

is in the *boat* conformation⁸ and is slightly staggered to relieve the transannular strain due to the intraannular interactions of the hydrogen atoms on carbons 4, 5, 7 and 8. The interatomic distances and the relevant bond angles are summarized in Fig. 1.

The infrared spectra of the complexes were measured in potassium bromide. In all cases the absorption bands characteristic of the cyclooctadiene double bonds at 1660 cm.⁻¹ (C=C) and 710 cm.⁻¹ (=CH) were absent. New bands appearing at 1612 cm.⁻¹ and 746 cm.⁻¹ were assigned to the complexed olefin. The spectrum of Ia exhibited a pair of bands at 1230 cm.⁻¹ and 1192 cm.⁻¹ of equal intensity, complexes Ib and Ic exhibited a similar pair of bands at 1238 cm.⁻¹ and 1188 cm.⁻¹, the intensity of the former being approximately twice that of the latter. A minor difference was also observed in a pair of bands that occurred at 971 cm.⁻¹ and 966 cm.⁻¹ in Ia and at 971 cm.⁻¹ and 957 cm.⁻¹ in Ib and Ic. X-Ray powder diffraction data also show that the structure of complex Ia is different from complexes Ib and Ic.

Hendra and Powell⁹ have suggested that the cuprous chloride-COD-1,5-complex prepared from hydrochloric acid solution involves the *chair* conformer of the olefin rather than the *boat*. The infrared spectra of complexes Ia-c are virtually identical with that reported by these authors. Since the crystal structure determination of Ic has shown that the complexed olefin exists in the *boat* conformation, it would certainly appear that complexes Ia-c all involve the *boat* conformation of the olefin. If this were not the case, then the various complexes should exhibit major differences in the 1000-500 cm.⁻¹ region where most of the absorption bands are due to the skeletal vibrations of the eight-membered ring. We believe that the minor spectral differences observed between Ia and Ib and Ic may be attributed to two structurally different complexes. Complexes Ib and Ic possess the determined dimeric structure; complex Ia is polymeric and consists of COD molecules in the *boat* conformation joined by exocyclic cuprous chloride bridging. The spectral differences may then reside in the non-symmetrical nature of Ib and Ic as opposed to the more symmetrical structure of Ia.

A more complete structural analysis of this complex will be reported elsewhere.

(8) COD-1,5 has been found to exist in the *boat* configuration in its rhodium chloride complex; J. A. Ibers and R. G. Snyder, *Acta Cryst.*, **15**, 923 (1962).

(9) P. J. Hendra and D. B. Powell, *Spectrochim. Acta*, **17**, 913 (1961).

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RECEIVED JANUARY 11, 1963

EVIDENCE FOR THE EXISTENCE OF AN ORGANODITIN DIHYDRIDE¹

Sir:

We wish to record what we believe to be the first preparation of an organoditin dihydride, specifically, 1,1,2,2-tetra-*n*-butyl-1,2-dihydroditin.

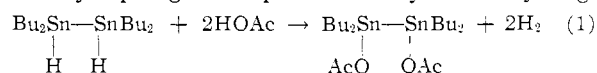
1,1,2,2-Tetra-*n*-butyl-1,2-dichloroditin,² prepared by treating 1,1,2,2-tetra-*n*-butyl-1,2-diacetoxyditin with hydrogen chloride in anhydrous ether, was reduced³

(1) We thank M and T Chemicals, Inc., for support of a portion of this work.

(2) A. J. Gibbons, A. K. Sawyer and A. Ross, *J. Org. Chem.*, **26**, 2304 (1961).

