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MACROCYCLIC BIPYRIDINES FOR ALKYLTIN TRICHLORIDE DEACTIVATION

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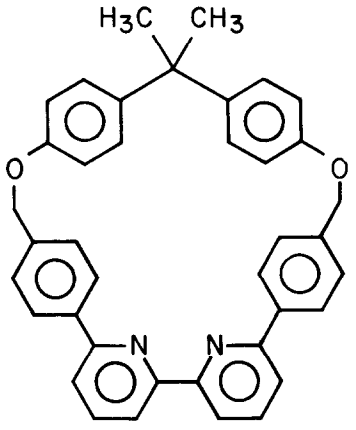
The synthesis of two macrocyclic bipyridines whose frameworks are suitable for alkyltin trichloride encapsulation is described.

The applicability of monoalkyltin(IV) compounds as stabilizer systems for poly(vinyl chloride) is limited because of the formation in situ of alkyltin trichlorides ($RSnCl_3$) as Lewis acidic byproducts.[1] A recent model study[2] has indicated that monodentate Lewis bases can lower the degradative activity of these Lewis acids. As an extension of this model study, we wished to determine whether a greater deactivation could be attained using bidentate macrocyclic ligands to sequester the electron-demanding tin species. Although organotin chlorides have been reported[3] to interact with 18-crown-6 as a bridging ligand, no macrocyclic encapsulating agents for $RSnCl_3$ have been noted in the literature. Described herein are syntheses of two macrocycles, **1** and **2**, whose cavities (as well as those of their N,N'-dioxides) are of the appropriate size and shape to make possible the formation of inclusion complexes with $RSnCl_3$. These cyclic hosts contain the 2,2'-bipyridyl coordinating group, whose incorporation into macrocycles is of current interest.[4]

The Grignard reagent[5] from 4-bromobenzyl methyl ether (10.3 g, 51.2 mmol) was coupled with 6,6'-dibromo-2,2'-bipyridine[6] (5.3 g, 17 mmol) in 500 ml of Et_2O at reflux using 1 g of $(PPh_3)_2NiCl_2$ as catalyst. Quenching with aqueous NH_4Cl followed by crystallization of the Et_2O-soluble organic material from MeOH gave 1.6 g (24%) of **3**,[7] mp 166-9°C. The product could also be chromatographed on silica gel, using CH_2Cl_2-EtOAc as eluant. (This method is an alternative to the procedure of Dietrich-Buchecker et al.,[8] and leads to facile isolation of the desired material, since the pyridyl byproducts are sparingly soluble oligomers.) Diether **3** (0.58g) was then treated with HBr-AcOH (35ml) for 2 d at 25°C. The resulting solution was poured into CH_2Cl_2 and H_2O, the mixture neutralized with Na_2CO_3, and separated into layers. The unfiltered organic layer was concentrated and crystallized from $ClCH_2CH_2Cl$ to yield dibromide **4**[7] (0.48 g, 66%, mp 237-8°C).

Compound **4** is the first 6,6'-diaryl-2,2'-bipyridine which can serve as the bis electrophile in a macrocyclization reaction. As such, it was reacted with dinucleophiles **5** and **6**[9] in dimethylformamide containing suspended Cs_2CO_3[10] at 50°C under high dilution conditions to obtain macrocycles **1**[7] and **2**[7] in 36% and 22% yields respectively. Purification of the products was accomplished by chromatography (CH_2Cl_2-EtOAc on silica gel) and crystallization. Gel permeation chromatography indicated that cyclic monomers had been prepared, rather than



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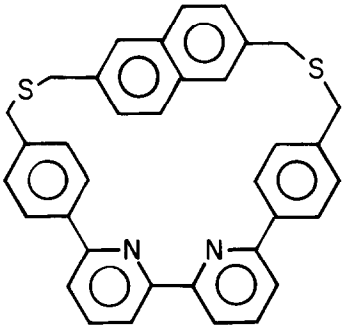

