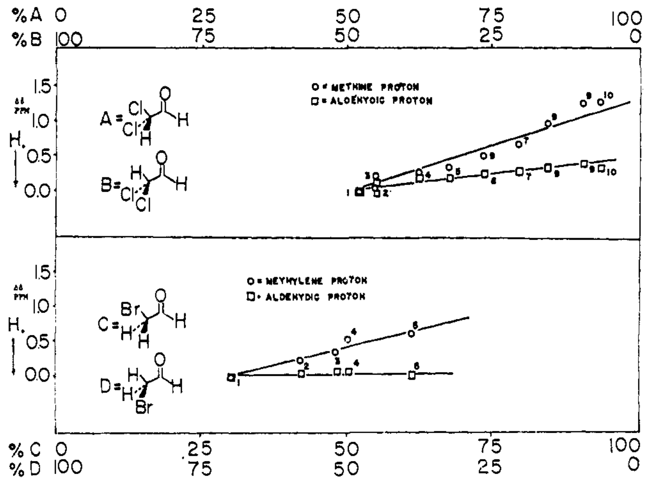
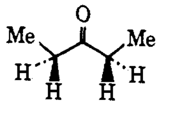
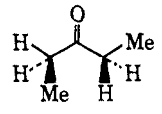


Figure 1. Dependence of the chemicals shifts of α protons and aldehydic protons of dichloroacetaldehyde and bromoacetaldehyde on rotamer populations. The chemical shifts of dichloroacetaldehyde were determined in the following solvents: (1) pentane; (2) *trans*-decalin; (3) carbon tetrachloride; (4) chloroform; (5) methylene chloride; (6) neat; (7) nitrobenzene; (8) acetone; (9) dimethylformamide; (10) dimethyl sulfoxide. The chemical shifts of bromoacetaldehyde were determined in the following solvents: (1) pentane; (2) methylene chloride; (3) nitrobenzene; (4) acetone; (5) formamide.

steroidal α-acetoxy[7] and α-halo ketones[8] and α-bromocyclohexanones[9,10] α-protons resonate at lower magnetic fields when axial than when equatorial. Additionally, $\delta(CH_2)$ of diethyl ketone shifts upfield[11] by 0.08 ppm and $\delta(CH_3)$ downfield by 0.05 ppm when the temperature changes from -61 to 104°. As rotamer VIII is more stable[12] than IX, the ratio IX/VIII increases


VIII


IX

with increase of temperature. Model II, therefore, correctly predicts the respective upfield and downfield shift of $\delta(CH_2)$ and $\delta(CH_3)$; model I predicts the reverse.

Acknowledgment. We thank the Petroleum Research Fund (2722-A1,4), administered by the American Chemical Society, and the National Science Foundation (GP-3343) for financial support.

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[8] A. Nickon, M. A. Castle, R. Harada, C. E. Berkoff, and R. O. Williams, *ibid.*, **85**, 2185 (1963).

[9] E. W. Garbish, Jr., *ibid.*, **86**, 1780 (1964).

[10] K. M. Wellman and F. G. Bordwell, *Tetrahedron Letters*, 1703 (1963).

[11] R. N. Jones and K. Noack, *Can. J. Chem.*, **39**, 2214 (1961).

[12] C. Romers and J. E. G. Creutzberg, *Rec. Trav. Chim.*, **75**, 331 (1956).

[13] National Science Foundation Predoctoral Fellow, 1966–1967.

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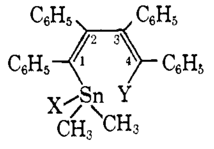
Hindered Diene Rotation by Virtue of Intramolecular Sn–Br Coordination

Sir:

Our original observation that the nmr spectra of the stannole dihalides[1] (I–III) display nonequivalent methyl



I, X = Y = Br
II, X = Y = Cl
III, X = Y = I
IV, X = Br; Y = H

resonances in carbon tetrachloride solution has prompted a detailed investigation of the conformation of I in both the solid state and in solution. The results reveal that molecular dissymmetry is introduced into diene I by an internal Sn–Br interaction which stabilizes a nonplanar cisoid conformation. This molecule is believed to be the first example of a diene whose rotational barrier about the central single bond is directly observable, as well as to represent the first X-ray crystallographic report of an organotin compound involving intramolecular Sn–Br interaction.[2]

The two equal-intensity methyl resonances exhibited at 36° by I at δ 0.48 and 0.98 in CCl_4 merge into a single broad peak when warmed to the coalescence temperature of $\sim$87°. There is also a pronounced solvent effect on the methyl bands: use of solvents of marked Lewis basicity (ethers, alcohols, etc.) or addition of 6 *M* excess of pyridine to the CCl_4 solution leads to a sharp singlet at 0.73. However, in thionyl chloride, a nonbasic but strongly ionizing solvent, the coalescence temperature was closely similar to that in CCl_4, thus ruling out any methyl equilibration mechanism involving ionization of Br (on Sn).

