the $N_2C_5Cl_4$ molecule is not known. The Ir–N(1) (1.819, 1.794 Å) and N(1)–N(2) (1.171, 1.159 Å) distances, while similar, are consistent with less π back-bonding from metal to atom N(1) in the N_2R species.

We believe that the route to a variety of metal–N_2R complexes described here is a general one and that the comparative reaction and structural chemistry of these complexes and their CO, NO^+, and N_2Ph^+ analogues will prove to be diverse and interesting.

Acknowledgments. This research was supported by the National Science Foundation. We thank Matthey Bishop Inc. for the generous loan of iridium.

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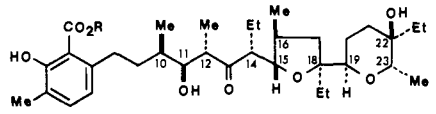
A Total Synthesis of Lasalocid A

Sir:

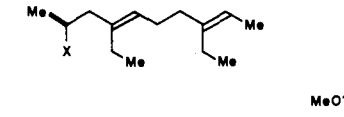
Lasalocid A (**1**), produced by *Streptomyces lasaliensis*, is a member of the class of naturally occurring ionophores known as polyether antibiotics.[1] Isolation,[2] structure elucidation,[3,4]



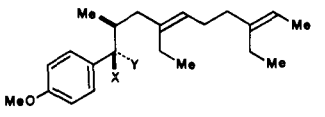
1, R = H (lasalocid A)
15, R = $CH_2C_6H_5$

biosynthesis,[5] and biological activity[6] of lasalocids have been reported. Polyether antibiotics present a formidable challenge for synthetic chemists; lasalocid A has ten chiral centers on the carbon backbone. We would like to report the first total synthesis of lasalocid A (**1**) with regio- and stereocontrol.

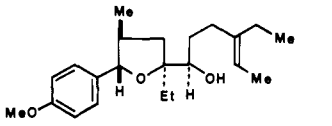
(4*E*,8*E*)-Ethyl 2-methyl-4,8-diethyldecadienoate (**2**)[7] (bp 88–90 °C (0.17 mmHg); ^{1}H NMR ($CDCl_3$) δ 5.12 (1 H, t, J = 7 Hz), 5.17 (1 H, q, J = 7 Hz)), readily synthesized by adapting Johnson's method,[8] was converted to the aldehyde **3**[7] (bp 83–85 °C (0.22 mmHg); ^{1}H NMR ($CDCl_3$) δ 5.10 (1 H, t, J = 7 Hz), 5.14 (1 H, q, J = 7 Hz), 9.59 (1 H, d, J = 2 Hz)) in 95% yield by two steps: (1) $LiAlH_4/Et_2O$, room temperature; (2) pyridinium chlorochromate/CH_2Cl_2, room temperature.[9] Treatment of **3** with *p*-methoxyphenylmagnesium bromide in ether, followed by Jones oxidation, gave the ketone **4**[7] (oil; ^{1}H NMR ($CDCl_3$) δ 5.06 (1 H, t, J = 7 Hz), 5.10 (1 H, q, J = 7 Hz)) in 72% overall yield. Highly stereospecific reduction of **4** to the alcohol **5**[7] (oil; ^{1}H NMR ($CDCl_3$) δ 4.36 (1 H, d, J = 7 Hz), 5.10 (1 H, t, J = 7 Hz), 5.13 (1 H, q, J = 7 Hz)) was realized by a combination of lithium aluminum hydride and *dl*-2-(*o*-toluidinomethyl)pyrrolidine.[10] Assignment of the stereochemistry of **5** was made based on Cram's rule.[11] The ratio of **5** and its diastereomer obtained by this method was at least 10:1 (97% yield), whereas other reducing reagents including hindered borohydrides gave less satisfactory results.[12] Optical resolution of **5** was achieved by preparative HLC separation of the *l*-α-methylbenzylurethane derivative of **5**.[13]