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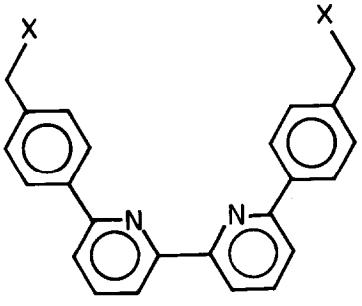
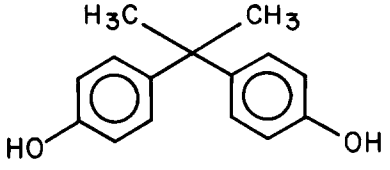


3, X = OCH_3

4, X = Br



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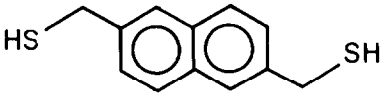

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cyclic dimers. Attempts to perform similar cyclizations in $(CH_2)_4O$ with NaH as base were unsuccessful.

The formation of 1:1 complexes between CH_3SnCl_3 and ligands 1 and 2 in dilute 1:1 v/v $CDCl_3$-CD_3CN solution was verified by ^1H NMR spectroscopy. In addition, the complex with 1 was precipitated from CH_2Cl_2-C_6H_6. The chemical shifts of the pyridyl hydrogens in the complexes (8.4-8.5 ppm for the hydrogens not adjacent to the phenylenes) are consistent with those previously reported[11] for the analogous protons in n-$C_4H_9SnCl_3$·bipyridine. Both host and guest chemical shifts when measured as a function of guest/host mol ratio display points of inflection at about 1 equiv of added guest (Figures 1 and 2).

Examination of CPK models of uncomplexed 1 and 2 reveals that the macrocycles cannot collapse into their cavities, although the cavities are partially occupied by aromatic C-H groups. Upon coordination[12] of the bipyridine nitrogens with a guest $RSnCl_3$, the hosts assume toroidal conformations with the tin atom surrounded by arylene groups. Thus, the tin compound should be sterically and electronically deactivated as a Lewis acid. Further characterization of $RSnCl_3$ complexes with macrocyclic bipyridines and their N-oxides, as well as determinations of the reactivities of the complexes in the presence of labile substrates, are currently in progress.[13]

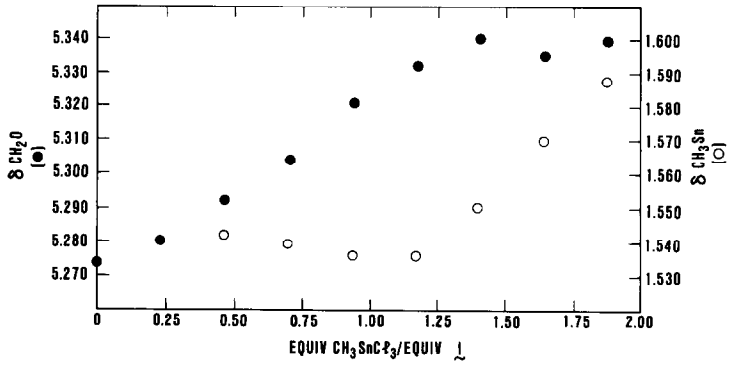

Figure 1

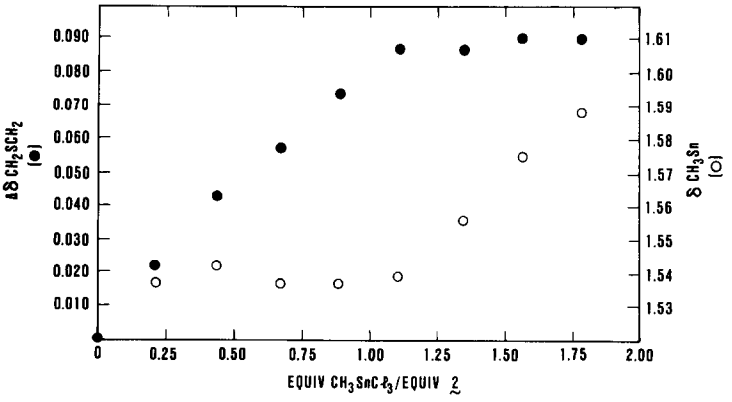

Figure 2

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