The origin of the methyl nonequivalence may be attributed to one of the following possibilities:[3] (a) the presence of two rotamers (*cf. s-cis* and *s-trans*) in which each methyl singlet represents both methyls of a particular rotamer and these are interconverted by rotation about C(2)–C(3) at elevated temperatures, (b) hindered rotation about the C(1)–Sn bond, but free rotation about C(2)–C(3), and (c) a nonplanar diene conformation in which methyl nonequivalence is inherent in the molecular dissymmetry thus produced and disappears when rotation about C(2)–C(3) becomes fast.

Since mechanism a requires exactly equal populations of the two different rotamers, we regard it as extremely unlikely. Further, the solvent effects are not easily explainable with this mechanism. Likewise, mechanism b can be rejected on the basis of the solvent studies: bulky solvents which can coordinate with the tin would be expected to hinder rather than accelerate rotation, in contrast to the observed results. Mechanism c re-

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[1] H. H. Freedman, *J. Org. Chem.*, **27**, 2208 (1962).

[2] The subject of pentacoordinate Sn has recently been reviewed: M. Gielen and N. Sprecher, *Organometal. Chem. Rev.*, **1**, 455 (1966). Structures of intermolecular pentacoordinate tin compounds have been published; *cf.* H. C. Clark, R. J. O'Brien, and J. Trotter, *Proc. Chem. Soc.*, **85** (1963); I. R. Beattie, G. P. McQuillan, and R. Hulme, *Chem. Ind.* (London), 1429 (1962).

[3] A monomer–dimer equilibration mechanism has been ruled out by isopiestic molecular weight determinations which indicate that I is monomeric in CCl_4.

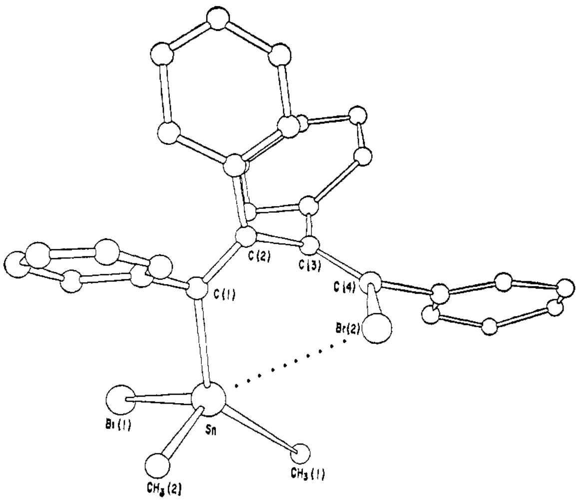

Figure 1. Molecular conformation of (4-bromo-1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadienyl)dimethyltin bromide (I). The intramolecular Sn–Br(2) interaction is shown by the dotted line.

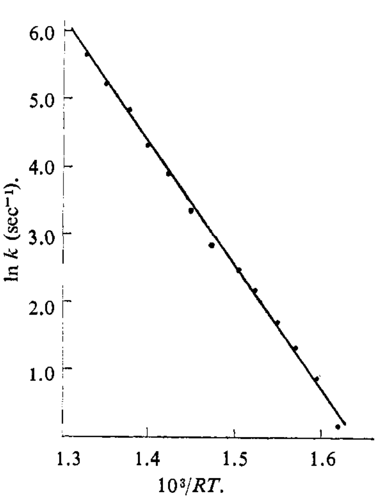

Figure 2. Temperature dependence (°K) of the rate constant (k) for methyl interchange of I in CCl_4.

mains as the most likely possibility. The magnetic nonequivalence of similar nuclei in an asymmetric environment has been well established,[4] and in this study magnetic nonequivalence arising from a preferred dissymmetric diene conformation is analogous to the nonequivalence observed in the dissymmetric biphenyls.[5]

To explain the absence of rotation about the C(2)–C(3) bond in I–III, we speculated that an internal tin–halogen bond served to stablize an unusual cisoid-skew conformation[6] at lower temperatures in nonbasic solvents. Diene rotation and methyl equivalence could be restored by breaking this weak bond, and this has been experimentally accomplished by (1) warming the sample, (2) adding a base to compete with Br for coordination to Sn, or (3) replacing the 4-halogen of I–III by H, as in IV.

