

although there is evidence from the electronic spectrum for its presence. Thus, at nominal physiological pH some mixed mode of bonding may be present as neither the O,O or the N,O complex forms exclusively when metal and ligand are mixed.

We have found that two distinct bis complexes are isolated at opposite sides of pH 7. The amino acid type of complex is isolated at a lower pH presumably because only one proton need be removed to produce the unprotonated ligand donor atoms while for the catecholate binding two protons must be removed. Thus, in gross agreement with the predictions of solution studies,² the pH is a sensitive determinant of the binding mode of Cu and dopa, and at physiological pH both modes of bonding are possible.

Another potential determinant of the bonding mode is the nature of other ligands in the coordination sphere of Cu. Thus, Sigel and coworkers¹³ have shown that certain ternary complexes of Cu²⁺ have unexpected stability. In particular, if one of the ligands in the ternary complex is 2,2'-bipyridine (bipy) then the stable ternary complexes are formed when the second ligand is of the O,O-bidentate type such as oxalate, pyrophosphate, or catecholate. Thus, a ternary complex of Cu²⁺, bipy, and dopa might be expected to favor formation of the complex containing the O,O-dopa ligand. To test this idea we carried out solution studies by monitoring the appearance of the 23,000-cm⁻¹ absorption band as the pH was raised. This band has been assigned to ligand-to-metal charge transfer^{11,13} and is thus a clear diagnostic of the formation of the Cu-O,O-dopa linkage. We find, however, that in this case no substantial difference occurs in the pH at which this band first appears in the presence or absence of bipyridyl.

The two factors which we have discussed above, pH and other ligands in the coordination sphere, may finely tune the way in which Cu binds to dopa. In the present case the pH seems to be the dominant factor. These same considerations apply to metal complexes of adrenaline, noradrenaline, and other biogenic amines which are under investigation in our laboratory. Copper containing enzymes are known to be strongly involved in the metabolism of these molecules. Our discussion here thus points to two ways in which an enzyme (or perhaps a membrane receptor) could control the mode of binding of these ambidentate ligands.

(13) H. Sigel, D. B. McCormick, and F. A. Walker, *Inorg. Chem.*, **11**, 2756 (1972).

(14) Recipient of Camille and Henry Dreyfus Foundation Teacher-Scholar Award.

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Bicyclotropones

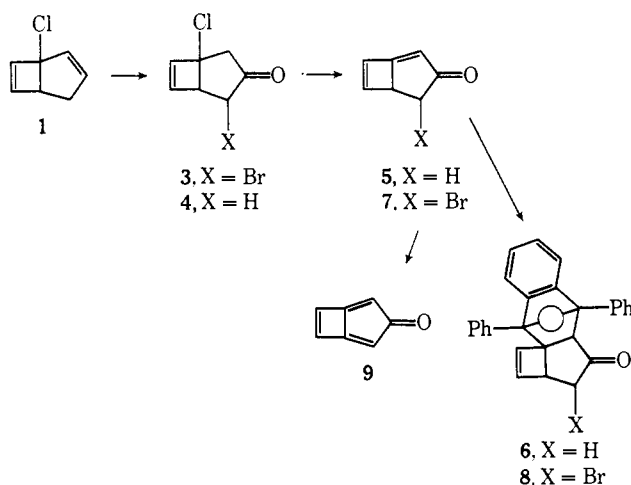
Sir:

Among the most interesting fused-ring compounds are those in which two systems with $4n$ π -electrons are fused to give a composite with $4n + 2$ π -electrons.

Such systems as octalene,¹ cyclooctatetraenocyclopentadienone,² cyclooctatetraenocyclobutadiene,³ and the fleetingly transient butalene⁴ (cyclobutadienocyclobutadiene) are examples. We now wish to report the detection of another member of this class, cyclobutadienocyclopentadienone (**9**), and some evidence contrasting the properties of **9** with those of an isomer **12**. Both compounds are formally derived from tropone (cycloheptatrienone) by bridging it in alternate ways.

The syntheses started with 1-chlorobicyclo[3.2.0]-hepta-3,6-diene (**1**).⁵ Reaction of this compound with *N*-bromosuccinimide in aqueous 90% dimethyl sulfoxide afforded the trans bromohydrin⁶ **2** which could be oxidized with Jones' reagent to the bromo ketone **3**.⁶ For model spectroscopic studies, this was converted with sodium iodide and boron trifluoride etherate to the chloro ketone **4**.⁶ On treatment with triethylamine in chloroform, this was converted to a solution of dienone **5**, with nmr signals at δ 7.48, 6.75, 5.56, and 3.84 for the vinyl and methine hydrogens, and a two-proton multiplet at δ 2.35 for the methylene group. In the uv, dienone **5** showed λ_{max} at 273 nm (THF solution). When the conversion of **4** to **5** was carried out in the presence of diphenylisobenzofuran, the adduct⁶ **6**, mp 170–171°, was obtained in 91% yield.

