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$_2$Cl$_2$ (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$_2$Cl$_2$. 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); [α]$^{23}_D$ +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$_4$Cl solution, and extracted with ether. The organic phase was washed with brine, dried over anhyd K$_2$CO$_3$, 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); [α]$^{30}_D$ +21.2° (c 1.03, EtOH) [lit.[6] [α]$^{25}_D$ +21.3° (c 1.01, EtOH)]. ^{1}H NMR and IR data are in good agreement with those reported.[6]

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

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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)
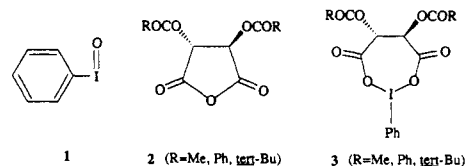
rt).[2b] The isolation and characterization of iodine(III) tartrates was not reported. However, it was assumed that the cyclic tartrates 3 were "generated in situ", and, since the oxidation of methyl *p*-tolyl sulfide with a reagent prepared from 1 and acetyl L-lactic acid proceeded with little induction, 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
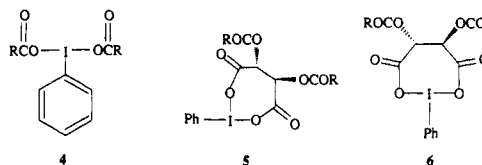
general are T-shaped about the iodine atom.[3] Cyclic species 5 are more consistent with the geometric constraints at iodine(III), but even they incorporate a high energy configuration; i.e., among aryliodinanes, ArIL$_1$L$_2$, the heteroatom ligands L$_1$ and L$_2$ are invariably colinear and not perpendicular as 5 requires.[3]   Symmetrical

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(2) (a) Merkushev, E. B.; Novikov, A. N.; Makarchenko, S. S.; Moskal'chuk, A. S.; Glushkova, V. V.; Kogai, T. I.; Polyakova, L. G. *J. Org. Chem. USSR (Engl. Transl.)* 1975, *11*, 1246. (b) Imamoto, T.; Koto, H. *Chem. Lett.* 1986, 967. (c) Hatzigrigoriou, E.; Varvoglis, A.; Bakola-Christianopoulou, M. *J. Org. Chem.* 1990, *55*, 315. (d) Ray, D. G., III; Koser, G. F. *J. Am. Chem. Soc.* 1990, *112*, 5672. (e) Ochiai, M.; Takaoka, Y.; Masaki, Y.; Nagao, Y.; Shiro, M. *J. Am. Chem. Soc.* 1990, *112*, 5677.

(3) See ref 1c (pp 729–740) and papers cited therein.
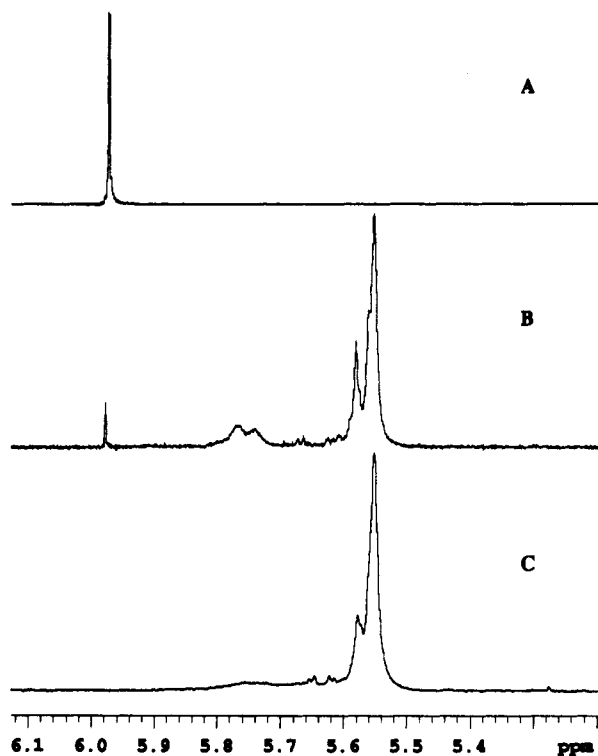
Figure 1. 300-MHz ^{1}H NMR spectra (methine region) of dibenzoyl-L-tartaric anhydride (A) and the iodine(III) dibenzoyl-L-tartrates derived from iodosobenzene (B) and (diacetoxyiodo)benzene (C).

structures **6**, in which the T-configuration at iodine is maintained, might be somewhat strained since the I–O bonds of bis(acyloxy)iodinanes are known to be substantially elongated.[4]

In an effort to clarify these structural issues, we investigated the reactions of iodosobenzene with L-**2** (R = Ph) and (diacetoxyiodo)benzene (**4**, R = Me) with dibenzoyl-D- and L-tartaric acids **7**. Iodine(III) tartrates are indeed produced. However, the materials isolated by us are noncyclic polymers capable of effecting the asymmetric oxidation of *p*-tolyl methyl sulfide despite the absence of a "C$_2$-symmetric ring system".

