dinuclear complexes where the hydrides are terminal but no reasonable mechanism exists for simultaneously placing both hydrides on the same metal. Our search for that and related photoactivity is continuing.

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A Novel Series of Macrocyclic Lactones

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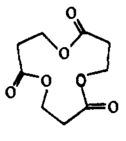
A variety of macrocyclic polyethers have been synthesized and shown to bind metal and ammonium ions efficiently[1,2] and to effect transport or catalytic modification.[3-14] Naturally occurring cyclic ionophores, on the other hand, contain not only ether groups but often amides and lactones arranged in a "head-to-tail" fashion around the ring.[15] Investigations on synthetic macrocyclic compounds with amide or lactone groups have largely been confined to cyclic peptides[16] or lactones with mirror plane symmetry,[17] whereas lactones with rotational symmetry have received only limited attention. The few examples reported in the literature include the penta- and hexalactones derived from glycolic acid[18] and the di-, tetra- and hexalactones synthesized from a bicyclic monomer.[19] We wish in this communication to describe a series of novel macrocyclic lactones with rotational symmetry axes derived from 3-hydroxypropionic acid. An efficient and convenient method for preparing them will also be described as will the X-ray structure of the lowest homolgue, the trilactone **2** with a cyclic backbone analogous to that of the natural iron carrier enterobactin.[20-22] The method of synthesis is based on the use of cyclic tin-oxygen compounds as templates[23] in order to catalyze the condensation of propiolactone to form macrocyclic products in up to 80% yields.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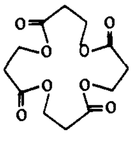
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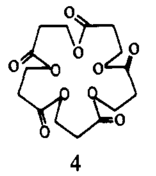
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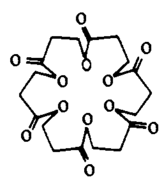
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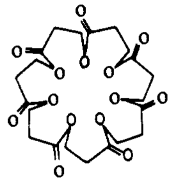
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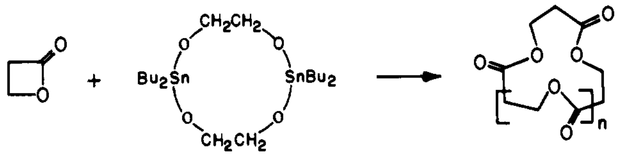
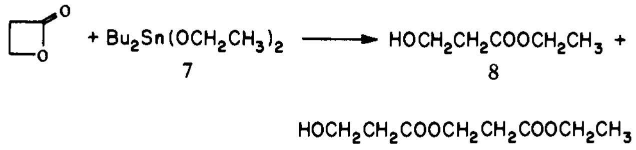


1

2, $n = 1$
3, $n = 2$
4, $n = 3$
5, $n = 4$
6, $n = 5$

Distannoxane **1** (24) (1.18 g, 2.0 mmol) and propiolactone (9.84 mL, 133 mmol) are heated in 800 mL of chloroform overnight. On concentrating the reaction mixture and chromatographing it on silica gel (elution with benzene-ethyl acetate), the following cyclic oligomers can be isolated as major products: 2.126 g (9.84 mmol, 22.2%) of the trimer **2**, 1.16 g (4.03 mmol, 12%) of the tetramer **3**, 1.067 g (3.04 mmol, 11.4%) of the pentamer **4**, 0.65 g (1.58 mmol, 6.7%) of the hexamer **5**, and 0.231 g (0.45 mmol, 2.4%) of the heptamer **6**, in addition to mixtures of the five macrocycles (2.5 g, 26%).[25]

The unique properties of a stannoxane as a template and the importance of its cyclic structure were demonstrated by experiments with linear stannoxanes. Refluxing propiolactone (0.54 mL, 8.6 mmol) with dibutyltin diethoxide (**7**) (1.4 g, 4.31 mmol) in 100 mL of chloroform did not yield any macrocyclic compounds but rather the hydroxy esters **8** and **9** (131 mg, 1.12 mmol, 12%; 91 mg, 0.313 mmol, 3.6%). However, on replacing the distannoxane **1** by the cyclic stannoxane 1,1-dibutyltin 4,4-dimethyl-1,2-dioxacyclohexane all macrocyclic oligomers are formed in



$$+ Bu_2Sn(OCH_2CH_3)_2 \longrightarrow HOCH_2CH_2COOCH_2CH_3 + HOCH_2CH_2COOCH_2CH_2COOCH_2CH_3$$

7 8 9

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(1) C. J. Pedersen, *J. Am. Chem. Soc.*, **87**, 7017 (1967).