2, X = CO_2Et
3, X = CHO



4, X = Y = O (ketone)
5, X = H; Y = OH



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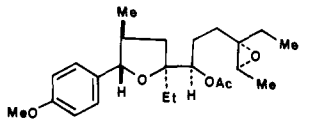

7

Epoxidation of the levorotatory alcohol **5** (*t*-BuOOH/VO(acac)$_2$/NaOAc/C_6H_6, room temperature[14]), followed by acetic acid workup, gave the tetrahydrofuran **6**[7] (75% yield; oil; ^{1}H NMR ($CDCl_3$) δ 3.65 (1 H, br), 4.30 (1 H, d, J = 9 Hz), 5.20 (1 H, q, J = 7 Hz)) along with a small amount of its stereoisomer in a ratio of 8:1.[15] As the C-15[16] hydroxy group was expected to control the stereochemistry of the epoxidation reaction,[15] structure **6** was assigned to the major product. Repetition of epoxidation of **6** under the same conditions, followed by acetylation (Ac_2O/Py, room temperature),[17] allowed isolation of the epoxide **7**[7] (oil; ^{1}H NMR ($CDCl_3$) δ 2.82 (1 H, q, J = 6 Hz), 4.25 (1 H, d, J = 9 Hz), 5.03 (1 H, br)), which was transformed to the tetrahydrofuran **8**[7] (oil; ^{1}H NMR ($CDCl_3$) δ 3.72 (1 H, q, J = 7 Hz), 4.08 (1 H, m), 4.28 (1 H, d, J = 10 Hz); $[\alpha]^{22}_D$ + 1.74° (*c* 1.44, $CHCl_3$)) by four steps ((1) 0.1 N H_2SO_4/aqueous acetone, room temperature;[18] (2) TsCl/Py, room temperature; (3) K_2CO_3/CH_3OH, room temperature; (4) AcOH, room temperature) in 45% overall yield. The first three steps were necessary to invert the stereochemistry of the epoxide ring. The overall stereoselectivity

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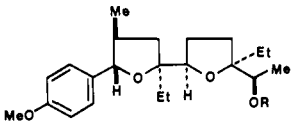
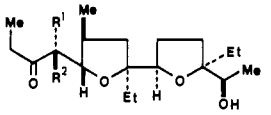
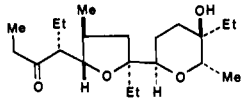


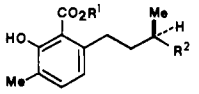
8, R = H
9, R = CH_2OCH_3



10, R^1 = H; R^2 = Et
11, R^1 = Et; R^2 = H



12



13, $R^1 = CH_2C_6H_5$; R^2 = CH = CH_2
14, $R^1 = CH_2C_6H_5$; R^2 = CHO

from **6** to **8** and its stereoisomer was 5:1. Bromomethyl methyl ether treatment of **8** (KH/THF, room temperature) gave the ether **9**[7] (oil; ^{1}H NMR ($CDCl_3$) δ 3.64 (1 H, q, J = 7 Hz), 3.95 (1 H, m), 4.35 (1 H, d, J = 9 Hz); $[\alpha]^{22}_D$ −25.4° (*c* 1.80, $CHCl_3$)) in 88% yield.

