

Synthesis of Tetraphenylstannacyclopentadienes (Stannoles).

1. Alkylation of 1,1-Dihalostannoies Leading to Lithium 1,1-Bis(η^1 -cyclopentadienyl)-1-halo-2,3,4,5-tetraphenylstannole, an $[R_4SnX]^-$ Anion with Pseudorotating Axial- and Equatorial-Fluxional η^1 -Cyclopentadienyl Groups

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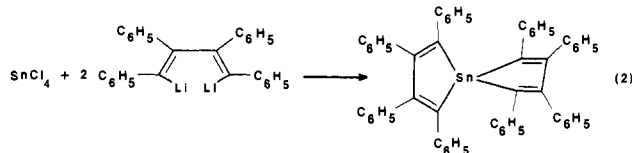
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Abstract: 1,1-Dibromo- and 1,1-diiodo-2,3,4,5-tetraphenylstannacyclopentadienes (dibromo- and diiodostannoies) formed from controlled phenyltin cleavage of hexaphenylstannole by elemental bromine and iodine, respectively, undergo conventional alkylation by methyllithium to form the expected 1,1-dimethylstannole, but treatment with excess lithium or thallium cyclopentadiene yields cubic crystals whose analytical data agree with the formulation $X(C_5H_5)_2SnC_4(C_6H_5)_4M$ where $X = Br$ and $M = Li$ and Tl and where $X = I$ and $M = Li$. Infrared ν_{asym} and ν_{sym} (Sn-Br) absorptions in the starting dibromostannole are replaced by a single feature at 225 cm^{-1} in the $X = Br$ products, and absorptions in the $3000\text{--}1595\text{--}695\text{ cm}^{-1}$ region specify the η^1 -cyclopentadiene nature of the C_5H_5Sn unit. The products exhibit two upfield resonances in both the proton and carbon-13 NMR with couplings to tin [$^2J(^{13}Sn-C^{-1}H)$] = 25.4 Hz for the $X = Br$ and $M = Li$ product and 23.2 Hz for the $X = I$ and $M = Li$ product] and the correct integration ratios for two cyclopentadiene rings per stannole unit. Only slight broadening of the fluxional C_5H_5 resonances is observed on cooling to $-100\text{ }^\circ\text{C}$; however, the two resonances of equal intensity undergo reversible collapse to a single, unshifted peak at $90\text{ }^\circ\text{C}$ for $X = Br$ and $100\text{ }^\circ\text{C}$ for $X = I$. From the slopes of the Arrhenius plots, ΔE^\ddagger is 12.2 and 11.4 kcal/mol , respectively. The tin-proton coupling constants remain relatively constant over the ca. $200\text{ }^\circ\text{C}$ range studied. Conductivity data in dilute acetonitrile are typical of weak 1:1 electrolytes. An ionic formulation is proposed in which a five-coordinated stannacyclopentadiene with one halogen atom remaining from the starting material and containing fluxional η^1 -cyclopentadiene groups undergoes pseudorotation to interconvert axial and equatorial positions in an $[R_4SnX]^-$ anion. The appearance of both cyclopentadienyl resonances in the NMR from the onset of the reaction rules out the intermediacy of a 1-(η^1 - C_5H_5), 1-halostannole, with subsequent adduct formation with $C_5H_5^-$ anion. An alternative mechanism would proceed via $(\eta^1-C_5H_5)_2SnC_4(C_6H_5)_4$ with subsequent metal halide uptake, but the addition of 1,4-dithio-1,2,3,4-tetraphenylbuta-1,3-diene to bis(η^1 -cyclopentadienyl)tin dichloride fails to yield a pure material.

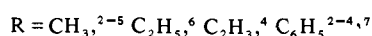
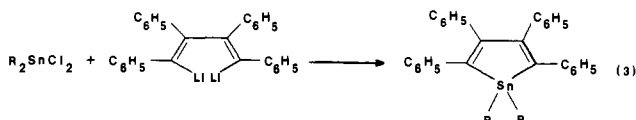
The discovery in 1941 that diphenylacetylene (tolan) undergoes dimerization by the action of lithium metal to form *cis,cis*-1,4-dilithio-1,2,3,4-tetraphenylbutadiene (eq 1)¹ was developed be-



ginning in 1959 into an apparently general reaction with organometallic and organometalloidal di- and tetrahalides to yield monocyclic and spiro heterocyclopentadienes (metalloles), respectively.^{2,3} In the tin series, octaphenyl-1,1-spirobistannole can be prepared from tin(IV) chloride (eq 2)^{2,3} and the 1,1-di-

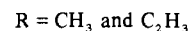
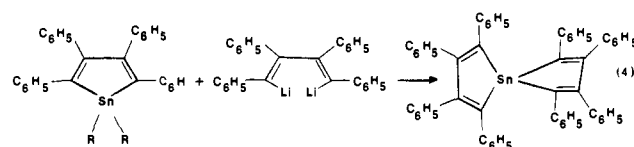


organo-2,3,4,5-tetraphenylstannoies from the corresponding diorganotin(IV) dichlorides (eq 3). When the dilithium reagent

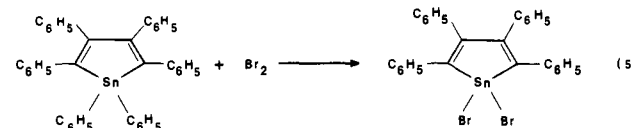


is added to the dihalide, the latter is always in excess, and the expected stannoies as shown in eq 3 are formed. Reverse addition,

on the other hand, leads to alkytin bond cleavage-cyclization by the dilithium reagent (eq 4).⁴



The key precursor intermediate in the development of the derivative chemistry of the stannoies is the dihalide. Our synthesis of the dibromostannole from phenyltin bond cleavage of the hexaphenylstannole by elemental bromine has been reported in a preliminary form, eq 5.⁸ In this series of papers we report our



results on the derivative chemistry of the stannoies. We begin by describing the synthesis of the 1,1-dihalostannoies and their alkylation which produced an unexpected result.