In a typical experiment, (diacetoxyiodo)benzene (10 mmol) was mixed with dibenzoyl-L-tartaric acid (10 mmol) in CH$_2$Cl$_2$ at room temperature. After 23 min, the solution was extracted with water, dried, and concentrated. The residual "glass" was pulverized, triturated with hexanes, and dried in vacuo to give a white powder (82% yield, mp 135–153 °C) exhibiting an elemental composition (C, H, I) consistent with a 1:1 adduct and an *average* molecular weight (i.e., 5870) corresponding to 10.5 monomer units (eq 1). The structure of the iodine(III) tartrate was further
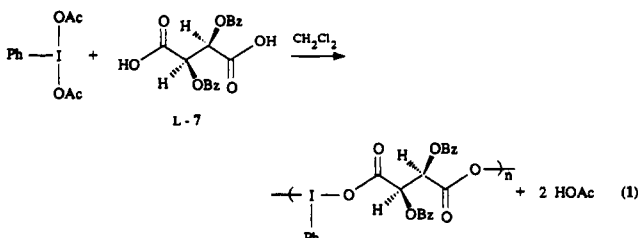
substantiated by NMR (^{13}C, 300-MHz ^{1}H) analysis, the various resonances being somewhat broadened as expected

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Table I. Specific Rotations of Iodine(III) Dibenzoyl Tartrate Polymers Derived from (Diacetoxyiodo)benzene

	$[\alpha]_D{}^a$ (deg)	
concn (w/v) (%)	L-tartrate polymer	D-tartrate polymer
0.50	+22	−21
1.00	+27	−30
2.00	+34	−36
3.00	+40	−41
5.00	+45	−45

^{a} Determined in CHCl$_3$ at 28–29 °C.

Table II. Asymmetric Oxidation of Methyl *p*-Tolyl Sulfide with Iodine(III) Dibenzoyl Tartrate Polymers

	methyl *p*-tolyl sulfoxide			
polymer, source	$[\alpha]_D{}^a$ (deg)	config	ee % (rotation)	ee % (NMR)
L-Tartrate, PhI(OAc)$_2$	−35	S	19	20
D-Tartrate, PhI(OAc)$_2$	+40	R	22	21
L-Tartrate, PhIO	−54	S	30	30

^{a} Determined in CHCl$_3$ at 27 °C. ^{b} Determined in CDCl$_3$ with (S)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol.

for a polymeric material. The methine region of the proton spectrum consists of several closely spaced resonances of unequal intensity and not the sharp singlet anticipated for highly symmetrical species such as **3** and **6**. The spectrum is compared in Figure 1 with that of dibenzoyl-L-tartaric anhydride selected as a model compound with a symmetrical cyclic structure.

Similar treatment of (diacetoxyiodo)benzene with dibenzoyl-D-tartaric acid gave an iodine(III) tartrate with a nearly identical ^{1}H NMR spectrum. It is interesting to note that the material derived from the L-acid is dextrorotatory while that from the D-acid is levorotatory and that the specific rotations (Table I) depend upon sample concentrations.

When iodosobenzene was mixed with dibenzoyl-L-tartaric anhydride in dry acetone, the conditions employed by Imamoto and Koto for the in situ oxidations of sulfides,[2b] a 1:1 iodine(III) tartrate polymer (MW = 6009) was likewise obtained having an ^{1}H NMR spectrum very similar to those of the polymers made from (diacetoxyiodo)benzene.

The ability of the iodine(III) tartrate polymers to effect the asymmetric oxidation of *p*-tolyl methyl sulfide in acetone was examined (Table II). The degree of chiral induction achieved in these studies was comparable to that reported (i.e., 36%) for the in situ oxidation of *p*-tolyl methyl sulfide with 1/L-**2** (R = Ph).[2b] One of the byproducts of polymer reduction was identified as dibenzoyl tartaric anhydride.

