Iodinanes with Iodine(III)-Bound Homochiral Alkoxy Ligands: Preparation and Utility for the Synthesis of Alkoxysulfonium Salts and Chiral Sulfoxides

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Iodinanes, $ArIL_1L_2$, with one aryl and two heteroatom ligands are versatile reagents for the oxidation and functionalization of organic compounds.¹ However, despite their potential utility for asymmetric syntheses, iodinanes of any kind with iodine(III)-bound homochiral ligands are rare.²⁻⁴ We now report the preparation of the first iodinanes with homochiral alkoxy ligands and a study of their reactions with sulfides to give chiral alkoxysulfonium salts. The alkoxysulfonium salts can be employed, in turn, as precursors to chiral sulfoxides of high optical purity.

Methoxyiodinanes,⁵ primary alkoxyiodinanes,^{5a,6} and tert-alkoxyiodinanes⁷ are known, but sec-alkoxyiodinanes have not been reported. We now find that the menthyloxy ligand can be appended to iodine(III) via a ligand-exchange reaction. [[(+)-Menthyloxy](tosyloxy)iodo]benzene [1a, (+)-MnTIB] was prepared almost quantitatively by the concentration of solutions of [methoxy(tosyloxy)iodo]benzene (MTIB)⁸ and equimolar (1S,2R,5S)-(+)-menthol in dichloromethane under aspirator vacuum, eq 1. [[(-)-Menthyloxy](tosyloxy)iodo]benzene (1b,



(-)-MnTIB) was made in the same way from MTIB and (1R, 2S, 5R)-(-)-menthol.⁹ The (menthyloxy)iodinanes thus obtained are moisture-sensitive powders of about 95% purity (i.e., contaminated with unreacted MTIB) and were generally prepared as needed and used under nitrogen without further purification. Analytically pure (+)-MnTIB was obtained by recrystallization of the crude product from liquified (+)-menthol (spiked with CH₂Cl₂) with hexanes and appropriately characterized.¹⁰

When sulfides were mixed with either (+)- or (-)-MnTIB in

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 (10) The structure of (+)-MnTIB was confirmed by NMR (300 MHz, ¹H, ¹³C, 2D) and elemental analysis (C, H, I values within ±0.26% of calculated values). Iodometric tritrations of four samples from a batch of crude (+)-MnTIB gave an average MW of 536.6 [calcd MW, 530.5 (>98% "purity")].

Table I. (Menthyloxy)sulfonium Tosylates 2 from Reactions of Sulfides with (Menthyloxy)iodinanes^a

		2							
iodinane		R ₁	R ₂	yield, ^b %	$\begin{array}{c} [\alpha]_{D} \\ (CH_{2}Cl_{2}), \\ deg \end{array}$	de,' %			
(+)-MnTIB ^d	(+)-2a ^g	p-tolyl	Me	92	+85	16			
(+)-MnTIB ^e	(+)- 2b	Me ₃ C	Me	87	+52	57			
(-)-MnTIB ^{e,d}	(-)-2b ^g	Me ₃ C	Me	86, 89	-54, -55	50, 57			
(-)-MnTIB ^d	(-)-2cg	PhCH ₂	Me	98	-40	4			
(+)-MnTIB ^f	(+)-2d ^g	PhCH ₂	PhCH ₂	91					

^a For unsymmetrical sulfides, reaction mixtures were kept for ca. 1 min at -78 °C (dry ice) and allowed to warm to room temperature. With dibenzyl sulfide, the initial temperature was ca. 4 °C. ^bThe sulfonium salts were isolated after solvent removal and trituration of the residual materials with hexanes (removes Ph]). Yields of (+)-2a, (+)-2b, and (-)-2b corrected for MeOS⁺R₁R₂, TsO⁻ (ca. 3-4 mol %)¹¹ and H₂O content. ^{c1}H NMR (300 MHz) analysis. ^dOn 10-mmol scale. ^cOn a 5-mmol scale. ^fOn a 29.8mmol scale. 8 The elemental compositions (C, H) of analytical samples of (+)-2a and (+)-2d were within $\pm 0.3\%$ of the calculated values while those of (-)-2b and (+)-2c (made from (+)-MnTIB) were consistent with $1/2^{-1}$ molar hydrates: (-)-2b-1/₂H₂O [$\Delta C = -0.10\%$, +0.55%; $\Delta H = -0.16\%$, -0.26% (two samples)]; (+)-2c-1/₂H₂O [$\Delta C = -0.23\%$, -0.46%; $\Delta H =$ -0.17%, -0.37% (second analysis after heating for 10 min at 100 °C).

Table II. Optically Active Sulfoxides from the Hydrolysis of (Menthyloxy)sulfonium Tosylates

	$R_1R_2S=O$						
sulfonium tosylate (de, %) ^a	R ₁	R ₂	$[\alpha]_{D}$ (CHCl ₃), deg	ee, ^b % (configurn)	yield,' %		
(+)-2a (>99)	p-tolyl	Me	-183	$\sim 99 (S)$	88		
(+)-2b (57)	Me ₃ C	Me	+4.9	56 (S)	71		
(-)- 2b (51)	Me ₃ C	Me	-4.9	49 (<i>R</i>)	69		
(−)- 2b (95) ^d	Me ₃ C	Me	-8.1	81 (<i>R</i>)	69		
$(-)-2c \ (>99)^d$	PhCH ₂	Me	+52.7	94.5 (R)	94		