The predicted molecular conformation of I has now been confirmed by a single-crystal X-ray diffraction study. The parameters of the monoclinic cell, a = 14.82, b = 18.65, c = 13.60 A, and β = 131.2°, give a calculated density of 1.562 g cm^{-3} with four molecules per unit cell. Absence of 0k0 reflections with k odd and $h0l$ with l odd indicates the centrosymmetric space group $P2_1/c$. The intensities of 1137 independent reflections were measured with Cu Kα radiation on the Picker automatic diffractometer using the 2θ scan technique. After the Sn and Br atoms had been located in the Patterson function, the C atoms were identified in an electron density map calculated using the heavy-atom phases. Refinement of the structure was terminated after four cycles of full-matrix least-squares variation of the positions and isotropic temperature factors of the Sn, Br, and C atoms, giving a value of R = 0.147. Additional X-ray intensity data are presently being collected, and further refinement is contemplated.

The structure (Figure 1) confirms the presence of a weak bond between Sn and Br(2) of length 3.769 ± 0.007 A, approximately 0.4 A less than the sum of the van der Waals radii.[7] To provide room for this interaction, the angle C(1)–Sn–CH_3(1) has opened to 130.3° from the normal tetrahedral value of 109.5°. Further evidence for pentacoordinate bonding is given by the increases in the lengths of the bonds at Sn from their normal values and an apparent lengthening of the C(4)–Br(2) bond. Observed and "normal" distances (parentheses)[8] for these bonds are (in angstroms): Sn–Br(1), 2.507 ± 0.007 (2.46); Sn–Cl(1), 2.19 ± 0.04 (2.14); Sn–CH_3(1) = Sn–CH_3(2), 2.24 ± 0.04 (2.18); and C(4)–Br(2), 2.01 ± 0.04 (1.89).

Because of the internal bonding and the steric requirements of the bulky substituents, I suffers considerable loss of conjugation energy as shown by the unusually large skew angle between the olefinic planes (73° from cisoid coplanar) and the large angles (50–70°) between the planes of the phenyl rings and the double bonds.

Rates of rotation about the C(2)–C(3) bond of I in CCl_4 at various temperatures were obtained by matching computer-generated[9] curves with the experimental spectra according to Sack[10] and Gutowsky.[11] A least-squares analysis of the Arrhenius plot (Figure 2) gave E^* = 18.30 ± 0.23 kcal/mole with log A = 13.

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(4) H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2196 (1962); E. I. Snyder, *J. Am. Chem. Soc.*, **85**, 2624 (1963), and references cited therein.

(5) W. L. Meyer and R. R. Meyer, *ibid.*, **85**, 2170 (1963).

(6) The usual preferred transoid coplanar diene conformation has been found to occur even in *cis,cis*-1,2,3,4-tetraphenylbutadiene, a close, though less sterically hindered, analog of I: I. L. Karle and K. S. Dragonette, *Acta Cyst.*, **19**, 500 (1965).

(7) The radius for Br is taken as 1.95 A (L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 263). The radius for Sn, 2.2 A, is estimated by extrapolating the values of neighboring elements (Sb, Te, I) on the periodic chart (see p 260), or alternatively by using the heuristic rule (p 263): r(van der Waals) = 0.8 + r(single bond).

(8) L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958, pp S10, S12, and S19. The covalent radius of the sp^2 C(1) is assumed to be about 0.04 A shorter than that of the methyl carbons.

(9) We are grateful to G. M. Whitesides for making available his EXCH 10 program.

(10) R. A. Sack, *Mol. Phys.*, **1**, 163 (1958).

(11) H. S. Gutowsky, R. L. Vold, and E. J. Wells, *J. Chem. Phys.*, 43, 4107 (1965).

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The Ionization of Dimethyl Sulfoxide

Sir:

We wish to report the results of a study of the rates of the base-catalyzed tritiation of dimethyl sulfoxide