We have not yet obtained molecular weight distributions for the iodine(III) tartrates. However, it seems likely that they are comprised of oligomers of varying molecular weights. Indeed, the reaction of iodosobenzene with L-**2** (R = Ph) in acetone gave a second material of low MW (1328) and low iodine content still capable of effecting the asymmetric oxidation (23% ee) of *p*-tolyl methyl sulfide. Furthermore, various reprecipitation experiments gave materials with significantly different PMR spectra. Thus far, we have not detected any cyclic iodine(III) tartrates although we cannot rule out their possible existence as one species among others in the solution phase.

Finally, we caution that acetone may not always be the solvent of choice for either in situ oxidations of sulfides with the system 1/**2** or with the preisolated iodine(III) tartrate polymers. When the dibenzoyl-L-tartrate polymer was heated under reflux in acetone, it was degraded by the

solvent and a 1:3 mixture of the mono- and bisacetonate esters **8** and **9** was obtained. These compounds are easily distinguished by ^{1}H NMR analysis since the methine hydrogens of **8** appear as an AB multiplet while those of **9** give rise to a sharp singlet.
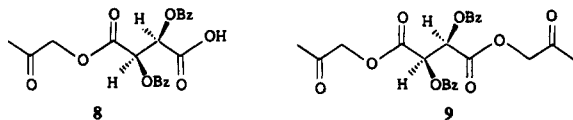
Preliminary investigations in our laboratory of the reactions of **1** with (Z)-L-glutamic acid and **4** (R = Me) with (+)-camphoric acid indicate that the production of iodine(III) carboxylate polymers may be a general phenomenon. This is consistent with a previously reported study of the treatment of succinic anhydride with **1**, adipic acid with **4** (R = Me), and silver sebacate with (dichloroiodo)benzene.[5] It was concluded that hypervalent iodine polymers were produced although little structural evidence was given and molecular weights were not reported.[5] An earlier report[6] of the preparation of a cyclic iodine(III) succinate from succinic acid and **1** in acetone or by the treatment of (dichloroiodo)benzene with silver succinate bears reinvestigation in light of these studies, especially since the assigned structure was based only on elemental analysis.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz respectively. Elemental analyses were performed by Midwest Microlab, LTD (Indianapolis, IN). Molecular weights (vapor pressure osmometry, CH_2Cl_2) were determined by Galbraith Laboratories, Inc. (Knoxville, TN). Melting points are uncorrected. (Diacetoxyiodo)benzene[7] and iodosobenzene[8] were prepared by standard literature methods. (+)-Dibenzoyl-D- and (−)-dibenzoyl-L-tartaric acids were purchased. (+)-Dibenzoyl-L-tartaric anhydride was prepared by the treatment of (−)-dibenzoyl-L-tartaric acid with acetic anhydride: mp 192–195 °C (lit.[9] mp 173 °C); $[\alpha]_D$ +196° (c 1.07, CHCl$_3$); FT-IR (Nujol) 1709 (ester C=O), 1740, 1825 cm^{-1} (anhydride C=O); ^{1}H NMR (CDCl$_3$) δ 5.97 (s, 2 H), 7.45–7.53 (complex d of d, 4 H), 7.61–7.69 (complex d of d, 2 H), 8.04–8.10 (complex d of d, 4 H).

Preparation of Dibenzoyl-L- and -D-tartrate Polymers from (Diacetoxyiodo)benzene. A mixture of dibenzoyl-L-tartaric acid (3.58 g, 10.0 mmol) and (diacetoxyiodo)benzene (3.22 g, 10.0 mmol) in CH_2Cl_2 (50 mL) was stirred for 23 min at room temperature. The resulting solution was washed with H_2O (3 × 20 mL), dried (MgSO$_4$), and concentrated to a "glassy" solid. The solid was pulverized (mortar and pestle), triturated with hexanes, and dried in vacuo (Kugelrohr, 2.5 h, 60–70 °C) to give the L-tartrate polymer as a white powder: yield, 4.57 g (82%); mp 135–153 °C; FT-IR (Nujol) 1724 cm^{-1} (broad C = O); ^{1}H NMR (CDCl$_3$) δ 1.92 and 2.02 (weak singlets, 0.3 H, end groups?), 2.2–2.8 (broad "s", 0.9 H, H_2O), 5.40–5.94 (complex m, 2 H, methine hydrogens), 6.70–8.06 (complex m, 15 H); ^{13}C NMR (CDCl$_3$) δ 70.8 (methine C), 122.9 (quat C), 128.5, 128.9, 130.1, 130.9, 131.95 (quat C), 133.6, 134.2, 134.7, 165.2 (C=O), 169.65 (C=O); MW (three-point determination) 5870. Anal. Calcd for $C_{24}H_{17}O_8I$ (monomer unit): C, 51.45; H, 3.06; I, 22.65. Found: C, 50.81; H, 2.99; I, 22.61.

