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$(p \rightarrow d)\pi$ BONDING IN PHENYLTRICHLORO-TIN, -GERMANE, AND -SILANE

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SUMMARY

The deuterium-decoupled ^1H NMR spectra of the aryl groups of several compounds having the structure RMX_3 (R=phenyl-2,5-d_2 and MX_3=$SiEt_3$, $GeEt_3$, $SnEt_3$, $PbEt_3$, CCl_3, $SiCl_3$, $GeCl_3$, and $SnCl_3$) have been analyzed to obtain chemical shift values for the protons *ortho*, *meta*, and *para* to the substituents. Comparison of *para* chemical shifts within this series of compounds suggests that $(p \rightarrow d)\pi$ bonding to carbon is significant in determining these ^1H NMR spectral parameters, and indicates that while the order of effectiveness of this π bonding in the compounds $RM(alkyl)_3$ is the expected $C < Si > Ge \simeq Sn > Pb$, the corresponding order in the compounds $RMCl_3$ is $C < Si < Ge < Sn$. A possible rationalization of this difference is discussed.

INTRODUCTION

The factors responsible for the striking differences[1] between corresponding carbon–metal and silicon–, germanium–, or tin–metal bonds have been the subject of active investigation, with special interest attached to questions concerning the relative importance of σ and π contributors to these bonds[2–6]. Comparisons of the properties of compounds containing $-MCl_3$ and $-M(alkyl)_3$ groups (M=Sn, Ge, Si) have resulted in the suggestion that the unusual properties of the groups containing tin may be due in part to their ability to act as π acceptors in metal–metal bonding. The importance of $(p \rightarrow d)\pi$ bonding between silicon, germanium, tin, and carbon has been extensively explored[†]. We have in this work attempted to determine the *relative* ability of MCl_3 and MR_3 groups to participate in π bonding with carbon, using as an experimental probe a technique yielding readily interpretable results: *viz.*, examina-

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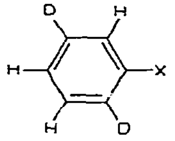
[†] See for reviews ref. 7.

tion of the chemical shifts of protons on benzene rings bearing representative MCl_3 and $M(alkyl)_3$ groups as substituents[8].

Examinations of the interaction of substituents with benzene rings using NMR spectroscopy have commonly been approached through study of the ^{19}F spectra of benzene derivatives monofluorinated in the positions *meta* and *para* to the substituent. Although there are several advantages to the use of ^{19}F NMR spectroscopy* [9] we have chosen to infer details of substituent interactions directly from ^1H chemical shifts in non-fluorinated rings. Our reasons for this choice are two. First, our interests lie specifically with non-fluorinated arylmetallic compounds. The striking differences in stabilities and properties of fluorinated and non-fluorinated organometallic reagents suggests that it may not be possible to infer the properties of non-fluorinated substances from study of their fluorinated analogs, particularly when relatively small changes in structure can have a pronounced influence on properties such as extent of aggregation or aggregate structure. Second, theoretical understanding of factors relating details of electronic structure, and particularly charge distributions, to ^1H chemical shifts is considerably more advanced than understanding of similar considerations in ^{19}F spectroscopy**.

NMR studies of organometallic compounds are of necessity frequently carried out using samples giving rise to spectra characterized by low signal-to-noise ratios and relatively broad lines. In order for accurate ^1H chemical shift analysis for monosubstituted benzene derivatives to be a practical matter under these conditions, it is necessary either to work at very high magnetic fields, or to simplify the spectra by isotopic substitution. Two features of the substitution pattern represented by (I) are uniquely convenient for the latter alternative***. First, the deuterium-decoupled spectrum of compounds of structure (I) are usually of the ABX type, and spectral analysis to obtain coupling constants and chemical shifts is straightforward[14]. Second and more important, the three chemical shifts obtained by analysis of (I) can be assigned uniquely to *o*, *m*, and *p*-protons, since each chemical shift is associated in the analysis with two distinct coupling constants, and since the relative magnitudes of coupling constants in benzene derivatives are well established to be $|J_o| > |J_m| > |J_p|$[8,14].



