J. Am. Chem. Soc. 1990, 112, 5672–5673

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

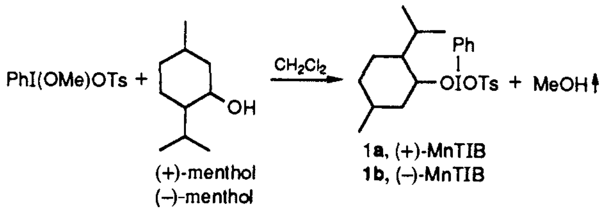
Dale G. Ray III and Gerald F. Koser*

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

Received April 5, 1990

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*-alkoxyiodinanes[7] 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 (1*S*,2*R*,5*S*)-(+)-menthol in dichloromethane under aspirator vacuum, eq 1. [[(−)-Menthyloxy](tosyloxy)iodo]benzene (**1b**, (−)-MnTIB) was made in the same way from MTIB and (1*R*,2*S*,5*R*)-(−)-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 CH_2Cl_2) with hexanes and appropriately characterized.[10]



(1)

When sulfides were mixed with either (+)- or (−)-MnTIB in 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 CH_2Cl_2/Et_2O 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.

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

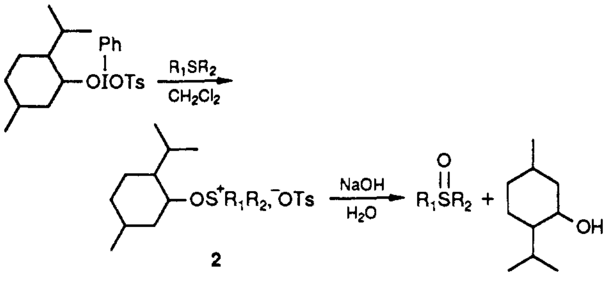
	2					
iodinane		R_1	R_2	yield,[b] %	$[\alpha]_D$ (CH_2Cl_2), deg	de,[c] %
(+)-MnTIB[d]	(+)-**2a**[g]	*p*-tolyl	Me	92	+85	16
(+)-MnTIB[e]	(+)-**2b**	Me_3C	Me	87	+52	57
(−)-MnTIB[e,d]	(−)-**2b**[g]	Me_3C	Me	86, 89	−54, −55	50, 57
(−)-MnTIB[d]	(−)-**2c**[g]	$PhCH_2$	Me	98	−40	4
(+)-MnTIB[f]	(+)-**2d**[g]	$PhCH_2$	$PhCH_2$	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. [b] The sulfonium salts were isolated after solvent removal and trituration of the residual materials with hexanes (removes PhI). Yields of (+)-**2a**, (+)-**2b**, and (−)-**2b** corrected for $MeOS^+R_1R_2$, TsO^- (ca. 3–4 mol %)[11] and H_2O content. [c] ^1H NMR (300 MHz) analysis. [d] On 10-mmol scale. [e] On a 5-mmol scale. [f] On a 29.8-mmol scale. [g] The elemental compositions (C, H) of analytical samples of (+)-**2a** and (+)-**2d** were within ±0.3% of the calculated values while those of (−)-**2b** and (+)-**2c** (made from (+)-MnTIB) were consistent with $^1/_2$-molar hydrates: (−)-**2b**·$^1/_2H_2O$ [ΔC = −0.10%, +0.55%; ΔH = −0.16%, −0.26% (two samples)]; (+)-**2c**·$^1/_2H_2O$ [ΔC = −0.23%, −0.46%; ΔH = −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,[c] %
(+)-**2a** (>99)	*p*-tolyl	Me	−183	~99 (*S*)	88
(+)-**2b** (57)	Me_3C	Me	+4.9	56 (*S*)	71
(−)-**2b** (51)	Me_3C	Me	−4.9	49 (*R*)	69
(−)-**2b** (95)[d]	Me_3C	Me	−8.1	81 (*R*)	69
(−)-**2c** (>99)[d]	$PhCH_2$	Me	+52.7	94.5 (*R*)	94

[a] ^1H NMR (300 MHz) analysis ($CDCl_3$). [b] ^1H NMR (300 MHz) analysis ($CDCl_3$) with (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol. [c] Based on isolation and corrected for H_2O content (NMR analysis). [d] Isolated from diastereomeric mixtures with efficiencies of about 57% [(−)-**2b**] and 58% [(−)-**2c**].