The D-tartrate polymer was prepared similarly from dibenzoyl-D-tartaric acid and isolated as a white powder: yield 4.05 g (72%); mp 131–163 °C; FT-IR (Nujol) 1721 cm^{-1} (broad C=O); ^{1}H NMR (CDCl$_3$) δ 1.92 and 1.99 weak singlets, 0.3 H), 2.8–3.8

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(weak *broad* resonance, 0.44 H), 5.40–5.90 (complex m, 2 H), 6.70–8.06 (complex m, 15 H); ^{13}C NMR (CDCl$_3$) δ 70.85, 122.7, 128.3, 128.6, 129.9, 130.7, 131.7, 133.4, 134.0, 134.45, 164.9 (C=O), 169.3 (C=O).

Preparation of Dibenzoyl-L-tartrate Polymer from Iodosobenzene. A mixture of dibenzoyl-L-tartaric anhydride (3.40 g, 10.0 mmol) and iodosobenzene (2.20 g, 10.0 mmol) in *dry* acetone (40 mL) was stirred mechanically for 35 min at room temperature. The insoluble solid that remained was isolated by filtration, washed with dry acetone, and dried under reduced pressure: yield 3.21 g (57%); mp 125–164 °C. This material (1.01 g) was pulverized, washed with hexanes and Et$_2$O, and dried in vacuo (Kugelrohr, 2.5 h, 60–70 °C) to give the L-tartrate polymer (0.77 g) as a white solid: mp 139–160 °C; FT-IR (Nujol) 1721 cm^{-1} (broad, C=O); ^{1}H NMR (CDCl$_3$) δ 1.21 (s, 0.1 H), 2.14 ("d", 0.1 H) and 2.60 (s, 0.06 H) (impurities or end groups derived from Me$_2$C = O?) 2.8–3.6 (broad peak, 0.8 H, H_2O?), 5.47–5.85 (complex m, 2 H, methine H), 6.72–8.04 (complex m, 15 H); ^{13}C NMR (CDCl$_3$) δ 70.9, 122.8, 128.2, 128.7, 129.95, 130.7, 131.8, 133.5, 133.7, 134.1, 165.0 (C=O), 169.4 (C=O); MW (three point determination) 6009. Anal. Calcd for $C_{24}H_{17}O_8I$ (monomer unit): C, 51.45; H, 3.06; I, 22.65. Found: C, 50.86; H, 3.17; I, 21.23.

The acetone filtrate was concentrated to an oil which, when kept under reduced pressure, solidified to a "glass": yield 1.32 g; mp 64–85 °C. A solution of this material (310 mg) in a minimum quantity of CH_2Cl_2 was added with stirring to hexanes (50 mL) at room temperature. The tan solid that separated (140 mg) was isolated, washed with hexanes, and dried in vacuo (Kugelrohr, 1.5 h, 60–70 °C); mp 80–135 °C; ^{1}H NMR (CDCl$_3$) δ 4.0–4.9 (broad s), 5.57–5.62 (m), 5.75–5.82 (complex m), 5.94–5.99 (m), 6.85–7.10 (arom. m), 7.30–8.15 (arom m) (relative areas 14.8:1.0:4.0:4.4:4.2:47.6—structure unknown); MW (single point determination) 1328. Found: C, 55.63; H, 3.67; I, 9.18.

Reaction of the Dibenzoyl-L-tartrate Polymer (from PhI(OAc)$_2$) with Acetone. A mixture of freshly prepared dibenzoyl-L-tartrate polymer (from 10 mmol each of (diacetoxyiodo)benzene and dibenzoyl L-tartaric acid) in reagent-grade acetone (50 mL) was stirred and heated under reflux for 24 h. The resulting solution was concentrated to an oil which, upon treatment with hexanes (2 × 20 mL) and Me$_2$CHOH (10 mL), gave a solid. The solid was taken up in benzene, and the solution was concentrated to remove residual benzene. The white solid thus obtained was dried in vacuo and identified as a 1:3 molar mixture of the mono- and bis-acetonate esters of dibenzoyl-L-tartaric acid (i.e., **8** and **9**): yield 1.05 g; ^{1}H NMR (CDCl$_3$) δ 2.04 and 2.05 (closely spaced singlets, 9 H), 2.9–3.4 (broad s, –COOH, H_2O), 4.58–4.81 and 4.60–4.84 (overlapping AB m's, 6 H), 6.06–6.11 (AB m, methine H's of **8**) and 6.17 (s, methine H's of **9**) (combined int., 2 H; relative areas 1:3), 7.41–7.49 (complex m, 8 H), 7.55–7.63 (complex m, 4 H), 8.05–8.15 (complex m, 8 H).