(I)

RESULTS AND DISCUSSION

The unexceptional synthetic sequence outlined in Scheme 1 was used to prepare the benzene derivatives used in this study. NMR spectra were taken using

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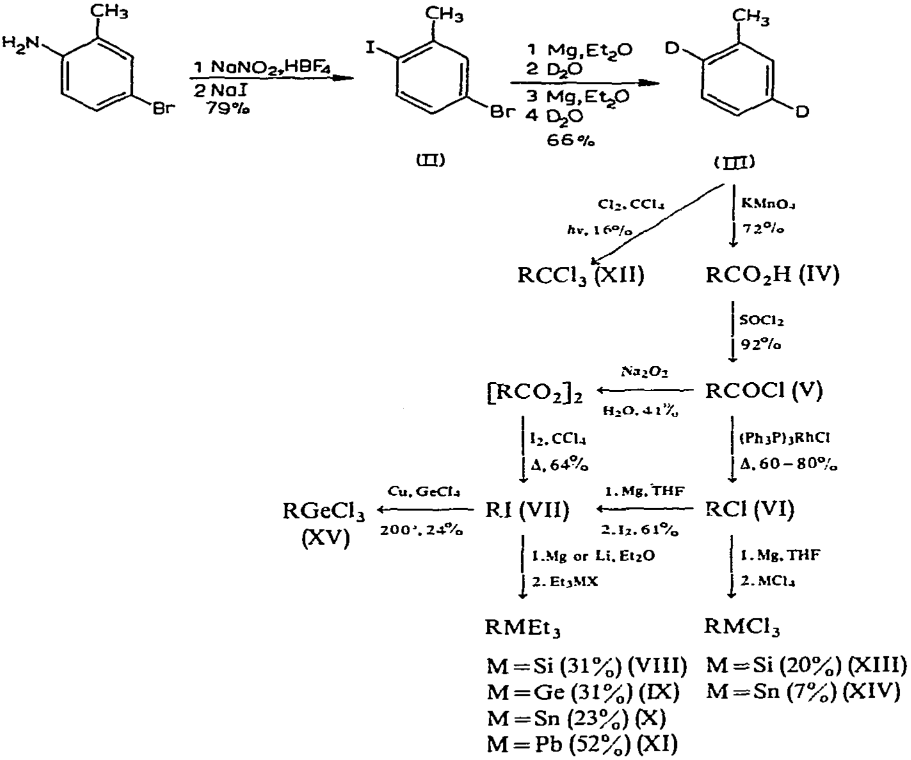
* Note, however, that the conclusions concerning π interactions in metal–ligand bonds derived from this type of investigation have not always been in agreement with conclusions from other types of studies[10,11].

** For recent calculations of ^1H chemical shifts see ref. 12.

*** For reviews of alternative schemes for the simplification of NMR spectra of monosubstituted benzene derivatives by isotopic substitution, see refs. 8 and 13.

SCHEME 1. SYNTHESIS OF DEUTERATED BENZENE DERIVATIVES (R = Phenyl-2,5-d_2)



samples 33 ± 3 % by weight in carbon tetrachloride, with tetramethylsilane as internal standard. Chemical shifts and coupling constants obtained by analysis of these spectra are listed in Table 1. Although in order to identify weak transitions in some of

TABLE 1

CHEMICAL SHIFTS (ppm) AND COUPLING CONSTANTS (Hz) FOR ARYL PROTONS[a]