Functionalization required for introduction of the ethyl ketone moiety to **9** was achieved by eight steps: (1) Li/EtOH/liquid NH_3; (2) MCPBA/aqueous $NaHCO_3/CH_2Cl_2$, room temperature; (3) HIO_4/aqueous dioxane, room temperature; (4) $LiAlH_4$/THF, reflux; (5) TsCl/Py, 0 °C; (6) $LiAlH_4/Et_2O$, room temperature; (7) B_2H_6/THF, room temperature; (8) Jones oxidation. Deprotection of the alcoholic group ($TrBF_4/CH_2Cl_2$, room temperature[19]) yielded exclusively the ketone **10**[7] (oil; ^{1}H NMR ($CDCl_3$) δ 3.53 (1 H, dd, J = 9, 5 Hz), 3.62 (1 H, q, J = 7 Hz), 3.95 (1 H, distorted t, J = 8 Hz); $[\alpha]^{22}_D$ + 18.9° (*c* 0.36, $CHCl_3$)). The overall yield from **9** to **10** was 13%. The stereochemistry at the C-14 position was deduced by comparison with the authentic ketone **11**, prepared from natural isolasalocid A.[4,20] Equilibration of **10** (NaOH/aqueous dioxane, room temperature) resulted in a 1:1 mixture (93% recovery) of **10** and **11**, which was well separated by silica gel preparative TLC (hexane–ether, 2:1). The recovered ketone **10** was recycled. The synthetic ketone **11**[7] (oil; ^{1}H NMR ($CDCl_3$) δ 3.56 (1 H, dd, J = 9, 7 Hz), 3.75 (1 H, q, J = 7 Hz), 3.98 (1 H, distorted t, J = 7 Hz); $[\alpha]^{22}_D$ −27.1° (*c* 1.69, $CHCl_3$)) was identical with the authentic ketone[4,20] in every respect (mass spectrum, NMR, IR, α_D, TLC).

The ketone **11**, belonging to the isolasalocid[4,20] series, was stereospecifically converted to the ketone **12**, belonging to the lasalocid series, in two steps; methanesulfonyl chloride–pyridine treatment of **11** afforded the mesylate, solvolysis of which in aqueous acetone in the presence of silver carbonate at room temperature gave a mixture of the ketones **12**[7] (65% yield; oil; ^{1}H NMR ($CDCl_3$) δ 0.74–1.10 (5 × 3 H), 1.20 (3 H, d, J = 7 Hz), ~2.5 (3 H, m), ~3.5 (2 H, m), 3.75 (1 H, q, J = 7 Hz); $[\alpha]^{22}_D$ −23.7 ° (*c* 0.19, $CHCl_3$)) and **11** (12% yield) which was recycled. The synthetic ketone **12** was identical with the authentic ketone, prepared from natural lasalocid A,[3,20] in every respect (mass spectrum, NMR, IR, α_D, TLC).

The left half of the lasalocids was synthesized as follows. Treatment of 2-acetoxy-2-methyl-6-carbobenzoxy-3,5-cyclohexadien-1-one[21] with lithium di(3-methyl-4-pentenyl)-cuprate, prepared from *l*-1-bromo-3-methyl-4-pentene ($[\alpha]^{22}_D$ −4.77° (*c* 3.02, CH_3OH)), gave the benzyl salicylate **13**.[7] Ozonization of **13** in a mixture of methylene chloride and methanol at −78°, followed by dimethyl sulfide workup, afforded the aldehyde **14**[7] (mp 29–30 °C; ^{1}H NMR ($CDCl_3$) δ 0.92 (3 H, d, J = 7 Hz), 2.20 (3, H, s), 5.37 (2 H, s), 6.57 and 7.53 (2 H, AB, J = 8 Hz), 9.34 (1 H, d, J = 2 Hz), 11.29 (1 H, s); $[\alpha]^{22}_D$ −0.92° (*c* 0.65, $CHCl_3$)). The overall yield from the cyclohexadienone to **14** was 50%. The synthetic aldehyde was identical with the authentic substance, prepared from lasalocid A,[20,23] in every respect (mass spectrum, NMR, IR, UV, α_D, TLC).