Experimental Section

Organotin starting materials were of commercial grade and were used without further purification. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Boiling points were determined at constant pressure with a still head thermometer and are uncorrected. Gas chromatographic analyses were performed on

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a Hewlett-Packard Model 5750 laboratory chromatograph equipped with a thermal conductivity detector using helium as the carrier gas. Volatiles were collected at -196°C in U-tubes. Elemental analyses were carried out by Galbraith Laboratory, Inc., Knoxville, TN, and by Instranal Laboratory, Inc., Rensselaer, NY. Organotin compounds with high molecular weight (over 700) would often not give consistent analyses. Tin was determined gravimetrically as the oxide, and chlorine, bromine, and iodine were determined by potentiometric titration with silver(I) nitrate. Molecular weights were determined in benzene (a suspected carcinogen) on a Hewlett-Packard Model 201A vapor pressure osmometer. Mass spectra were recorded on A.E.I. MS-902 and Hewlett-Packard 5985B GC/MS instruments at 70 eV. Nuclear magnetic resonance spectra were recorded on Varian A-60, HA-100, and XL-100 instruments. Tetramethylsilane was used as an external standard, and field width was calibrated with a solution of tetramethylsilane-benzene in carbon tetrachloride. Infrared spectra were recorded in the $4000\text{--}200\text{-cm}^{-1}$ range on Beckman IR-12 or 4250 infrared spectrophotometers and calibrated with polystyrene. Samples were run as liquid smears or Nujol mulls on potassium bromide plates or in polyethylene cells. A Beckman IR-11 spectrophotometer was used to examine the far-infrared region ($400\text{--}33\text{ cm}^{-1}$). Mössbauer spectra were recorded on a constant acceleration, cam-drive spectrometer previously described,⁹ with the sample mounted in a cryostat at liquid-nitrogen temperature, or on a Ranger Engineering constant acceleration spectrometer equipped with an NaI scintillation counter using $\text{Ca}^{119\text{m}}\text{SnO}_3$ (New England Nuclear Corp.) as both source and standard reference material for zero velocity. Velocity calibration was based on both β -tin and natural iron foils. Data were fitted to Lorentzian curves by standard, nonlinear, least-squares techniques. The Ranger Engineering variable-temperature liquid-nitrogen Dewar and controller used in this study are regulated by a variable-bridge, silicon-controlled rectifier circuit and are accurate to $\pm 1\text{ K}$.

1,4-Dilithio-1,2,3,4-tetraphenylbutadiene.¹⁰ To a solution of diphenylacetylene (tolan) (10.69 g, 0.06 mol) in anhydrous diethyl ether (30 mL) was added lithium wire (0.7 g, 0.1 mol), and the solution was stirred at room temperature under a nitrogen atmosphere for 4 h. After a 10-min induction period, an intense red color developed and a yellow solid began to precipitate. This induction time increased significantly with decreasing diphenylacetylene concentration and was about 30 min for a 0.3–0.4 M solution. At concentrations below 0.3 M, it was found that any moisture in the system greatly retarded the rate of reaction. If freshly dried equipment is not used, the surface moisture increases the induction period from ca. 30 min to as much as 12 h. The reaction is initially mildly exothermic, and if the concentration of diphenylacetylene is doubled, cooling with a rapid flow of nitrogen gas becomes necessary.

This procedure is favored over previous methods^{1,7} because the precautions necessary to exclude water are much less stringent.

1,1,2,3,4,5-Hexaphenylstannole.^{2,4,7,11} Diphenyltin dichloride (10.32 g, 0.03 mol) was placed in a three-neck flask equipped with a pressure-equalizing funnel, condenser, and gas inlet tube and dissolved in freshly distilled tetrahydrofuran (200 mL). A solution of the dilithium reagent was then added to the addition funnel via a hypodermic syringe. This technique separated the excess lithium which remains behind. The red solution and yellow precipitate were then added dropwise to the colorless diphenyltin dichloride solution. An additional 100 mL of diethyl ether was used to transfer the dilithio compound to the organotin solution, which was cooled in an ice bath during the addition. The reaction was mildly exothermic. The resulting green-yellow solution was stirred under nitrogen at reflux for 2 h. The ethers were removed in vacuo, dichloromethane (250 mL) was added to the residue, and the resulting suspension was filtered. After concentration to ca. 75 mL, absolute ethanol (100 mL) was added. The yellow title compound precipitated upon cooling with Dry Ice. Recrystallization from dichloromethane-ethanol (1:1) resulted in a yellow solid (mp $172\text{--}173^{\circ}\text{C}$), in a yield of 65% based on tolan. The compound was identified by comparison of melting point^{2,4,7} and Mössbauer (IS = $1.39 \pm 0.02\text{ mm/s}^4$) data with those of an authentic sample.

An additional tin-containing white powder (mp $108\text{--}110^{\circ}\text{C}$) was isolated in 20% yield based on tolan during an attempt to increase the yield of hexaphenylstannole. The Mössbauer spectrum contained a doublet with IS of 1.31 ± 0.02 and QS of $2.77 \pm 0.04\text{ mm/s}$, and the infrared spectrum contained prominent bands at 3060 (w), 3040 (w), 1600 (m), 1575 (w), 1432 (m), 1075 (m), 1023 (m), 1000 (m), 730 (s), 695 (s), and 440 (s) cm^{-1} . The (1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadi-

nyl)diphenyltin chloride structure is consistent with these data. Anal. Calcd for $\text{C}_{40}\text{H}_{31}\text{Cl}_2\text{Sn}$: C, 72.18; H, 4.66; Cl, 5.26; Sn, 17.89. Found: C, 69.87; H, 4.51; Cl, 4.92; Sn, 17.05.