Compound	δ_o	δ_m	δ_p	J_o	J_m	J_p
tert-Butylbenzene[b]	7.27	7.17	7.03	7.8	1.5	1.3
RSiEt$_3$ (VIII)	7.477	7.313	7.220	7.6	1.1	0.7
RGeEt$_3$[c] (IX)	7.343	7.20	7.20			
RSnEt$_3$[c] (X)	7.352	7.19	7.19			
RPbEt$_3$ (XI)	7.368	7.196	7.109	7.4	1.4	0.7
RCCl$_3$ (XII)	7.866	7.297	7.314	7.6	1.0	0.5
RSiCl$_3$ (XIII)	7.732	7.444	7.371	7.7	1.3	0.7
RGeCl$_3$ (XV)	7.674	7.515	7.458	7.6	1.3	0.7
RSnCl$_3$ (XIV)	7.553	7.53	7.50	(7.6)[d]	1.3	0.5

[a] Samples were 33 ± 3% w/w in CCl$_4$, unless otherwise noted. The estimated uncertainty in chemical shift values is ~0.002 ppm, except for compounds (IX), (X) and (XIV), in which it is ~ ±0.01 ppm; the estimated uncertainty in coupling constants is ~ ±0.2 Hz. [b] See ref. 35; sample concentration 25% v/v in CCl$_4$. [c] The degeneracy of the *m*- and *p*-chemical shifts makes it impossible to obtain values for individual coupling constants without using special techniques. [d] This value was assumed.

the spectra it was necessary to use samples too concentrated to yield reliable *absolute* chemical shifts, the relative shifts reported in Table 1 are significant[15]. To check for gross concentration dependences in the chemical shift values, several samples giving well-defined spectra were reanalyzed after dilution to ~5–10% in solute; changes in chemical shifts were less than 0.03 ppm.

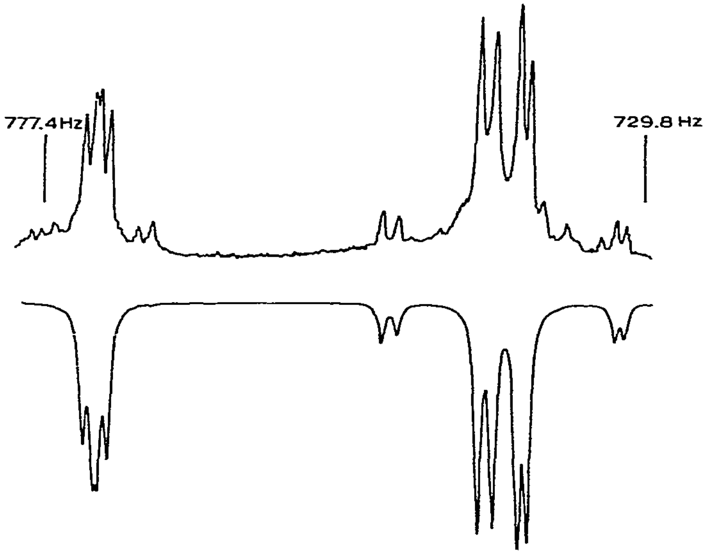


Fig. 1. Deuterium-decoupled ^1H NMR spectrum of the aryl protons of phenyl-2,5-d_2-trichlorosilane (XIII): observed (upper trace), calculated (lower trace).

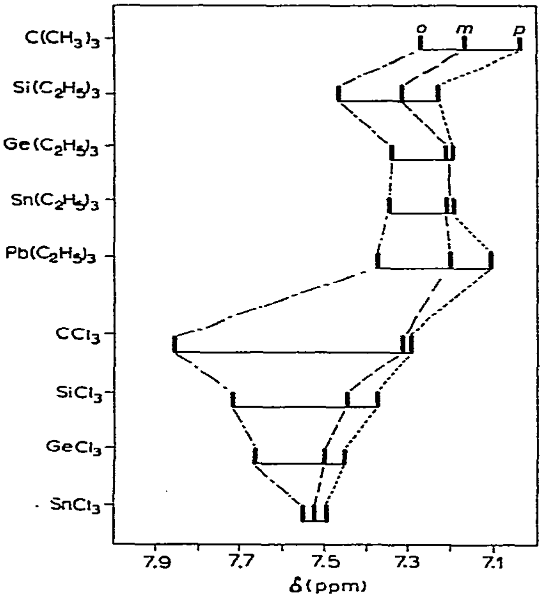


Fig. 2. Chemical shifts of the *ortho*-, *meta*-, and *para*-hydrogens of 1-substituted derivatives of benzene-2,5-d_2.

