has described the lipase-catalyzed enantioselective transesterification of *O*-trityl 1,2-diols and the practical synthesis of (*R*)-tritylglycidol.

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Further studies, including the synthesis of chiral 1,2-diols and β-blockers, are in progress in our laboratory.

Experimental Section

Materials and Methods. All 1,2-diols, triphenylmethyl chloride, and vinyl acetates were obtained from Aldrich. Lipase PS from *Pseudomonas* sp. was obtained from Amano, Japan. All other chemicals were reagent grade and used as received.

^{1}H NMR spectra were recorded on a Bruker AM-300 instrument with peaks referenced to tetramethylsilane in $CDCl_3$. IR spectra were recorded on a Perkin-Elmer 843 spectrometer. Optical rotations were measured using a JASCO polarimeter. Melting points were measured using a Thomas-Hoover apparatus. Enantiomeric excesses of acetates and oxirane were measured by ^{1}H NMR spectroscopy in the presence of Eu(hfc)$_3$. Enantiomeric excesses of alcohols were measured in the acetate forms.

(*R*)-Tritylglycidol [(*R*)-4]. A solution of **1a** (1.0 g, 9.05 mmol), triphenylmethyl chloride (2.78 g, 9.96 mmol), triethylamine (1.89 mL, 13.6 mmol), and 4-(dimethylamino)pyridine (0.044 g, 0.36 mmol) in CH_2Cl_2 (10 mL) was stirred overnight at 25 °C under a nitrogen atmosphere. After stirring for 24 h, the reaction mixture was poured into an ice–water mixture and extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous $MgSO_4$, concentrated, and chromatographed (*n*-hexane/ethyl acetate, 11:1) to give **2a** (colorless oil, 2.71 g, 85%): ^{1}H NMR δ 7.42 (m, 6 H), 7.28 (m, 9 H), 3.93 (m, 1 H), 3.70 (dd, *J* = 11.1 and 4.8 Hz, 1 H), 3.62 (dd, *J* = 11.1 and 6.0 Hz, 1 H), 3.32 (dd, *J* = 9.6 and 5.1 Hz, 1 H), 3.25 (dd, *J* = 9.6 and 5.4 Hz, 1 H), and 2.34 (d, *J* = 5.8 Hz, 1 H) ppm.

Enzymes (lipase PS, 0.2 g) were added to an organic solution containing **2a** (0.35 g, 1 mmol), vinyl acetate (0.74 mL, 8 mmol), and toluene (10 mL). The resulting mixture was stirred at rt. The reaction was followed by TLC and stopped when no further reaction progress was observed (4.5 days). The reaction mixture, after removal of enzymes, was concentrated and subjected to chromatography (*n*-hexane/ethyl acetate, 6:1) to give (*S*)-**3a** (0.17 g, 43%) and (*R*)-**2a** (0.19 g, 54%), separately. This reaction was repeated on a larger scale (**2a**, 4.43 g, 12.5 mmol; lipase PS, 2.02 g, vinyl acetate, 7.78 g, 90.3 mmol; toluene, 20 mL; 5 days) to obtain 2.30 g (47%) of (*S*)-**3a** and 2.00 g (45%) of (*R*)-**2a**. (*S*)-**3a**: ^{1}H NMR δ 7.41 (m, 6 H), 7.27 (m, 9 H), 5.15 (m, 1 H), 3.74 (m, 2 H), 3.30 (d, *J* = 5.1 Hz, 2 H), and 2.09 (s, 3 H) ppm.

Acetate (*S*)-**3a** (0.44 g, 1.13 mmol) dissolved in absolute EtOH (5 mL) was added to a solution of KOH (0.108 g, 1.93 mmol) in absolute EtOH (10 mL). The solution mixture was stirred at 25 °C for 8 h, filtered to remove KCl, and concentrated to yield white solid. The products were further purified by chromatography (*n*-hexane/ethyl acetate, 6:1) to give 0.29 g (0.92 mmol, 83%) of (*R*)-**4**. This reaction was repeated on a larger scale (3.5 g, 8.87 mmol) to obtain 2.40 g (7.59 mmol, 86%) of the target products. (*R*)-**4**: mp 97–97.5 °C (lit.[8] mp 86.5–87 °C for racemic **4**); $[\alpha]^{23}_D$ +9.3 (*c* 2.0, $CHCl_3$); >98% ee. Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.27; H, 6.32. ^{1}H NMR and IR data are in good agreement with those reported for the racemic compound.[8]