1,1-Dibromo-2,3,4,5-tetraphenylstannole.⁸ A solution of hexaphenylstannole (23.5 g, 37.3 mmol) in carbon tetrachloride (200 mL) was cooled in a dry ice-acetone bath to $-30\text{--}40^{\circ}\text{C}$ under a nitrogen atmosphere, and bromine (12.0 g, 75.0 mmol) in carbon tetrachloride (200 mL) was added dropwise. The original yellow-green color lightened with the addition of the halogen. The rate of decolorization decreased after half of the bromine had been added, and the remainder of the reaction was carried out at $-20\text{--}30^{\circ}\text{C}$ for a period of 2 h. The color of the solution passed from yellow-green to white to light brown to red-dish orange. The cloudy solution became clear when it was allowed to warm to room temperature. The solvent was then stripped in vacuo to leave a yellow oil which was dissolved in a methylene chloride-ethanol mixture to give white crystals (22.5 g, 35.4 mmol, mp $167.5\text{--}168.0^{\circ}\text{C}$ with decomposition) in 95% yield based on hexaphenylstannole. The concentrated mother liquor was found to contain bromobenzene, identified by its infrared spectrum.

The Mössbauer spectrum contained a doublet with IS of 1.48 ± 0.03 and QS of $2.88 \pm 0.06\text{ mm/s}$. The infrared spectrum contained prominent bands at 3075 (w, b), 3050 (w, b), 1600 (w, sh), 1575 (w, b), 1485 (w, b), 1445 (s, b), 763 (m), 732 (s, b), 692 (s), 576 (m), 553 (s), 525 (m), 445 (m), 330 (w, b), 271 (m), 252 (s), 232 (s), and 194 (m) cm^{-1} . The mass spectrum contained fragments up to m/e 638. An abundant, tin-containing fragment appeared at m/e 356, with a less abundant fragment at m/e 631. Anal. Calcd for $\text{C}_{28}\text{H}_{20}\text{SnBr}_2$: C, 52.96; H, 3.16; Sn, 18.69; mol wt, 634.97. Found: C, 51.69; H, 3.19; Sn, 18.21; mol wt, 636.

1,1-Diiodo-2,3,4,5-tetraphenylstannole. Hexaphenylstannole (5.9 g, 9.3 mmol) was dissolved in carbon tetrachloride (50 mL) and cooled while the solution was stirred under nitrogen to 0°C in an ice bath. To this was added a solution of iodine (4.8 g, 18.75 mmol) in carbon tetrachloride (150 mL). The color of the original solution lightened with the addition of iodine, passing from yellow to orange to pink to red to purple. The solution was stirred under nitrogen at room temperature for 2 h after the addition of the iodine was complete, the solvent was removed in vacuo, and the remaining red-brown oil was dissolved in methylene chloride and filtered. Precipitation resulted with the addition of absolute ethanol and cooling in Dry Ice. After recrystallization from methylene chloride-ethanol a white solid was obtained (mp $167\text{--}168^{\circ}\text{C}$, 5.02 g, 74% yield). The mother liquor from the solid was concentrated and found to contain iodobenzene, identified by its infrared spectrum.

The infrared spectrum contained prominent bands at 3050 (w, b), 1600 (w), 1574 (w), 1490 (w), 1442 (m), 762 (m), 731 (s), 695 (s), 565 (m), 548 (s), 513 (m), 444 (m), 345 (w), 208 (w), and 184 (m) cm^{-1} . The Mössbauer spectrum was a doublet with IS of 1.61 ± 0.03 and QS of $2.32 \pm 0.06\text{ mm/s}$. Anal. Calcd for $\text{C}_{28}\text{H}_{20}\text{SnI}_2$: C, 46.10; H, 2.74; Sn, 16.32; I, 34.84. Found: C, 45.77; H, 2.82; I, 36.62; Sn, 15.79.

1,1-Dimethyl-2,3,4,5-tetraphenylstannole.^{2,5} Methylolithium in ether (8.29 mL, 17.75 mmol) was added dropwise to an ether solution of dibromotetraphenylstannole (4.00 g, 6.26 mmol). The reaction was cooled in a Dry Ice-acetone bath under nitrogen, and the temperature slowly was raised to ambient when the solution became a yellowish green color. After removal of the solvent, the residue was treated with toluene (20 mL) and lithium bromide was removed by filtration. 1,1-Dimethyl-2,3,4,5-tetraphenylstannole was precipitated and washed with hexane to give yellow crystals (1.2 g, 2.38 mmol) (mp $189.5\text{--}189.0^{\circ}\text{C}$ vs. lit.⁵ $185\text{--}192^{\circ}\text{C}$) in 37.8% yield. The infrared spectrum consisted of prominent absorptions at 3060 (w), 3040 (w), 1600 (m), 1575 (w), 1450 (m), 1265 (w), 1150 (w), 1070 (m), 1020 (m), 919 (m), 880 (w), 840 (w), 780 (m), 759 (s), 745 (m), 729 (s), 690 (s), 540 (s), 520 (s), 510 (m), and 400 (w) cm^{-1} was consistent with this formulation.⁵ The NMR spectrum in CDCl_3 contained a sharp singlet of methyl proton resonance at δ 0.65 with $|^2J(^{119}\text{Sn-C-H})| = 56.2\text{ Hz}$, in addition to the phenyl group proton multiplet, and integration gave a ratio of 3.62:1 for phenyl:methyl protons (calcd 3.33:1).

Lithium 1,1-Bis(η^1 -cyclopentadienyl)-1-bromo-2,3,4,5-tetraphenylstannole. (a) Lithiation of Cyclopentadiene.¹² Technical dicyclopentadiene (100 mL, 87.5 g) was placed in a 250-mL, one-necked, round-bottom flask equipped with a calcium chloride drying tube and a Newman stopcock-type distilling head (Ace Glass Co.) and 100-mm Vigreux column with the receiver in a Dry Ice bath. The flask containing dicyclopentadiene was heated to 160°C until the cyclopentadiene distilled smoothly at $38\text{--}46^{\circ}\text{C}$ and a little dicyclopentadiene refluxed from the cold-finger condenser.

Freshly cracked cyclopentadiene monomer (1.30 mL, 15.75 mmol) in tetrahydrofuran (30 mL) was chilled in a Dry Ice bath and treated with

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n-butyllithium in hexane (6.10 mL, 1.6 M, 9.76 mmol) dropwise at -60°C to -70°C . The resulting clear solution then was allowed to warm to room temperature with stirring.