A representative deuterium-decoupled spectrum, that of $C_6H_3D_2SiCl_3$, is shown in Fig. 1, together with the spectrum calculated using the parameters of Table 1. For convenience, the chemical shift information pertinent to the discussion which follows is summarized graphically in Fig. 2.

Interpretation of these chemical shifts in terms of ring–metal π interactions rests on the approximately linear dependences established between the chemical shifts of protons *para* to substituents on a benzene ring and the π-electron density at the carbon atom to which they are directly bonded[8,16], and between these chemical shifts and the Hammett σ constants of the substituents[*]. However, the range of chemical shift variation observed in proton studies is not large. Thus, for example, a chemical shift difference of ~ 1.8 ppm is observed between protons *para* to amino and nitro groups, substituents which represent extremes of π-donation and π-acceptance in interaction with benzene rings. In light of this limited range of proton chemical shifts, and of the limitations on the absolute accuracy of the chemical shifts determined in this work, it seems prudent to restrict interpretation of these data to qualitative estimates of interaction between substituents and ring.

The chemical shifts of the *p*-hydrogens of benzene rings substituted with the $M(alkyl)_3$ substituents follows the pattern which has emerged from other studies of ring-substituent interactions in related systems[7]. The chemical shifts of *p*-hydrogens in compounds (VIII)–(XI) all occur at low field relative to that of the *p*-hydrogen of tert-butylbenzene. The downfield shift indicates decreased π-electron density at the *p*-carbon atom, and is consistent with weak resonance interaction between the ring and these substituents involving $(p\rightarrow d)\pi$ interaction. The order of these shifts ($C < Si > Ge \simeq Sn > Pb$) is that expected from previous work[7,18]. The *ortho* and *meta* chemical shifts in these compounds roughly parallel the *para* shifts. However, the factors which determine these shifts are sufficiently obscure that there would be no point in an attempt to draw structural inferences from their order[8].

The chemical shifts of the hydrogen nuclei *para* to trichlorosilyl, -germyl, and -stannyl substituents show a pattern distinctly different from that characterizing the $M(alkyl)_3$ groups. Each of these chemical shifts lies at lower field than that for the *p*-hydrogen nucleus of α,α,α-trichlorotoluene-2,5-d_2 (XII) again suggesting $(p\rightarrow d)\pi$ bonding. However, unlike the order of shifts observed for the $M(alkyl)_3$ substituents, the magnitude of these shifts relative to that of (XII), and presumably the magnitude of the π interaction between ring and substituent, *increases* in the order $C < Si < Ge < Sn$. Thus, the $SnCl_3$ moiety appears to be *most* effective of the groups examined in $(p\rightarrow d)\pi$ bonding to carbon.

Why the order of effectiveness in π bonding to carbon should be $Si > Ge > Sn$ for Et_3M groups but $Sn > Ge > Si$ for Cl_3M groups remains a topic of speculation. It is clear from previous work that $(p\rightarrow d)\pi$ bonding between M and Cl contributes substantially to the electronic properties of the MCl_3 groups by shifting charge density to the central atom from the chlorine atoms[2-4]. Thus, for the compounds

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[*] The correct constant of proportionality between chemical shift and π-electron density remains a subject of controversy[17].