2

(2)

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%

---

[1] (a) Banks, D. F. *Chem. Rev.* **1966**, *66*, 243. (b) Varvoglis, A. *Chem. Soc. Rev.* **1981**, *10*, 377. (c) Koser, G. F. Hypervalent Halogen Compounds. In *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, **1983**; Chapter 18. (d) Varvoglis, A. *Synthesis* **1984**, 709. (e) Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244.

[2] 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.

[3] Imamoto, T.; Koto, H. *Chem. Lett.* **1986**, 967.

[4] Hatzigrigoriou, E.; Varvoglis, A.; Bakola-Christianopoulou, M. *J. Org. Chem.* **1990**, *55*, 315.

[5] For example, see: (a) Baker, G. P.; Mann, F. G.; Sheppard, N.; Tetlow, A. J. *J. Chem. Soc.* **1965**, 3721. (b) Leffler, J. E.; Jaffe, H. *J. Org. Chem.* **1973**, *38*, 2719. (c) Balthazor, T. M.; Miles, J. A.; Stults, B. R. *J. Org. Chem.* **1978**, *43*, 4538. (d) Schardt, B. C.; Hill, C. L. *Inorg. Chem.* **1983**, *22*, 1563.

[6] Etter, M. C. *J. Solid State Chem.* **1976**, *16*, 399.

[7] (a) Tanner, D. D.; Gidley, G. C. *Can. J. Chem.* **1968**, *46*, 3537. (b) Amey, R. L.; Martin, J. C. *J. Org. Chem.* **1979**, *44*, 1779. (c) Nguyen, T. T.; Amey, R. L.; Martin, J. C. *J. Org. Chem.* **1982**, *47*, 1024. (d) Nguyen, T. T.; Wilson, S. R.; Martin, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3803.

[8] Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1980**, *45*, 4988.

[9] The use of menthol as a chiral alkoxy ligand for exchange with MTIB was suggested to us by Professor William G. Kofron (The University of Akron).

[10] The structure of (+)-MnTIB was confirmed by NMR (300 MHz, ^1H, ^{13}C, 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")].

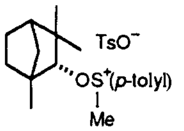
[11] The synthesis of methoxysulfonium tosylates from sulfides with MTIB has been reported: Koser, G. F.; Kokil, P. B.; Shah, M. *Tetrahedron Lett.* **1987**, *28*, 5431.

0002-7863/90/1512-5672$02.50/0

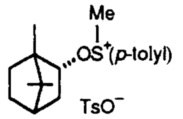
ee). With (−)-MnTIB as the starting reagent, (*R*)-(−)-*tert*-butyl methyl sulfoxide (49% ee) was ultimately obtained.

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 $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ 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]benzyl-*p*-tolylsulfonium 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/Et_2O and hydrolysis gave (−)-benzyl *p*-tolyl sulfoxide with an optical purity of 87%.[12]

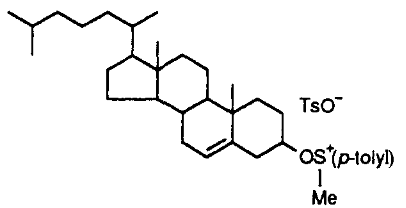
The method described herein for the synthesis of (menthyloxy)sulfonium tosylates has been applied to other chiral alcohols. For example, ligand exchange of MTIB with (1*R*)-*endo*-(+)-fenchyl alcohol, (1*S*)-*endo*-(−)-borneol, and (−)-cholesterol followed by the addition of methyl *p*-tolyl sulfide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



3



4



5

---

[12] Johnson, C. R.; Bacon, C. C.; Kingsbury, W. D. *Tetrahedron Lett.* **1972**, 501.

[13] The elemental analyses (C, H) of **3** and **4** are consistent with $^1/_2$-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

A. C. Harms, R. E. Leuchtner, S. W. Sigsworth, and
A. W. Castleman, Jr.*

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

Received March 26, 1990
Revised Manuscript Received May 21, 1990

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.