(b) Formation of Lithium 1,1-Bis(η^1 -cyclopentadienyl)-1-bromo-2,3,4,5-tetraphenylstannole. To a solution of lithium cyclopentadiene was added dibromotetraphenylstannole (3.0 g, 4.72 mmol) at room temperature to give a light brown solution which was stirred under argon for 3 h. The hexane-tetrahydrofuran solvent was removed in vacuo, and the yellowish white solid was treated with toluene (20 mL), the lithium bromide filtered through a Schlenk tube (Ace Glass Co. Model No. 7759), and the filtrate collected in the Schlenk reaction vessel (Ace Glass Co. Model No. 7756) and concentrated to a volume of 10 mL under vacuum before adding hexane (7 mL). A tan solid was obtained by cooling the mixture to Dry Ice temperature for 1 h. Recrystallization from toluene-hexane required 7 days to give cubic-shaped, tan crystals (0.8 g, 1.16 mmol) which started to shrink at 158.5°C and decomposed at 160.5°C to give a bright red material.

The infrared spectrum showed bands at 3060 (w, b), 1595 (w), 1570 (w), 1485 (m), 1524 (m), 1027 (m), 880 (s, d), 755 (s, sh), 710 (s), 695 (s), 578 (s, sh), 555 (m), 335 (s, sh), 252 (m), and 225 (w) cm^{-1} . The Mössbauer spectrum was a doublet with IS of 1.41 ± 0.06 and QS of $1.03 \pm 0.12\text{ mm/s}$. The proton and carbon-13 NMR spectra at room temperature appear similar, with two upfield resonances ascribable to the tin-cyclopentadienyl system in addition to the phenyl group multiplet: $^1\text{H } \delta$ 4.38 and 4.13 (in toluene, or δ 4.28 and 4.06 in CDCl_3), [$^2J(^{119}\text{Sn}-^1\text{H})$] = 25.4 Hz at 40°C ; ^{13}C 114.3 and 114.8 ppm (Me_4Si) standard, [$^2J(^{119}\text{Sn}-^{13}\text{C})$] = 30.2 Hz at ambient. The integration ratio (2.0:1 calcd; 2.2:1 found) correspond to two cyclopentadiene groups per stannole ring. The temperature-dependent NMR spectrum showed that the two cyclopentadienyl singlets coalesce at 90°C to give on sharp singlet at 5.92 ppm. Anal. Calcd for $\text{C}_{38}\text{H}_{30}\text{BrSnLi}$: C, 65.94; H, 4.37; Sn, 17.15; Li, 1.00. Found: C, 68.13; H, 4.48; Sn, 17.53; Li, 0.69.

Lithium 1,1-Dicyclopentadienyl-1-iodo-2,3,4,5-tetraphenylstannole. Freshly cracked cyclopentadiene monomer (1.30 mL, 15.75 mmol) in tetrahydrofuran (30 mL) was cooled in a Dry Ice-acetone bath and treated with *n*-butyllithium (2.76 mL, 3.53 M in hexane, 9.76 mmol) dropwise at -60 to -70°C . The resulting clear solution was then allowed to warm to room temperature with stirring under a nitrogen atmosphere.

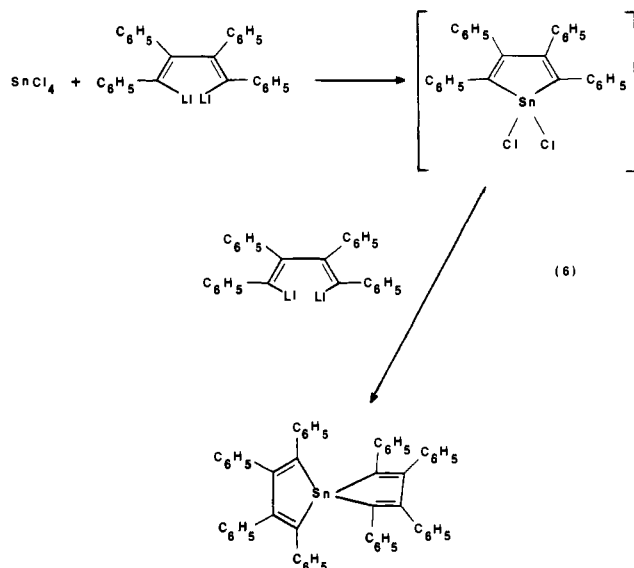
To the solution of lithium cyclopentadiene was added diiodotetra-phenylstannole (3.44 g, 4.72 mmol) at room temperature to give a light brown solution which was stirred under nitrogen for 4 h. The tetrahydrofuran-hexane solvent was removed in vacuo, the light brown solid treated with toluene (30 mL), and the lithium iodide removed by filtration under nitrogen. The solution was concentrated to 10 mL under vacuum and hexane (10 mL) added. A light brown solid was obtained by cooling to Dry Ice temperature (0.69 g, 0.94 mmol, 20% yield). The solid began to melt at 153°C and decomposed at 156°C .

The infrared spectrum showed bands at 3060 (w), 1595 (m), 1575 (m), 1485 (m), 1442 (s), 1075 (m), 1025 (s), 914 (m), 883 (s), 785 (s), 753 (s), 726 (s), 695 (s), 581 (s), 552 (s), 332 (m), 328 (s), and 255 (m) cm^{-1} . The Mössbauer spectrum was a doublet with IS of 1.49 ± 0.03 and QS of $0.96 \pm 0.05\text{ mm/s}$. The proton NMR spectrum at room temperature contained two resonances attributed to the tin-cyclopentadienyl system in addition to the phenyl group multiplet. The resonances were located at δ 4.54 and 4.21 (relative to Me_4Si) in CDCl_3 . The temperature-dependent NMR spectra showed that these two resonances coalesce to give one sharp singlet at 100°C . Anal. Calcd for $\text{C}_{38}\text{H}_{30}\text{SnI}$: C, 61.71; H, 4.06; Sn, 16.10; I, 17.19. Found: C, 62.93; H, 4.32; Sn, 15.62; I, 16.43.