We anticipated that the major product of the Aldol reaction between **12** and **14** would have the desired stereochemistry at the C-10, C-11, and C-12 positions, based on Cram's rule[11] and House's experiments.[24] After many unsuccessful attempts, this crucial step was realized using a procedure similar to that reported by House, which involved (1) LDA (2.2 equiv) treatment of **12** (1.0 equiv) in Et_2O at 0 °C; (2) $ZnCl_2$ (2.2 equiv) treatment of the resultant enolate at 0 °C; and (3) treatment of the resultant zinc enolate with **14** (1.0 equiv) at 0 °C for 3 min. Silica gel preparative TLC (hexane–ether 1:1) allowed isolation of four Aldol products (67% yield; 96% yield based on the recovered **14**), the ratio of which was 40:10:7:3.[25] As expected, the major product (oil; ^{1}H NMR ($CDCl_3$) δ 0.73–1.05 (6 × 3 H), 1.17 (3 H, d, J = 7 Hz), 2.19 (3 H, s), 2.4–3.2 (4 H), 3.3–3.95 (4 H), 5.40 (2 H, s), 6.60 and 7.10 (2 H, AB, J = 8 Hz), 7.35 (5 H), 11.25 (1 H, s); $[\alpha]^{22}_D$ −2.80° (*c* 0.80, CH_3OH)) was identical with benzyl lasalocid A (**15**),[7] prepared from natural lasalocid A,[20,23] in every respect (mass spectrum, NMR, IR, UV, α_D, TLC). The stereochemistry of the minor products has not yet been established. Better stereoselectivity (~8:1:1 for the first three isomers) of the Aldol reaction was observed in DME, but the efficiency of condensation was lower (~20% uncorrected yield). Buse and Heathcock[26] recently reported a different stereochemical outcome for the Aldol reaction in a similar system, due to different reaction conditions employed for these experiments. It is interesting to point out that the stereochemistry around the β-hydroxy ketone moiety (or its masked form) of some other polyether antibiotics such as salinomycin,[27] narasin,[28] lysocellin,[29] A23187,[30] monensin,[31] and dianemycin[32] is the same as that of the lasalocids.

Debenzylation of **15** was carried out under the standard conditions (H_2/Pd on C/MeOH, room temperature), and synthetic lasalocid A (**1**)[7] was quantitatively isolated as its sodium salt. The synthetic substance was identical with the sodium salt of natural lasalocid A[20] in every respect (melting point, mixture melting point, NMR, IR, UV, α_D, TLC).

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(11) For example, J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", American Chemical Society, Washington, D.C., 1976, p 87 ff.
(12) For example, $NaBH_4$ reduction of 4 in CH_3OH gave a 3:2 mixture of **5** and its diastereomer, and L-Selectride reduction in THF gave a 3:1 mixture.
(13) The alcohol **5** was optically resolved by three steps: (1) (−)-$C_6H_5CH(CH_3)N{=}C{=}O/Et_3N$, 60 °C; (2) preparative HLC separation (Waters System 500, silica, 20% ether–80% hexane); (3) $NaOCH_3/CH_3OH$, 100 °C. $[\alpha]^{22}_D$ −9.00° (c 5.31, $CHCl_3$) and +8.63° (*c* 1.35, $CHCl_3$) were observed for enantiomeric alcohols **5**.

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(15) A manuscript describing stereospecificity of epoxidation of bishomoallylic alcohols by this method[14] is in preparation (B. Vranesic, D. P. Negri, and Y. Kishi).
(16) Numbering in this paper corresponds to that of lasalocids: J. W. Westley, *J. Antibiot.*, **29**, 584 (1976).
(17) This acetylation was necessary to avoid formation of the undesired tetrahydrofuran ring at this stage.
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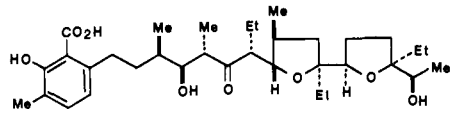
(20) We are indebted to Dr. J. W. Westley for samples of lasalocid A (1) and isolasalocid A (i).



i, isolasalocid A

(21) This substance was prepared by following the synthetic method of 2-acetoxy-2-methyl-6-carboethoxy-3,5-cyclohexadien-1-one: F. Wessely, E. Zbiral, and H. Sturm, *Chem. Ber.*, **93**, 2840 (1960).
(22) This optically active bromide was synthesized as follows: (1) $CH_3CH{=}CHCH_2OH/CH_3(OEt)_3$, 160 °C; (2) NaOH/aqueous dioxane, room temperature; (3) optical resolution as the α-methylbenzylamine salt; (4) $LiAlH_4/Et_2O$, room temperature; (5) $MsCl/Et_3N/CH_2Cl_2$, 0 °C; (6) LiBr/DMF, 100 °C.
(23) The authentic aldehyde 14 was prepared from natural lasalocid A in two steps: (1) $C_6H_5CH_2Br/K_2CO_3$/dioxane, 80 °C; (2) 230 °C (0.02 mmHg).[3]
(24) H. O. House, D. S. Crumrine, A. Y. Teranishi, and H. D. Olmstead, *J. Am. Chem. Soc.*, **95**, 3310 (1973).
(25) The Aldol condensation between **12** and dibenzylated aldehyde (cf. 14) was as good as the one reported.
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Additions and Corrections