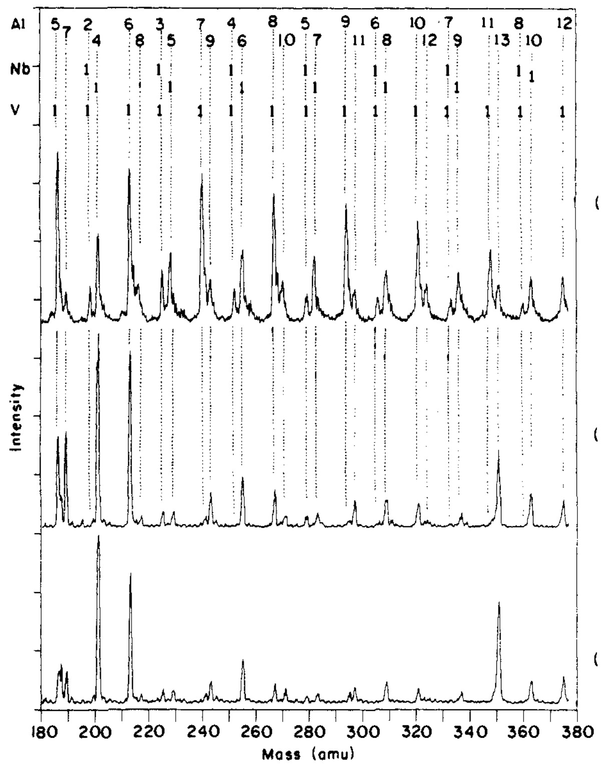


Figure 1. Reaction of metal clusters with O_2: (a) 0.0 sccm of O_2, (b) 30.6 sccm of O_2, and (c) 60.0 sccm of O_2. Intensity scales are arbitrary.

The jellium model,[1] which treats the nuclei (and core electrons) of the constituent atoms as smeared out in a specified potential well and allows all of the valence electrons of the cluster to fill electronic shells (as in the hydrogen atom), has been a useful model[2] in accounting for special abundances of small alkali clusters in terms of their electronic structure. In addition, recent results[3] on the thermal reactivity (etching action) of bare aluminum cluster anions with oxygen showed Al_{13}^- and Al_{23}^- as products, species that are also predicted shell closings of the spherical jellium model.[1] However, the jellium model has failed to account for the trends in aluminum cluster polarizabilities[4] 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 one of differing valence.[7] The present report deals with the reaction (etching action) of oxygen on aluminum clusters containing niobium and/or vanadium. Niobium and vanadium have five valence electrons each ($4d^45s^1$ and $3d^34s^2$, 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

---

[1] (a) Knight, W. D.; Clemenger, K.; de Heer, W.; Saunders, W.; Chou, M.; Cohen, M. *Phys. Rev. Lett.* **1984**, *52*, 2141. (b) Chou, M.; Cleland, A.; Cohen, M. *Solid State Commun.* **1984**, *52*, 645. (c) Chou, M.; Cohen, M. *Phys. Lett. A* **1986**, *113*, 420.

[2] Saito, Y.; Minami, K.; Ishida, T.; Noda, T. *Z. Phys. D.* **1989**, *11*, 87.

[3] Leuchtner, R. E.; Harms, A. C.; Castleman, A. W.; Jr. *J. Chem. Phys.* **1989**, *91*, 2753.

[4] de Heer, W.; Milani, P.; Châtelain, A. *Phys. Rev. Lett.* **1989**, *63*, 2834.

[5] (a) Leuchtner, R. E.; Harms, A. C.; Castleman, A. W., Jr. Aluminum Cluster Reactions, submitted. (b) Cox, D. M.; Trevor, D. J.; Whetten, R. L.; Kaldor, A. *J. Phys. Chem.* **1988**, *92*, 421.

[6] Klots, T. D.; Winter, B. J.; Parks, E. K.; Riley, S. J. *J. Chem. Phys.* **1990**, *92*, 2110.

[7] Kappes, M. M. *Chem. Rev.* **1988**, *88*, 382.

[8] (a) Castleman, A. W., Weil, K. G.; Sigsworth, S. W.; Leuchtner, R. E.; Keesee, R. G. *J. Chem. Phys.* **1987**, *86*, 3829 (b) Leuchtner, R. E.; Harms, A. C.; Castleman, A. W., Jr. Metal Cluster Cation Reactions: Carbon Monoxide Association to Cu_n^+ Ions. *J. Chem. Phys.*, in press.

0002-7863/90/1512-5673$02.50/0 © 1990 American Chemical Society