(2) G. W. Gokel and H. D. Durst, *Synthesis*, 168 (1976).

(3) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972).

(4) J. M. Lehn, *Struct. Bonding (Berlin)*, **16**, 1 (1973).

(5) *Prog. Macrocycl. Chem.*, **1**, 1 (1979).

(6) K. H. Wong, K. Yagi, and J. Smid, *J. Membr. Biol.*, **18**, 379 (1974).

(7) J. M. Lehn, *Pure Appl. Chem.*, **51**, 979 (1979).

(8) J. J. Christensen in "Bioenergetics and Thermodynamics: Model Systems", A. Brabanti, Ed., D. Reidel, Boston, 1980, pp 111.

(9) D. J. Cram and J. M. Cram, *Acc. Chem. Res.*, **11**, 8 (1978).

(10) F. Stoddart, *Chem. Soc. Rev.*, **8**, 85 (1979).

(11) J. M. Girodeau, J. M. Lehn, and J. P. Sauvage, *Angew. Chem.*, **87**, 813, (1975); *Angew. Chem., Int. Ed. Engl.*, **14**, 764 (1975).

(12) J. P. Behr, J. M. Lehn, and P. Vierling, *J. Chem. Soc., Chem. Commun.*, 621 (1976).

(13) Y. Chao, G. R. Weisman, G. D. Sogah, and D. J. Cram, *J. Am. Chem. Soc.*, **101**, 4948 (1979).

(14) J. P. Behr and J. M. Lehn, *J. Chem. Soc., Chem. Commun.*, 143 (1978).

(15) Yu. A. Ovchinnikov and V. T. Ivanov, *Tetrahedron*, **31**, 2177 (1975).

(16) C. M. Deber, V. Madison, and E. R. Blout, *Acc. Chem. Res.*, **9**, 106 (1976).

(17) J. S. Bradshaw and P. E. Stott, *Tetrahedron*, **36**, 461 (1980). J. S. Bradshaw, G. E. Maas, R. M. Izatt, and J. J. Christensen, *Chem. Rev.*, **79**, 375 (1979), and references cited therein.

(18) J. Dale, O. Sevaldsen, and K. Titlestad, *Acta Chem. Scand., Ser. B*, B32, 306 (1978).

(19) M. Okada, H. Sumitomo, and I. Tajima, *J. Am. Chem. Soc.*, **101**, 4013 (1979).

(20) K. N. Raymond and C. J. Carrano, *Acc. Chem. Res.*, **12**, 183 (1979).

(21) M. Llinas, D. M. Wilson, and J. B. Neilands, *Biochemistry*, **12**, 3836 (1973).

(22) W. H. Rastetter, T. J. Erickson, and M. C. Venuti, *J. Org. Chem.*, **45**, 5011 (1980).

(23) For earlier publications on the use of tin derivatives for the synthesis of macrocyclic compounds, see: A. Shanzer and N. Mayer-Shochet, *Chem. Commun.*, 176 (1980); A. Shanzer and F. Berman, *ibid.*, 259 (1980); A. Shanzer, N. Shochet, D. Rabinovich, and F. Frolow, *Angew. Chem., Int. Ed. Engl.*, **19**, 326 (1980); A. Shanzer, N. Shochet, D. Rabinovich, and F. Frolow, *J. Org. Chem.*, in press.

(24) W. J. Considine, *J. Organomet. Chem.*, **5**, 263 (1966).

(25) The melting points of the macrocyclic polylactones are 56-58 °C for the trilactone **2**, 116-120 °C for the tetralactone **3**, 80-85 °C for the pentalactone **4**, 133-135 °C for the hexalactone **5**, and 84-86 °C for the heptalactone **6**. Their IR, NMR, and mass spectra and elemental analyses are consistent with the assigned structures; see supplemental material.