Treatment of the bromochloro ketone **3** with triethylamine first led to bromodienone **7** in solution. This could be trapped if it were generated in the presence of diphenylisobenzofuran to afford adduct⁶ **8**, mp 203–206°. Solutions of **7** showed uv absorption with λ_{max} 278 nm, but, on standing in solution with base, **7** was converted to a new species which we identify as the bicyclotropone **9**. This has in the uv a



λ_{max} at 284 nm, and in the nmr it shows two vinyl absorptions of equal intensity at δ 6.85 and 6.56. The same uv spectrum could be produced from **3** using KO-*t*-Bu. The spectral shift is comparable to the 7-nm difference between tropone and 2,3-dihydrotropone.

(1) R. Breslow, W. Horspool, H. Sugiyama, and W. Vitale, *J. Amer. Chem. Soc.*, **88**, 3677 (1966).

(2) Ronald Breslow, William Vitale, and Kurt Wendel, *Tetrahedron Lett.*, **6**, 365 (1965).

(3) G. Schröder and H. Röttele, *Angew. Chem., Int. Ed. Engl.*, **7**, 635 (1968).

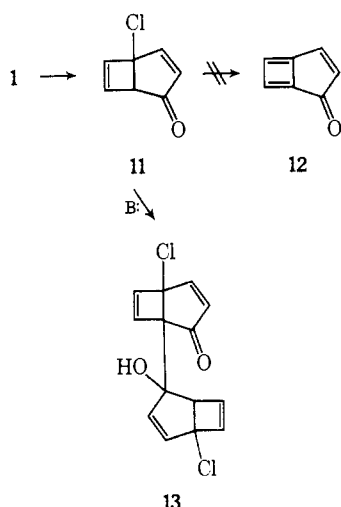
(4) R. R. Jones and R. G. Bergman, *J. Amer. Chem. Soc.*, **94**, 660 (1972); J. Napierski, Ph.D. Thesis, Columbia University, 1972.

(5) R. Breslow, W. Washburn, and R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 196 (1969).

(6) The structure is supported by mass and nmr spectra.

Solutions of **9** were not stable over time. Thus the uv spectrum disappeared over several hours at room temperature, while the more concentrated nmr solutions were generated at -48° and the signals assigned to **9** disappeared on warming the solution to -10° . This concentration dependence suggests a dimerization or polymerization of **9**, although well-defined adducts could not be obtained from the decomposition.

An approach to an isomeric trienone was undertaken by treating chlorodiene **1** with *N*-bromosuccinimide in CCl_4 under free radical conditions. A mixture^{6,7} of allylic bromides **10** was obtained which was converted with silver tosylate and DMSO, followed by sodium bicarbonate, to chlorodienone⁶ **11**, bp $40\text{--}42^\circ$ (0.7 Torr). By contrast with **7** this resisted all attempts at HX elimination, as did the bromodienone⁶ corresponding to **11** (derived from the bromodiene⁶ related to **1**). Thus treatment of **11** with strong bases such as DBN or NaH at reflux for many hours led to recovered starting material, and even with an excess of lithium diethylamide some starting material was recovered. The principal product from this latter reaction is, however, the dimer⁶ **13** obtained from an aldol re-



action; this dimer could be converted to the corresponding acetate,⁶ mp $134\text{--}135^\circ$. Thus when the enolate derived from **11** is in fact formed with base, it does not lose chloride ion but instead undergoes a bimolecular aldol addition reaction.

These data indicate clearly that the bicycloprenes **9** and **12** do not share the stability of tropone itself. While **9** seems to have some stability on solution and is thus perhaps a more stable molecule than is cyclopentadienone, **12** seems to be extremely unstable, as evidenced by the failure of the enolate derived from **11** to lose chloride ion. Thus the properties of **9** and **12** seem to reflect the stabilities of their component rings, rather than that of the peripheral trienone system.

Acknowledgment. Support of this work by the National Institutes of Health is gratefully acknowledged.

(7) W. Washburn, Ph.D. Thesis, Columbia University, 1971.