(3) This reduction was attempted by J. G. Noltes and G. J. M. van der Kerk, "Functionally Substituted Organotin Compounds," Tin Research Institute, Greenford, Middlesex, England, 1958. It was later shown by the following workers that the compound which they believed to be 1,1,2,2-tetra-*n*-butyl-1,2-dichloroditin was in reality bis-(di-*n*-butylchlorotin) oxide: (a) ref. 2; (b) D. L. Alleston and A. G. Davis, *Chem. Ind.* (London), 949 (1961); (c) O. H. Johnson, *J. Org. Chem.*, **25**, 2262 (1960).

by lithium aluminum hydride in anhydrous ether to give the colorless liquid, 1,1,2,2-tetra-*n*-butyl-1,2-dihydroditin (76%) (found: Sn, 50.51; calcd. for C₁₆H₃₆Sn₂H₂: Sn, 50.75), *n*_D²⁰ 1.5205. A large Sn-H absorption band was found at 1795 cm.⁻¹ with a faint shoulder at 1835 cm.⁻¹. The reaction of this hydride with a 100% excess of glacial acetic acid over that required by eq. 1 gave a quantitative yield of hydrogen



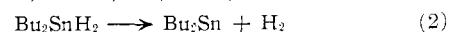
and 1,1,2,2-tetra-*n*-butyl-1,2-diacetoxyditin. That the product of this reaction is a ditin was shown by its quantitative reaction with bromine forming di-*n*-butylacetoxybromotin⁴ isolated in 70% yield. In previous work it has been shown that di-*n*-butyltin dihydride reacts with two moles of acetic acid to produce di-*n*-butyltin diacetate.⁴ It follows that di-*n*-butyltin dihydride is not present in appreciable amount in the reduction product, which, therefore, must be 1,1,2,2-tetra-*n*-butyl-1,2-dihydroditin.

This hydride is more reactive toward acid than is di-*n*-butyltin dihydride, and, on exposure to air, rapidly forms a white solid whose tin analysis corresponds to that for di-*n*-butyltin oxide.

Formation of this ditin dihydride, or a polytin dihydride,⁵ is indicated in other reactions of di-*n*-butyltin dihydride.

(a) Di-*n*-butyltin dihydride reacts with acetone to form isopropyl alcohol and di-*n*-butyltin.⁶ Infrared spectra of the reaction product mixture taken at intervals showed not only the disappearance of Sn-H absorption of di-*n*-butyltin dihydride at 1835 cm.⁻¹ but also the simultaneous appearance of new Sn-H absorption at about 1785 cm.⁻¹.

(b) Decomposition of di-*n*-butyltin dihydride at 100° constitutes a method for the preparation of di-*n*-butyltin. (Found: C, 41.34; H, 7.78; Sn, 51.10. Calcd.



for C₈H₁₈Sn: C, 41.45; H, 7.79; Sn, 50.96.) Infrared spectra of the reaction product mixture taken during the decomposition showed a decrease in the intensity of the Sn-H absorption at 1835 cm.⁻¹ accompanied by the appearance and increase in intensity of a Sn-H band at 1780 cm.⁻¹; when the decomposition was somewhat more than 70% complete, only the latter band remained. Decrease in intensity of this band required prolonged heating.

(c) Treatment of di-*n*-butyltin with di-*n*-butyltin dihydride in a 1:1 molar ratio results in new Sn-H absorption at about 1780 cm.⁻¹.

It has been reported by Neumann and König⁵ that, in the case of diphenyltin dihydride, substitution of one hydride hydrogen by tin results in a lowering of the frequency of Sn-H absorption to about 1790 cm.⁻¹.

(4) (a) A. K. Sawyer and H. G. Kuivila, *J. Am. Chem. Soc.*, **82**, 5958 (1960); (b) A. K. Sawyer and H. G. Kuivila, *J. Org. Chem.*, **27**, 610 (1962).

(5) W. P. Neumann and K. König, *Angew. Chem.*, **74**, 215 (1962).

(6) H. G. Kuivila and O. F. Beumel, *J. Am. Chem. Soc.*, **83**, 1246 (1961).

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RECEIVED JANUARY 31, 1963

THE ASSIGNMENT OF N.M.R. SPECTRA USING THE NUCLEAR OVERHAUSER EFFECT

Sir:

In the analysis of nuclear magnetic double resonance (n.m.d.r.) experiments, three main effects must be considered: the perturbation of individual spin systems by the second r.f. field which gives rise to transitions