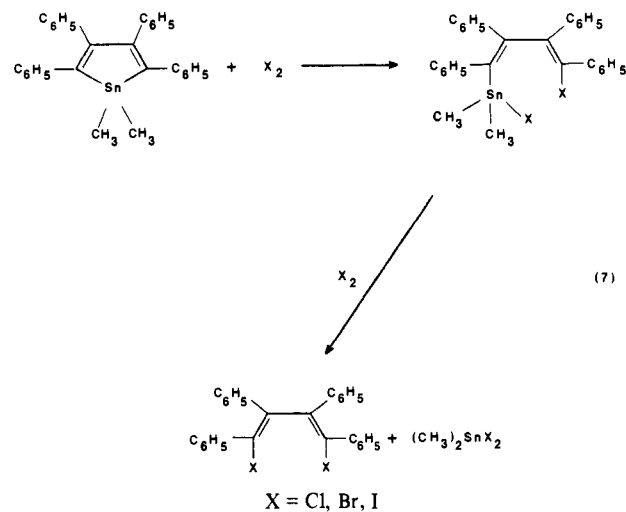
Discussion

The key step in working out the derivative chemistry of the stannoles is the development of a convenient synthesis of a 1,1-dihalostannole. While in the initial syntheses of the metalloles it was assumed that the 1,1-dichlorostannole was formed as an intermediate en route to the spiro compound (eq 6) and 1,1-dibromo-2,3,4,5-tetraphenylcyclopentadiene could be prepared by the addition of carbon tetrabromide to 1,4-dithio-2,3,4,5-tetraphenylbutadiene⁷ and the analogous dichloroformole by the addition of the dilithio reagent to germanium tetrachloride:¹³ all attempts to isolate the 1,1-dichlorostannole from the synthesis depicted in eq 6 or by other routes have thus far failed.

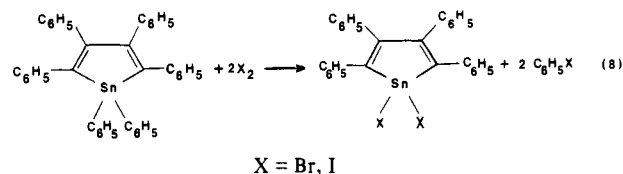
Instead, advantage can be taken of the well worked-out cleavage of tin-carbon bonds by elemental halogens. In these reactions R_4Sn species react stepwise, but the last two groups usually resist cleavage somewhat. Thus, R_2SnX_2 compounds can be prepared



in this manner. The ease of cleavage of the various organic groups from tin is known to decrease in the order aromatic > vinyl > alkyl.¹⁴⁻¹⁶ In the stannole series the action of elemental halogens on 1,1-dimethyl-2,3,4,5-tetraphenylstannole results in the cleavage of the olefinic ring carbon to tin bonds while preserving the methyltin bonds (eq 7).⁵ We have found, however, that controlled



bromination or iodination of hexaphenylstannole occurs preferentially at the exo-cyclic phenyltin bond to give the desired dihalostannole (eq 8). The far-infrared spectra of these compounds



contain absorption bands which can be assigned to the $\nu_{\text{asym}}(\text{Sn}-\text{Br})$ and $\nu_{\text{sym}}(\text{Sn}-\text{Br})$ modes at 252 and 233 cm^{-1} , respectively,^{17,18} and to the $\nu_{\text{asym}}(\text{Sn}-\text{I})$ and $\nu_{\text{sym}}(\text{Sn}-\text{I})$ modes at 208 and 184 cm^{-1} , respectively.¹⁷ The remainder of the spectrum resembles that of

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Table I. Tin-119m Mössbauer Data for the Dihalostannoles, Their Derivatives, and Related Organotin(IV) Compounds at 77 K in mm s⁻¹

compd	IS	QS	ρ
(η^1 -C ₅ H ₅) ₄ Sn ^a	1.48 ± 0.01		
(η^1 -C ₅ H ₅) ₂ SnCl ₂ ^{b,c}	1.44 ± 0.03	1.88 ± 0.06	
(η^1 -C ₅ H ₅) ₂ SnBr ₂ ^b	1.58 ± 0.06	1.67 ± 0.12	
(η^1 -C ₅ H ₅) ₂ SnI ₂ ^b	1.68 ± 0.06	1.43 ± 0.12	
(C ₂ H ₅) ₂ SnCl ₂ ^{d,e}	1.49–1.70	3.13–3.81	
(C ₂ H ₅) ₂ SnBr ₂ ^{d,e}	1.68–1.70	3.27–3.48	
(C ₂ H ₅) ₂ SnI ₂ ^{d,e}	1.31–1.78	2.97–3.24	
1,1-dibromostannole ^a	1.48 ± 0.03	2.88 ± 0.06	1.95
1,1-diiodostannole ^a	1.61 ± 0.03	2.32 ± 0.06	1.44
lithium 1,1-Bis(η^1 -cyclopentadienyl)-1-bromo-2,3,4,5-tetraphenylstannole ^a	1.41 ± 0.06	1.03 ± 0.12	0.73
lithium 1,1-Bis(η^1 -cyclopentadienyl)-1-iodo-2,3,4,5-tetraphenylstannole ^a	1.49 ± 0.03	0.96 ± 0.05	0.65

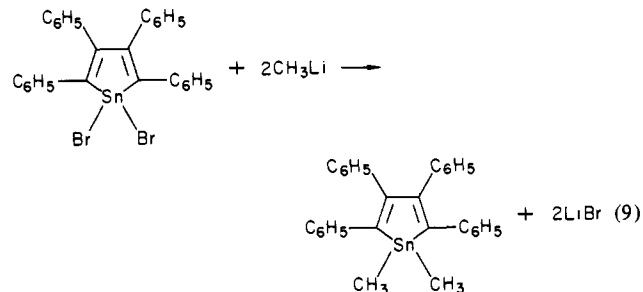
^a This work. ^b Reference 25. ^c Quoted as IS = 1.51 ± 0.06 and QS = 1.83 ± 0.12 mm/s in ref 25. ^d Reference 19. ^e Reference 44.

hexaphenylstannole.⁷ The tin-119m Mössbauer spectra are doublets with isomer shift (IS) and quadrupole splitting (QS) values consistent with four-coordinated diorganotin(IV) dihalides¹⁹ as shown in Table I. Variable-temperature Mössbauer spectroscopy can give further evidence for the structure of organotin solids.^{20,21} The plot of the logarithms of the areas under the resonance lines, ln(A_T/A₇₇), normalized to the area under the resonance curves at 77 K, vs. temperature for the dibromostannole between 77 and 95 K has a slope of $-2.22 \times 10^{-2} \text{ K}^{-1}$ (regression analysis data: intercept at $T = 0$, 1.719; correlation coefficient, $\gamma = -0.999$; number of points, 3). This rather steep decay of the Mössbauer effect is strong evidence that the dibromostannole exists in its crystal as an assemblage of individual, weakly held monomers.