Recrystallization of 0.23 g from Me$_2$CHOH (5 mL) and treatment of the recrystallized material with benzene and CH_2Cl_2 as described above gave 0.082 g of the *bis*-acetonate: white solid; mp 147–149 °C; $[\alpha]^{28}_D$ −53° (c 1.865, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ 1.53–1.66 (broad s, 1 H, H_2O), 2.05 (s, 6 H), 4.60–4.84 (AB m, 4 H), 6.16 (s, 2 H), 7.42–7.49 (t, 4 H), 7.56–7.63 (m, 2 H), 8.09–8.15 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ 25.6, 69.1, 71.1, 128.8, 128.7, 130.35, 133.9, 165.7 (C=O), 200.2 (C=O). Anal. Calcd for $C_{24}H_{22}O_{10}·^1/_2H_2O$: C, 60.12; H, 4.84. Found: C, 60.50; H, 4.65.

Asymmetric Oxidation of Methyl p-Tolyl Sulfide with the Dibenzoyl-L-tartrate Polymer Derived from Iodosobenzene. A mixture of methyl p-tolyl sulfide (0.28 g, 2.0 mmol) and the L-tartrate polymer (2.80 g, ca. 4 mmol of monomer units) in dry acetone (35 mL) was stirred for 2.5 h at room temperature. The unreacted polymer and dibenzoyl-L-tartaric anhydride (product of polymer reduction, identified by ^{1}H NMR analysis), both insoluble in acetone, were then removed by filtration. The filtrate was concentrated to an oil. Flash column chromatography of the oil on silica gel, first with CH_2Cl_2 to remove PhI and then with acetone/CH_2Cl_2 (5/95–15/85) gave methyl p-tolyl sulfoxide as a viscous oil which solidified upon drying (dry ice, acetone bath): yield 0.25 g (81%); mp 35–36 °C (lit.[10] mp 42–43 °C, 50–54 °C

(10) *Dictionary of Organic Compounds*, 5th ed.; Chapman and Hall: London, New York, 1989; 7th suppl, p 299.

(racemic sulfoxide); mp 74.5 °C (pure S enantiomer); $[\alpha]^{27}_D = -54°$ (c 1.98, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ 2.40 (s, 3 H), 2.69 (s, 3 H), 7.28–7.55 (AA'BB'm, 4 H); ^{1}H NMR analysis with the chiral shift reagent, (S)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol indicated the sulfoxide to be enriched in the S enantiomer (i.e., 30% ee).

Preparation of 1-Chloroalkyl Hydroperoxides by the Addition of Hydrogen Chloride to Carbonyl Oxides

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Carbonyl oxides, formed as intermediates in ozonolysis, are well-known to react with "participating solvents" such as water, alcohols, hydrogen peroxide, alkyl hydroperoxides, carboxylic acids, ammonia, amines, and hydrogen cyanide to yield α-heteroatom-substituted hydroperoxides.[1] We have previously made 1,1-dichloroalkyl hydroperoxides by the addition of anhydrous hydrogen chloride to α-chlorinated carbonyl oxides.[2,3] We report here the first examples of 1-chloroalkyl hydroperoxides, prepared by the analogous addition of HCl to carbonyl oxides that do not already have an α-chlorine atom.

The lack of selectivity in the cleavage of the primary ozonide from unsymmetrical olefins and the formation of a highly reactive aldehyde or ketone alongside the desired carbonyl oxide would be disadvantageous in attempts to obtain the title compounds selectively. We prepared the 1,1-dichloroalkyl hydroperoxides from symmetrical double-bond-dichlorinated olefins; the byproduct, an acid chloride, reacted slowly enough with the hydroperoxides that it could be stripped out of the mixture after the reaction. In general it is possible to obtain carbonyl oxides selectively from unsymmetrical olefins when one double-bond carbon has an electron-withdrawing substituent such as a halogen or an alkoxy group (eq 1). If there is a

$$R^1R^2C{=}CClR^3 + O_3 \rightarrow \underset{1}{R^1R^2C^+OO^-} + R^3COCl \quad (1)$$

chlorine atom on C-1 of a terminal olefin, there is the additional advantage that the acid chloride is formyl chloride, which rapidly decomposes into carbon monoxide and hydrogen chloride. This is the strategy that we have used in the present work to examine the reaction of HCl with a number of carbonyl oxides, most of which have no electronegative substituent in the α position.