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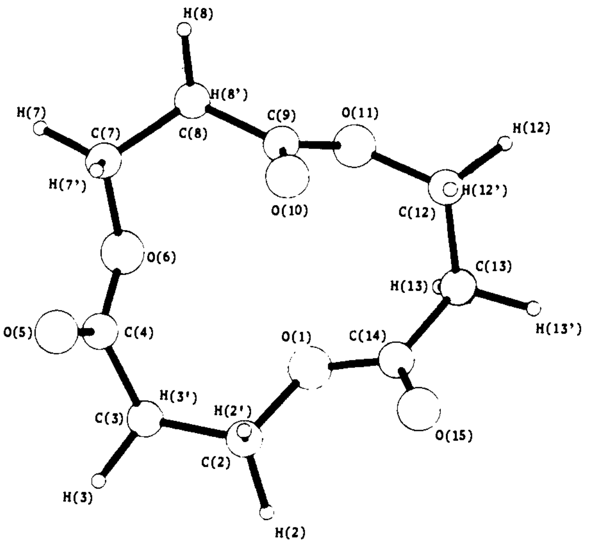


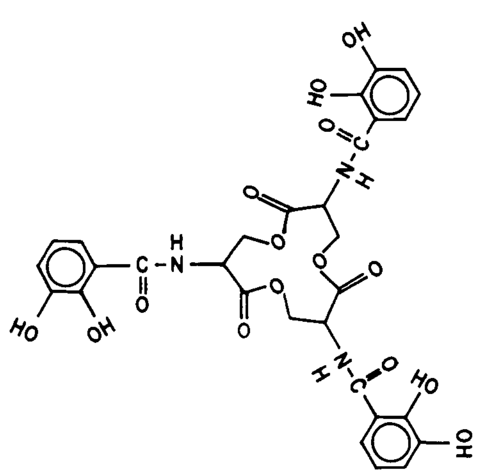
Figure 1.

comparable yields. No interconversion of macrocyclic polylactones into each other under the conditions of the reaction was observed, and trilactone **2** was recovered unchanged after heating with cyclic distannoxane **1** for 24 h.

This reaction may occur by insertion of several propiolactone molecules into the tin-oxygen bond and subsequent expulsion of the macrocyclic product. Propiolactone insertion into tin-oxygen compounds has been shown to be reversible and together with the possibility of multiple insertions support such a mechanism.[26] The reactions of cyclic stannoxanes may be compared with that of some organometallic compounds, which lead to cyclic rather than linear oligomerization of monomers.[27] It is, however, different from cationic oligomerization of bicyclooctanone which yields only even multiples of the monomeric unit.[19]

The structure of the trimer **2** has been confirmed by X-ray diffraction analysis as shown in Figure 1.[28] In the crystal the backbone of the trilactone **2** adopts a crown configuration, with all carbonyl groups on one side of the plane of the ether oxygens. Two enantiomeric conformations are therefore possible, both of which are present in the crystal.

The all-syn arrangement of the carbonyl groups observed in this compound has been reported for both synthetic and natural macrocyclic polycarbonyl compounds. Tri-*o*-thymotide, for instance, a trilactone which forms clathrate inclusion complexes with many guest molecules, assumes a similar conformation[29] as do many cyclic tripeptides, both in the solid state and in solution.[30] Of particular interest is, however, the iron carrier enterobactin, the cyclic skeleton of which is identical with the trilactone **2**. Although no X-ray diffraction studies of enterobactin or its iron complex have been reported, studies of this compound in solution indicate a propeller-like conformation of the aromatic residues with the ring carbonyl groups pointing down from the cyclic backbone.[21] We are in the process of applying this synthetic method to the preparation of a number of naturally occurring macrocycles in addition to structural investigations of these novel compounds.



Acknowledgment. We thank the Israel Academy for Sciences and Humanities for support.