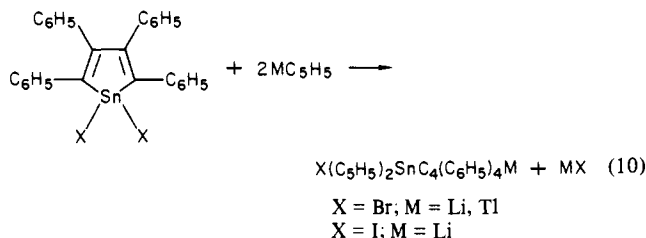
The mass spectra of both the dihalostannoles contain an abundant fragment at m/e 356 which can be assigned as [C₆H₅C=C(C₆H₅)-C(C₆H₅)=CC₆H₅]⁺; however, while the dibromo derivative exhibits a tin-bearing fragment centered at m/e 638, in the vicinity of the parent peak at m/e 641 (calcd), the mass spectrum of the iodo derivative does not contain its parent peak or, indeed, any peaks ascribable to organotin fragments. The most abundant tin-bearing peaks are found centered at m/e 120, 247, and 374. These polyisotopic peaks can be assigned to Sn, SnI, and SnI₂, respectively.

The dihalostannoles undergo substitution and complexation reactions typical of a diorganotin dihalide^{14–16} except that the stannole ring constrains the tin-carbon bond vectors into configurations different from those encountered in the conventional derivatives, and the unsaturated butadienoid residue exerts an electrical effect on the properties of the tin atom. In addition, the tetraphenyl substitution and presumably planar structure of the stannole ring will have a steric effect on the reactions of the dihalostannoles and on the properties of the resulting products.²² Nevertheless, alkylation of 1,1-dibromostannole by methyl lithium yields the expected 1,1-dimethylstannole (eq 9).^{2–5} All attempts to reduce the dibromostannole with lithium aluminum hydride resulted in a vile-smelling material which produced severe headaches in our personnel even when handled in an efficient fume hood. The presumed 1,1-dihydro-2,3,4,5-tetraphenylstannole product was not investigated further.

Treatment of either the dibromo- or diiodostannole with excess lithium cyclopentadiene, from *n*-butyllithium and cyclopentadiene monomer, at room temperature, followed by removal of the THF-hexane solvent and workup in toluene-hexane which pre-



cipitates the lithium halide, results, on the other hand, in the very slow formation of light brown cubic crystals which analyzed as X(C₅H₅)₂SnC₄(C₆H₅)₄Li where X = Br and I (eq 10).



The infrared spectra resemble those of the dihalostannole precursors. In the X = Br derivative, for example, the two bands assigned to the $\nu_{\text{asym}}(\text{Sn}-\text{Br})$ at 253 and $\nu_{\text{sym}}(\text{Sn}-\text{Br})$ at 240 cm⁻¹ are replaced by a single absorption of weaker intensity at 225 cm⁻¹. Absorptions at 1485 and 1027 cm⁻¹ can be assigned to the $\nu(\text{C}-\text{C})$ and ring breathing modes, respectively, of η^1 -bonded cyclopentadienyl groups.²³ New bands which appear 335 and 332 cm⁻¹ in the bromide and at 332 and 328 cm⁻¹ in the iodide can be assigned to the $\nu_{\text{asym}}(\text{Sn}-\eta^1\text{-C}_5\text{H}_5)$ and $\nu_{\text{sym}}(\text{Sn}-\eta^1\text{-C}_5\text{H}_5)$ modes as found in Sn($\eta^1\text{-C}_5\text{H}_5$)₄²⁴ and the mixed methyl and phenyl derivatives.^{25,26} Other absorptions above 3000 and between 1595 and 695 cm⁻¹ specify the diene nature of the cyclopentadienyl ligands.^{27,28}

The proton NMR spectra of the two derivatives appear similar at room temperature with two upfield resonances ascribable to the tin-cyclopentadienyl system [for X = Br, 5.72 and 5.94 ppm for X = I, 5.79 and 5.46 ppm in CDCl₃ with $|^2J(^{117,119}\text{Sn}-^1\text{H})| = 25.4$ and 23.2 Hz, respectively, for both resonances at 40 °C]. The integration ratio [found for X = Br 2.5:1; and for X = I 2.4:1; calcd 2.0:1] reveals two cyclopentadienyl groups per stannole ring. Data derived from the derivative prepared from the action of 2 mol equiv of cyclopentadienylthallium on the dibromostannole are also similar [5.42 and 5.63 ppm, $|^2J(^{117,119}\text{Sn}-^1\text{H})| = 26.0$ Hz for both resonances at 40 °C]. Both resonances in the cyclopentadienyl region appear simultaneously from initial addition of the C₅H₅Tl. The proton NMR data are consistent with those for analogous η^1 -cyclopentadienyltin derivatives,^{29–31} and the carbon-13 spectrum of the lithium derivative of the dibromostannole appears similar, with the two upfield resonances at 114.3 and 114.8 ppm and $|^2J(^{117,119}\text{Sn}-^{13}\text{C})| = 30.2$ and 26.2 Hz at ambient, respectively. Analogous carbon-13 chemical shifts^{32,33} in the series ($\eta^1\text{-C}_5\text{H}_5$)_nSnR_{4-n} in which R = CH₃ and C₆H₅ and