In Tables I and II we show the olefins that we have subjected to ozonolysis in methyl formate in the presence of HCl and the carbonyl oxides presumed to be intermediates in the reactions. Table I has the carbonyl oxides that were found to add HCl, and Table II those that did not do so. Carbonyl oxides **1a–e** are clearly formed under these conditions and readily add HCl (eq 2).

$$\underset{2}{1 + HCl \rightarrow R^1R^2CClOOH} \quad (2)$$
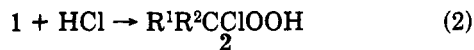
Hydroperoxide **2b** proved to be stable enough to be distilled and to give fair elemental analyses. This stability

is comparable with that of the analogous α-methoxy hydroperoxide ClCH$_2$CH(OCH$_3$)OOH, which has been described by others.[4] The β-brominated hydroperoxide **2c** was not distilled, but it was similarly stable. The methoxy and acetoxy analogues **2d** and **2e** were more labile; thus, although some NMR samples of **2d** were unchanged after 1 h at 35 °C, others decomposed with the evolution of considerable heat when allowed to warm above 0 °C.

The lower part of Table I shows some chlorinated hydroperoxides that have previously been reported (**2g–i**) and one (**2f**) made in this study, in all of which the carbonyl oxide already has an α-chlorine substituent.

The yield of trichloromethyl hydroperoxide (**2g**) is unknown; since the ozonolysis of C$_2$Cl$_4$ is very slow, the alternative preparation of **2g** by light-induced oxidation of chloroform is preferable.[5] Nevertheless, the known ester CCl$_3$OOCOCH$_3$ was prepared in detectible amounts by prolonged treatment of C$_2$Cl$_4$ with ozone in the presence of HCl and acetyl chloride; it was identified by comparison with authentic material.[5]

Except for the simplest carbonyl oxide, **1a**, all those so far found to add HCl have electron-withdrawing groups in either the α or the β position. That this is not a sufficient criterion, however, is attested by the failure of carbonyl oxide **1m** to produce C$_6$H$_5$CCl$_2$OOH. It is uncertain just how the failure occurs in this example: in the formation of **1m**, in the addition of HCl, or in some instability of the hydroperoxide once formed.

In some of the other cases, the course of the reaction was clearer. Thus, ozonolysis of 1-methoxycyclopentene gave the same products (polymers) with HCl as without.[6] This appeared also to be the case for β-bromostyrene (benzaldehyde and diphenyltetroxane as the main products). Ozonolysis of two olefins that are expected to yield the carbonyl oxide (CH$_3$)$_2$C$^+$OO$^-$ (**1k**) failed to give any evidence for the formation of (CH$_3$)$_2$CClOOH (**2k**). Instead, the major product was acetone peroxide (the cyclic dimer or trimer of **1k**). In this context it must be mentioned that other workers, carrying out the ozonolysis of 2-methyl-3-chloro-2-butene on the surface of polyethylene, found evidence from NMR spectra and product studies for the formation of the acetate ester of hydroperoxide **2k**.[7] It was suggested that the ester arose by rearrangement of the normal ozonide; in contrast to the esters of the 1,1-dichloroalkyl hydroperoxides we have previously described, however, it was both thermally and chemically unstable, reacting spontaneously with either water or silica gel. If hydroperoxide **2k** is equally sensitive, it may well not have survived our reaction conditions.

The only α-chlorinated hydroperoxides that we have been able to acetylate with acetyl chloride are **2g–i**, and all of the esters have been described previously.[2,3,5,8] The failure of the others to yield acetates cannot in all cases be due to instability of the hydroperoxides: **2b**, for example, is stable for days in acetyl chloride at 4 °C. This resistance toward acetylation with acetyl chloride is particularly surprising in light of the fact that 1,1-dichloroethyl hydroperoxide was readily acetylated in good yield when allowed to stand in acetyl chloride.[3]

These results led us to question the assigned structures, but the spectroscopic evidence for them is strong (the

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