Electrochemical Synthesis and Structural Characterization of the Iron–Sulfur Cluster Cation $[(\eta\text{-}C_5H_5)_2Fe_2(S_2)(SC_2H_5)_2]^+$ [*J. Am. Chem. Soc.*, **98**, 1980 (1976)]. By P. J. VERGAMINI,* R. R. RYAN, and G. J. KUBAS, The University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87545.

An error has been found in the atomic position parameter table published as Supplementary Material. A revised table is deposited herewith.

Supplementary Material Available: A listing of atomic positional parameters (Table I) (1 page). Ordering information is given on any current masthead page.

Ionization of Group 6 and 7 Protonic Acids in Dimethyl Sulfoxide [*J. Am. Chem. Soc.*, **99**, 808 (1977)]. By EDWARD M. ARNETT* and LEONARD E. SMALL, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260.

Page 814: The captions for Figures 3 and 4 are reversed.

Add as ref 7a: F. A. Long and P. Ballinger, "Electrolytes", B. Pesce, Ed., Pergamon Press, New York, N.Y., 1962, pp. 152–165.

An Anionic Equivalent of the Friedel–Crafts Cycloacylation [*J. Am. Chem. Soc.*, **99**, 4822 (1977)]. By R. J. BOATMAN, B. J. WHITLOCK, and H. W. WHITLOCK, JR.,* Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706.

It has been called to our attention that our references 4 and 6 to Professor W. E. Parham's work in this area were not very explicit. Since our primary concern is with the synthesis of anthracyclinones, we did not give a detailed literature review, but we would point out now that a comparable synthesis of 1-indanone by him is described in the paper referred to in ref 6, which also indicates the potential generality and utility of this synthetic approach.

Magnesium Bromide–Tetrahydrofuran Complexes: $MgBr_2(C_4H_8O)_2$, $MgBr_2(C_4H_8O)_3$, $MgBr_2(C_4H_8O)_4$, and $MgBr_2(C_4H_8O)_4(H_2O)_2$. A Reagent for the Preparation of Anhydrous Magnesium Phosphodiester Salts [*J. Am. Chem. Soc.*, **99**, 5285 (1977)]. By FAUSTO RAMIREZ,* RAGHUPATHY SARMA,* YU FEN CHAW, TERENCE M. MCCAFFREY, JAMES F. MARECEK, BRIAN MCKEEVER, and DAVID NIERMAN, Chemistry and Biochemistry Departments, State University of New York at Stony Brook, Stony Brook, New York 11794.

Experimental Section, page 5287, line 11: For "The solution was concentrated to ca. 200 mL . . . ", read "The solution was concentrated to ca. 50 mL . . . ".

Orientation in Nucleophilic Substitution at the Cycloheptatrienone Nucleus: Failure of Predictions from Either Electron Spin Resonance Data or Molecular Orbital Treatments [*J. Am. Chem. Soc.*, **99**, 5997 (1977)]. By MARINO CAVAZZA, M. PERLA COLOMBINI, MASSIMO MARTINELLI, LAMBERTO NUCCI, LUCIO PARDI, FRANCESCO PIETRA,* and SERGIO SANTUCCI, Department of Chemistry and GNSM, Istituto di Fisica, Università di Pisa, 56100 Pisa, Italy, and Facoltà di Scienze, Libera Università di Trento, 38050 Povo (Trento), Italy.

UV data for 3-thiomethyltropone are correct as they stand in Table VI while those reported in the Experimental Section refer instead to 2-thiomethyltropone.