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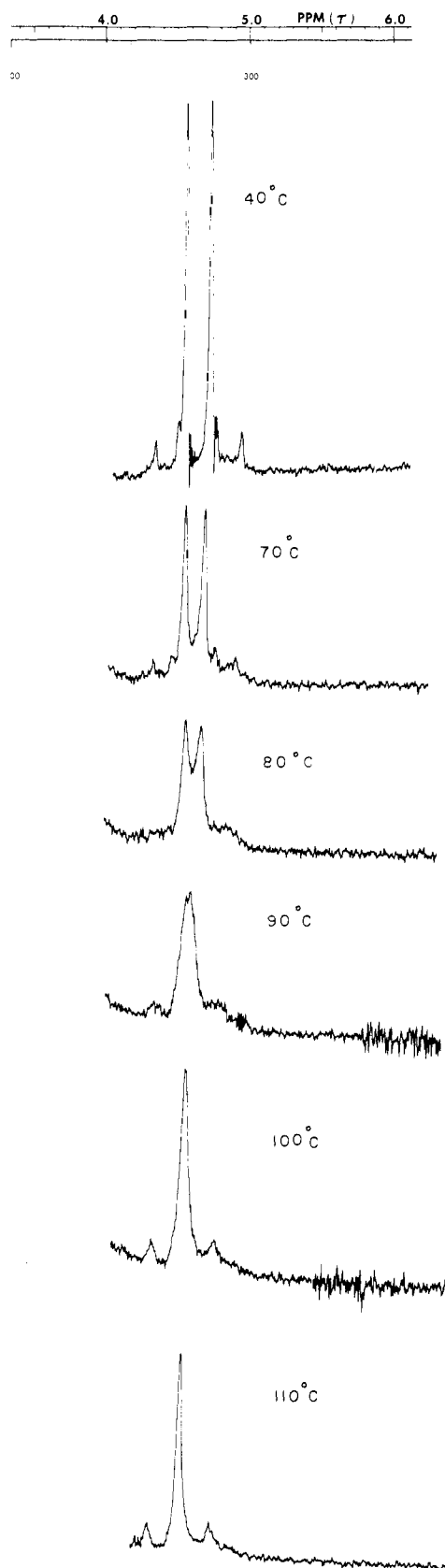


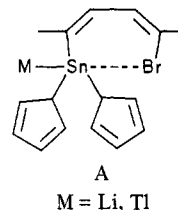
Figure 1. Variable-temperature proton NMR spectrum of lithium 1,1-dicyclopentadienyl-1-bromo-2,3,4,5-tetraphenylstannole in toluene at 60 MHz.

$n = 1-4$ lie in the range 113.6–114.3 ppm with the resonance in $(\eta^1\text{-C}_5\text{H}_5)_3\text{SnCl}$ at 114.8 ppm.²⁸ Tin-proton couplings in the related $(\eta^1\text{-C}_5\text{H}_5)_2\text{SnBr}_2$ (41.0 Hz),³⁴ $(\eta^1\text{-C}_5\text{H}_5)_2\text{SnI}_2$ (37.0 Hz),³⁴

and $(\eta^1\text{-C}_5\text{H}_5)_3\text{SnCl}$ (33.5 Hz,³³ with $|^1J(^{117,119}\text{Sn}-^{13}\text{C})|$ for the latter at 26.0 Hz²⁸ have also been recorded.

The pair of cyclopentadienyl proton resonances undergo only slight broadening at -100°C consistent with previous studies on $\eta^1\text{-C}_5\text{H}_5\text{Sn}$ compounds for which fast metallotropic 1,2 shifts have been proposed.^{31,33} However, as shown in Figure 1 for the lithium derivative of the dibromostannole, the two resonances of equal intensity observed at 40°C merge into a single, unshifted peak at 90°C (100°C for the lithium derivative of the diiodostannole). From the slopes of the Arrhenius plots (-2660 and -2490 K for the bromo and iodo derivatives, respectively), ΔE^\ddagger is 12.2 and 11.4 kcal/mol for the processes occurring in the bromo and iodo derivatives, respectively. The tin-proton couplings remained relatively constant over ca. 200°C temperature range studied, and the changes observed were reversible.

Preservation of the tin-proton couplings through the high-temperature region specifies an intramolecular process, and the lack of shift on changing temperature rules out an equilibrium process such as the dissociation of a dimer or ion pair. The origin of the cyclopentadienyl group nonequivalence may lie in hindered diene-rotation in an $\text{LiSnR}_3\text{-XR}$ system arising from intramolecular $\text{X} \rightarrow \text{Sn}$ coordination of the type studied in the solid state for (4-bromo-1,2,3,4-tetraphenylbuta-1,3-dienyl)dimethyltin bromide in which a *cis-cis* conformation is adopted to bring the tin and the 4-bromo atoms into contact for intramolecular coordination.³⁵ Structure A depicts such a situation in which



hindered rotation about C(2)–C(3) gives rise to a diene dissymmetry in a compound of the formulation $\text{MSnR}_3\cdot\text{BrR}'$. However, our products show none of the properties of the triorganolithium compounds described in the literature.³⁶ Moreover, conductivity measurements over the concentration range $(1.8-9) \times 10^{-6}$ M for the bromo and $(1.8-80) \times 10^{-6}$ M for the iodo derivative gave $\Lambda_0 = 123$ and $133 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$ at infinite dilution in acetonitrile, characteristic of a weak 1:1 electrolyte. Only negligible conductivity was recorded for the solvent itself, which was freshly distilled from phosphorus pentoxide, and no conductivity was shown by the bromo derivative in nitrobenzene.