Supplementary Material Available: X-ray data and specifically atom coordinates (Table 1), hydrogen atom coordinates (Table 2), bond lengths (Table 3), bond angles (Table 4), and physical data (Table 5) as well as the drawing of the packing arrangement (Figure 2) are available (6 pages). Ordering information is given on any current masthead page.

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[26] K. Itoh, S. Kobayashi, S. Sakai, and Y. Ishii, *J. Organomet. Chem.*, **10**, 451 (1967).

[27] W. Brenner, P. Heimlich, H. Hey, E. W. Mueller, and G. Wilke, *Liebigs Ann. Chem.*, **727**, 161 (1969).

[28] Compound **2** crystallizes as monoclinic crystals from petroleum ether; space group $P2_1/n$; $a = 8.398$ (8), $b = 8.184$ (4), $c = 14.643$ (5) Å; $\beta = 92.48$ (5°); $Z = 4$. Intensity data were collected on a CAD-4 diffractometer (1326 unique reflections, $\theta < 23°$), and the structure of the compound (Figure 1) was solved by MULTAN and refined by full-matrix least squares to $R = 0.06$ and $R' = 0.05$.

[29] D. R. Wilson, *Chem. Soc. Rev.*, **7**, 65 (1978), and references therein.

[30] M. E. Druyan, C. L. Coulter, R. Walter, G. Kartha, G. K. Ambady, *J. Am. Chem. Soc.*, **98**, 5496 (1976); G. Kartha and G. Ambady, *Acta Crystallogr., Sect. B*, **31**, 2035 (1975); C. M. Deber, D. A. Torchia, and E. R. Blout, *J. Am. Chem. Soc.*, **93**, 4893 (1971).

Synthesis of the First Homoleptic Trifluorosilyl σ-Bonded Metal Compounds by Cocondensation of Metal Vapor with Trifluorosilyl Radicals

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The first homoleptic trifluorosilyl metal compounds, bis(trifluorosilyl)tellurium, tris(trifluorosilyl)bismuth, and bis(trifluorosilyl)mercury have been formed in moderate yields by cocondensation of tellurium, bismuth, and mercury vapor with trifluorosilyl ($SiF_3\cdot$) radicals in a low-temperature matrix:

$$M(g) + nSiF_3\cdot \xrightarrow{-196\ °C} M(SiF_3)_n$$

The trifluorosilyl radicals are cleanly generated from hexafluorodisilane in a low-temperature glow discharge:

$$Si_2F_6 \xrightarrow[\substack{10\ MHz \\ 30\ W}]{} 2SiF_3\cdot$$

Hexafluorodisilane is an excellent precursor for the synthesis of trifluorosilyl compounds because the silicon-silicon bond energy of 50 kcal/mol is considerably lower than the silicon-fluorine bond energy of about 140 kcal/mol.[1,2] The large difference in bond energies leads primarily to plasma generation of trifluorosilyl radicals and production of byproducts such as $Si_2F_5\cdot$, $SiF_2:$, and SiF_4 in quantities too low to detect among the reaction products. The reactor[3] used in this work consisted of a metal evaporation source and a radio-frequency generator for production of $SiF_3\cdot$ radicals. Both species were directed at a −196 °C surface. Normally, at least a tenfold stoichiometric excess of Si_2F_6 is used, and of the unreacted Si_2F_6, 95% may be recycled for other reactions.

Synthesis of $Hg(SiF_3)_2$. Mercury (1.5 g) was evaporated over a 3-h period and cocondensed with $SiF_3\cdot$ radicals. The volatile

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[1] T. C. Ehlert and J. L. Margrave, *J. Chem. Phys.*, **41**, 1066 (1964).

[2] J. D. McDonald, C. H. Williams, J. C. Thompson, and J. L. Margrave, "Mass Spectrometry in Inorganic Chemistry", American Chemical Society, Washington, DC, 1968, Adv. Chem. Ser. No. 72, p 261.

[3] T. J. Juhlke, R. W. Braun, T. R. Bierschenk, and R. J. Lagow, *J. Am. Chem. Soc.*, **101**, 3229 (1979).

0002-7863/81/1503-7340$01.25/0