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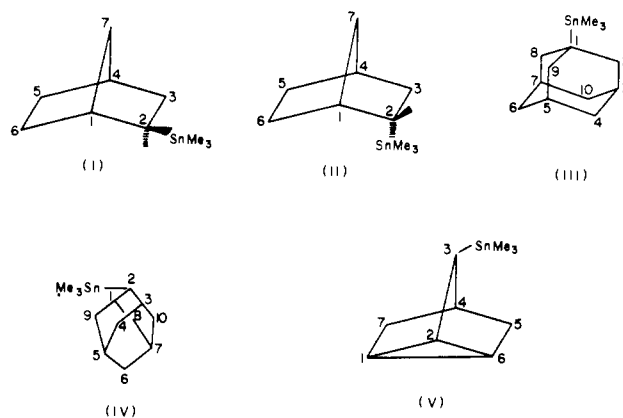
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Karplus-Type Dependence of Vicinal $^{119}\text{Sn}\text{--}^{13}\text{C}$ Coupling¹

Sir:

It has been reported recently that the magnitude of 3J ($^{119}\text{SnCC}^{13}\text{C}$) is dependent upon the dihedral angle between the coupling nuclei.¹ In the present communication, we report the ^{13}C nmr parameters for a series of compounds which incorporate a range of SnCCC dihedral angles and define more precisely the relationship between $^3J(\text{SnCCC})$ and the dihedral angle.

The new compounds studied are *exo*- and *endo*-2-norbornyl, 1- and 2-adamantyl, and 3-nortricyclyltrimethylstannane (I–V), respectively. All yielded satisfac-



factory elemental analysis and ^1H nmr spectra. The ^{13}C chemical shift and coupling constant data are given in Table I. Assignments were made by (i) off-resonance decoupled spectra, (ii) the magnitude of $^1J(^{119}\text{Sn}\text{--}^{13}\text{C})$ for ^{13}C nuclei directly attached to ^{119}Sn , (iii) comparisons of the chemical shift with the parent hydrocarbons and of the shifts of ^{13}C resonances on substitution in other hydrocarbons, (iv) the relative magnitudes of vicinal $J(^{119}\text{SnCC}^{13}\text{C})$ coupling constants, and (v) general considerations of compression effects on ^{13}C nuclei in γ positions.

Pure I (from *exo*-2-bromonorbornane and $(\text{CH}_3)_3\text{SnLi}$)² was examined in conjunction with a mixture of I and II (from³ the Grignard reagent of *exo*-2-bromonorbornane and $(\text{CH}_3)_3\text{SnCl}$). Note that C_7 in I (γ effect -0.1 ppm) is upfield from C_7 in II (γ effect $+2.2$ ppm) by 2.3 ppm, while C_6 in II (γ effect -0.4 ppm) is upfield from C_6 in I (γ effect $+3.3$ ppm) by 3.9 ppm.⁴ (The corresponding γ effects for C_7 are 3.7 ppm in *exo*-2-methylnorbornane and $+0.2$ in *endo*-2-methylnorbornane. For C_6 , γ effects of -1.1 and -7.7 ppm are observed for *exo*- and *endo*-2-methylnorbornanes, respectively.)⁵ Because of difficulties in differentiating C_5 and

(1) (a) This is paper II of the series " ^{13}C Fourier Transform Nmr Study of the Organotin Compounds," by the group from Albany; Paper I of this series: H. G. Kuivila, J. L. Considine, R. J. Mynott, and R. H. Sarma, *J. Organometal. Chem.*, **55**, C11 (1973). (b) See also D. Doddrell, M. L. Bullpitt, C. J. Moore, C. W. Ford, W. Kitching, W. Adcock, and B. D. Gupta, *Tetrahedron Lett.*, 665 (1973).

(2) For method used, see (a) G. S. Koerner, M. L. Hall, and T. G. Traylor, *J. Amer. Chem. Soc.*, **94**, 7206 (1972); (b) H. G. Kuivila, J. L. Considine, and J. D. Kennedy, *ibid.*, **94**, 7202 (1972).

(3) F. R. Jensen and K. L. Nakamaye, *J. Amer. Chem. Soc.*, **88**, 3437 (1966).

(4) Notice that the γ -shifts are slightly negative for situations of strong compressional interaction with $(\text{CH}_3)_3\text{Sn}$, but positive (*i.e.*, to lower field) otherwise. These γ -shifts are small considering the data for the *exo,endo*-2-methylnorbornanes.

(5) Data from G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance," Wiley-Interscience, New York, N. Y., 1972, p 46, and references therein.