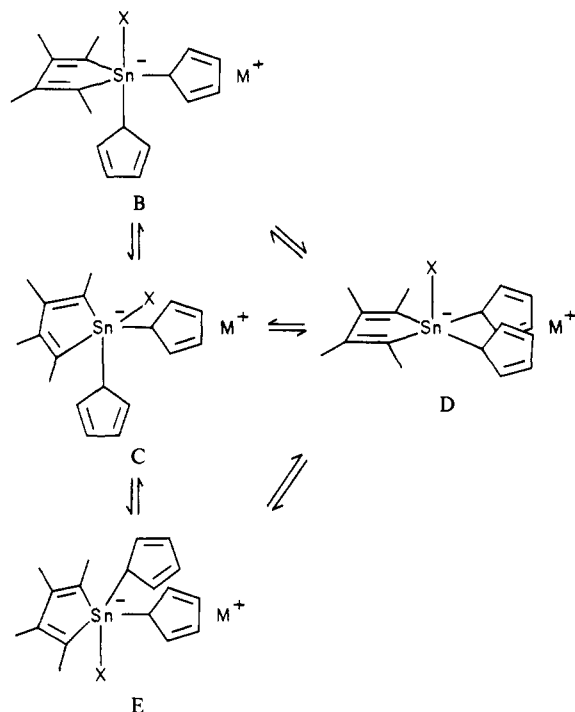
Ionic formulations, $[\text{R}_4\text{SnX}]^-\text{M}^+$ must thus be considered, based upon the usual trigonal-bipyramidal arrangement of ligands at the tin atom,³⁷ as shown in structures B, C and D, and the tetragonal-pyramidal E into which they could convert by a pseudorotation mechanism. Structures B and D are drawn with the halogen ($\text{X} = \text{Br}, \text{I}$) in the presumably favored, axially most electronegative position, but structure D cannot rationalize the nonequivalence of the two cyclopentadiene groups at tin on the basis of positional isomerism on the trigonal bipyramid. In structure B the stannole ring spans two equatorial positions on the trigonal bipyramid at the tin atom, in C axial and equatorial positions are spanned. Based upon structures B and C and hybridization arguments, we can assign the downfield resonance in the carbon-13 spectrum which has the smaller $|^1J(^{119}\text{Sn}-^{13}\text{C})|$ value to the axial cyclopentadiene group. The tin coupling in the proton NMR spectrum is smaller for the downfield resonance only at lower temperatures. Structure D could give rise to the observed cyclopentadienyl group nonequivalence through a stannole ring nonplanarity. Such magnetic nonequivalence arising from a preferred dissymmetric diene conformation has been proposed for the related open-chain (4-bromo-1,2,3,4-tetraphenyl-*cis,cis*-buta-1,3-dienyl)dimethyltin bromide^{35,38} but is less likely for our

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heterocycles. While no structural data are available for any of the fourth group metalloles,³⁷ the heterocyclic ring in the related pentaphenylaluminum diethyl ether complex is completely planar.³⁹ Structure B in which the stannole ring spans two equatorial positions would require an unreasonable expansion of the carbon-tin-carbon bond angles. Conversion of structure B to the square pyramidal form E would thus be expected to be accompanied by considerable release of strain. Square-pyramidal intermediates have been proposed to rationalize the temperature-dependent proton NMR of 2-biphenyl-bis(4,4-bitolyl)antimony whose singlet tolyl methyl resonance becomes a quartet at -60

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°C ($\Delta E^\ddagger = 11.6$ kcal/mol).^{40,41} Solid pentaphenylantimony has a square-pyramidal structure.^{42,43}

An alternative proposal based upon lithium ion association with the stannole ring in 1,1-bis(η^1 -cyclopentadienyl)stannole and a bromide gegenion would rationalize the temperature-dependent spectra in terms of a dissociation of the metal-heterocycle complex, but this is ruled out by the lack of chemical shift dependence on temperature and by the presence of an easily assignable tin bromide stretching frequency in the infrared. The chemical shifts of the bromo derivative are sensitive to the change in metal ion from lithium to thallium, however, the lack of appreciable conductivity in nitrobenzene and easy solubility in hydrocarbons suggests significant ion pairing.

The synthesis of the $[X(\eta^1-C_5H_5)_2SnC_4(C_6H_5)_4]^-M^+$ species can proceed through either a 1-(η^1 -C₅H₅)-1-halostannole, followed by adduct formation with C₅H₅⁻ anion or via (η^1 -C₅H₅)₂SnC₄(C₆H₅)₄ with subsequent metal halide uptake. The appearance of both cyclopentadienyltin resonances from the onset of reaction rules out the former, and the addition of 1,4-dilithio-1,2,3,4-tetraphenylbuta-1,3-diene to bis(η^1 -cyclopentadienyl)tin dichloride²⁵ from the redistribution reaction between tetrakis(η^1 -cyclopentadienyl)tin(IV)²⁴ and tin(IV) chloride did not, in our hands, yield a pure tin-containing material. The oily product gave a Mössbauer spectrum arising from more than one tin site.

Tetraorganotin compounds show no Lewis acid activity, but the as yet unisolated 1,1-bis(η^1 -cyclopentadienyl)-2,3,4,5-tetraphenylstannole apparently takes up halide ion during its formation from lithium or thallium cyclopentadiene in THF-hexane to form the $[X(\eta^1-C_5H_5)_2SnC_4(C_6H_5)_4]^-$ anion rather than precipitating the metal halide. The addition of pyridine has no effect on these products.

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Synthesis and Carbon-13 Nuclear Magnetic Resonance Studies of Some Bridgehead Fluorides: Carbon-Fluorine Coupling Constants

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Abstract: The synthesis of 1-fluorobicyclo[2.2.1]heptane, 1-fluorobicyclo[3.1.1]heptane, 1-fluorobicyclo[2.1.1]hexane, and 1-fluorobicyclo[1.1.1]pentane is described. The ¹³C NMR spectra of these fluorides together with that of 1-fluorotricyclo[3.3.0.0^{2,6}]octane were examined in order to gauge, in particular, the importance of Fermi contact contributions to the one-bond ¹³C-F spin-spin coupling constants. It is found that the magnitude of ¹J(¹³C-F) increases with enhanced s character of the carbon bonding orbital. At the same time it is noted that vicinal ¹³C-F coupling involving bridgehead carbons increases dramatically as the number of three-bond paths also increases, although through-space interactions appear to play a significant role in determining the magnitude of this parameter. It is suggested that these nonbonded interactions also account for the shielding effect exerted by the antiperiplanar fluorine atoms on the bridgehead γ -carbon atoms. Such shielding increases markedly as the system becomes more constrained.

There is, currently, widespread interest in spin-spin coupling between various nuclei and the factors which influence this

phenomenon. Some time ago Ramsey¹ discussed the theory appropriate to such coupling in terms of the following electron-