^{a1}H NMR (300 MHz) analysis (CDCl₃). ^{b1}H NMR (300 MHz) analysis (CDCl₃) with (S)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol. ^c Based on isolation and corrected for H₂O content (NMR analysis). ^d Isolated from diastereomeric mixtures with efficiencies of about 57% [(-)-2b] and 58% [(-)-2c].

dichloromethane, (menthyloxy)sulfonium tosylates 2 were obtained (eq 2, Table I).¹¹ For example, the treatment of methyl *p*-tolyl



sulfide with (+)-MnTIB gave [(+)-menthyloxy]methyl-p-tolylsulfonium tosylate [(+)-2a] in 92% yield as a mixture (ca. 16% de) of diastereomers. The major diastereomer was separated with 49% efficiency by recrystallization of the mixture from CH₂Cl₂/Et₂O and hydrolyzed in 1 N NaOH to optically pure (S)-(-)-methyl p-tolyl sulfoxide (88% yield, ~99% ee), eq 2. Since (+)-menthol and not (+)-isomenthol is also produced during the hydrolysis of (+)-2a, it seems likely that the major diastereomer of (+)-2a is of the R configuration at sulfur.

Regulation of the configuration at sulfur can be achieved, at least in some cases, by an appropriate choice of iodine(III) reagent. When tert-butyl methyl sulfide was treated with (+)-MnTIB, a 3.7:1.0 mixture (57% de) of the (menthyloxy)sulfonium diastereomers (+)-2b was obtained. Hydrolysis of the mixture and chromatography of the crude product on silica gel gave enantiomerically enriched (S)-(+)-tert-butyl methyl sulfoxide (56%)

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ee). With (-)-MnTIB as the starting reagent, (R)-(-)-tert-butyl methyl sulfoxide (49% ee) was ultimately obtained.

The degree of asymmetric induction at sulfur in 2 appears to be largely regulated by steric effects and, in the case of benzyl methyl sulfide, was almost nonexistent. However, even when induction is low, the separation of the *major* diastereomer from CH₂Cl₂/Et₂O appears to be general, and sulfoxides of high optical purity can be prepared (Table II). We note that Johnson and his co-workers previously synthesized [(-)-menthyloxy]benzylp-tolysulfonium fluoroborate by the sequential treatment of benzyl p-tolyl sulfide with 1-chlorobenzotriazole, (-)-menthol, and silver fluoroborate.12 Recrystallization of the sulfonium salt from benzene/Et₂O and hydrolysis gave (-)-benzyl *p*-tolyl sulfoxide with an optical purity of 87%.¹²

The method described herein for the synthesis of (menthyloxy)sulfonium tosylates has been applied to other chiral alcohols. For example, ligand exchange of MTIB with (1R)-endo-(+)fenchyl alcohol, (1S)-endo-(-)-borneol, and (-)-cholesterol followed by the addition of methyl p-tolyl sulfide gave the alkoxysulfonium tosylates 3 (89%), 4 (93%), and 5 (13%), all with low diastereoselectivities (0.6-5% de).13



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(13) The elemental analyses (C, H) of 3 and 4 are consistent with $1/2^{-1}$ molar hydrates [4 slightly off (+0.49%) on carbon] while the elemental composition of 5 indicates that it is the unhydrated sulfonium salt.

Gas-Phase Reactivity of Metal Alloy Clusters

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Study of the production and reactivity of gas-phase mixed-metal clusters in a well-characterized flow reactor offers a unique opportunity to investigate the complex and interesting properties that often accompany the corresponding heterogeneous alloys. Determining the reactivity trends of small metal alloy particles provides a promising way not only of investigating the evolution of bulk behavior but also of elucidating the electronic and geometric makeup of metallic entities of finite dimensions. These latter aspects are currently the focus of intense experimental and theoretical activity.

The jellium model,¹ which treats the nuclei (and core electrons) of the constituent atoms as smeared out in a specified potential



Figure 1. Reaction of metal clusters with O_2 : (a) 0.0 sccm of O_2 , (b) 30.6 sccm of O₂, and (c) 60.0 sccm of O₂. Intensity scales are arbitrary.

well and allows all of the valence electrons of the cluster to fill electronic shells (as in the hydrogen atom), has been a useful model² in accounting for special abundances of small alkali clusters in terms of their electronic structure. In addition, recent results³ on the thermal reactivity (etching action) of bare aluminum cluster anions with oxygen showed Al13 and Al23 as products, species that are also predicted shell closinings of the spherical jellium model.¹ However, the jellium model has failed to account for the trends in aluminum cluster polarizabilities⁴ and in some of their reactivity behavior.⁵ Moreover, magic numbers have been seen for cobalt clusters pointing to icosahedral structures,⁶ but none have been seen that can be attributed to the electronic structure of transition-metal clusters, raising questions about the general validity of the model.

One particularly useful way of investigating the importance of the electronic contribution to stability is by examining the influence of substituting one or more atoms in the cluster with The present report deals with the one of differing valence.⁷ reaction (etching action) of oxygen on aluminum clusters containing niobium and/or vanadium. Niobium and vanadium have five valence electrons each (4d⁴5s¹ and 3d³4s², respectively), and aluminum has three $(3s^23p^1)$. Determination of the trends in reactivity with cluster size, the produced magic number alloy clusters, and comparison of the results with the bare aluminum results sheds light on the jellium model, the importance of electronic effects, and the free electrons involved.

The details of the apparatus have been reported previously.⁸ The metal clusters are produced in a laser vaporization source

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