(*S*)-(+)-3-(Phenylthio)-1,2-propanediol [(*S*)-(+)-6]. Benzenethiol (0.4 mL, 4 mmol) was added to NaH (powder, 50 mg, 2 mmol) suspended in dry THF (4 mL) at 0 °C under nitrogen atmosphere,[9] and to this solution was added (*R*)-**4** (50 mg, 0.16 mmol). The resulting mixture was stirred at 25 °C for 2 h, quenched with saturated aqueous NH_4Cl solution, and extracted with ether. The organic phase was washed with brine, dried over anhyd K_2CO_3, and evaporated to give **5** (white solid, 60 mg, 89%). The white solid was dissolved in MeOH (10 mL), and then a catalytic amount of *p*-toluenesulfonic acid was added into the reaction mixture. The reaction was carried out at 25 °C until all the starting material was consumed (about 5 h). The reaction mixture was evaporated, and the residue was applied to a silica gel column (*n*-hexane/ethyl acetate, 8:1) to give the desired product **6** (27 mg, 92%): mp 79–80 °C (from benzene) (lit.[6] mp 79–81 °C); $[\alpha]^{30}_D$ +21.2° (*c* 1.03, EtOH) [lit.[6] $[\alpha]^{25}_D$ +21.3° (*c* 1.01, EtOH)]. ^{1}H NMR and IR data are in good agreement with those reported.[6]

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Registry No. (±)-**1a**, 52340-46-2; (±)-**2a**, 69161-65-5; (±)-**2b**, 71697-18-2; (±)-**2c**, 138384-31-3; (±)-**2d**, 138457-82-6; **3a**, 138384-30-2; **3b**, 138407-35-9; **3c**, 138384-32-4; **3d**, 138384-33-5; **4**, 65291-30-7; **5**, 138407-34-8; (*S*)-(+)-**6**, 97798-48-6.

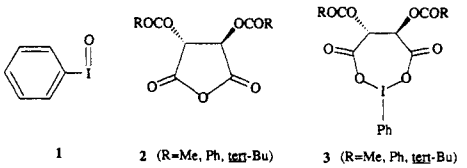
Iodinanes with Chiral Ligands. Synthesis and Structure of Iodine(III) Dibenzoyl Tartrates

Dale G. Ray III and Gerald F. Koser*

Department of Chemistry, The University of Akron, Akron, Ohio 44325

Received July 22, 1991

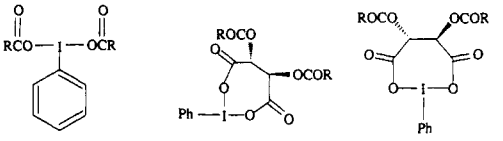
Although iodine(III) compounds (i.e., iodinanes) have been known for over a century and are widely employed as oxidation and functionalization reagents,[1] only several studies of iodinanes with iodine(III)-bound homochiral ligands have been published.[2] Of particular interest here is a 1986 report of the asymmetric oxidations of *o*- and *p*-tolyl methyl sulfides to the corresponding sulfoxides in moderate optical yields (i.e., 30–53%) with iodosobenzene (**1**) in the presence of the L-tartaric anhydrides **2** (acetone,



1 **2** (R=Me, Ph, tert-Bu) **3** (R=Me, Ph, tert-Bu)

rt).[2b] The isolation and characterization of iodine(III) tartrates was not reported. However, it was assumed that the cyclic tartrates **3** were "generated in situ", and, since the oxidation of methyl *p*-tolyl sulfide with a reagent prepared from **1** and acetyl L-lactic acid proceeded with little induction, it was concluded that the "C_2-symmetric ring system...is an important factor for the efficient asymmetric oxidation of sulfides".[2b]

Molecules such as **3**, if demonstrated to exist, would be unique since bis(acyloxy)iodinanes **4** and iodinanes in



4 **5** **6**

general are T-shaped about the iodine atom.[3] Cyclic species **5** are more consistent with the geometric constraints at iodine(III), but even they incorporate a high energy configuration; i.e., among aryliodinanes, $ArIL_1L_2$, the heteroatom ligands L_1 and L_2 are invariably colinear and not perpendicular as **5** requires.[3] Symmetrical

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(3) See ref 1c (pp 729–740) and papers cited therein.

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