studied here, chemical shift data for MEt_3 groups indicate that $SiEt_3$ is slightly more effective than $SnEt_3$ in π bonding to carbon. The π-acceptor capacity of both tin and silicon increases on substitution of a chlorine atom for an ethyl group, as expected on the basis of the electronegativities of chlorine and carbon; however, the increase in the π-acceptor capacity of silicon accompanying chlorine substitution is significantly smaller than that of tin, since $SnCl_3$ is a *more* effective group than $SiCl_3$ in π bonding to carbon. This difference in the response of silicon and tin to changes in their directly bonded substituents is most easily rationalized using an argument discussed by Brown and Harris[3], and by Graham[2]. Efficient $(p \rightarrow d)\pi$ bonding between chlorine and silicon results in transfer of charge density from chlorine onto silicon, and consequently decreases the capacity of silicon to accept electron density from the phenyl ring relative to that expected for a hypothetical $SiCl_3$ group in which no chlorine–silicon π bonding occurs; less efficient $(p \rightarrow d)\pi$ bonding between tin and chlorine results in less charge transfer to tin, with a correspondingly smaller decrease in the capacity of the tin to accept charge by π bonding to carbon.

EXPERIMENTAL

General

Melting points were determined using a Thomas–Hoover capillary melting point apparatus and are uncorrected. Boiling points are uncorrected. IR spectra were taken in sodium chloride cells using a Perkin–Elmer Model 237-B grating spectrophotometer. Mass spectra were determined on a Hitachi–Perkin–Elmer RMU-6D mass spectrometer. Magnesium sulfate was used as a drying agent.

2-Iodo-5-bromotoluene (II)

To 360 ml of 48% fluoroboric acid in a 1l flask fitted with a mechanical stirrer was added 46.5 g (0.250 mole) of 2-methyl-4-bromo-aniline. The resulting mixture was heated on a steam bath to form a uniform suspension, then cooled in an ice/salt bath. An aqueous solution (40 ml) containing 19.7 g (0.285 mole) of sodium nitrite was added slowly with stirring while maintaining the temperature of the reaction mixture below 4°. After the addition was complete, the solution was stirred at 0° for 3 h. The resulting orange diazonium salt was collected on a filter and added slowly to a solution of 39.7 g (0.265 mole) of sodium iodide in 300 ml of acetone. The dark reaction mixture was diluted with 100 ml of water, and extracted with three 150-ml portions of pentane. The combined organic phases were extracted with three 60-ml portions of saturated aqueous sodium thiosulfate, and 60 ml of water. The solvent was removed from the dried organic layer at reduced pressure, and the residual red liquid distilled through a 55-cm platinum spinning band column to give 58.9 g (79%) of product, b.p. 80–97° (0.09–0.12 mm) (lit.[19] b.p. 260°).

Toluene-2,5-d_2 (III)

A 500-ml three-necked flask was fitted with a reflux condenser, a pressure-equalizing dropping funnel, and a magnetic stirrer. The apparatus was flamed under dry nitrogen and charged with 12.3 g (0.506 mole) of magnesium powder and 290 ml of anhydrous ether. A small portion of a 134 g (0.451 mole) sample of (II) and 0.5 ml of iodomethane were added to the ether, and the resulting mixture refluxed to initiate the reaction. The remaining (II) was added over 0.5 h and refluxing was continued for 3 h. To the resulting Grignard reagent solution was added slowly with stirring 19 g (0.95 mole) of deuterium oxide. After the mixture had again been warmed to reflux temperature, the inorganic salts were dissolved by addition of 500 ml of 1 *N* aqueous HCl. The phases were separated, and the aqueous phase was extracted with 50 ml of ether. The combined organic phases were extracted with two 75-ml portions of saturated aqueous NaCl and 75 ml of water. The ethereal solution was dried and concentrated. The resulting deuterated monohalide was subjected to the same procedure without further purification. Distillation of the final concentrate through a 20-cm Vigreux column yielded 28.0 g (66%) of (III), b.p. 110–112°.

Benzoic-2,5-d_2 acid (IV)

Toluene-2,5-d_2 (III) (22.5 g, 0.239 mole) was added in one portion with mechanical stirring to a mixture of 82.2 g (0.520 mole) of potassium permanganate in 400 ml of water at 85°. The mixture was heated at 90° for 8 h and then cooled. Methanol (50 ml) was added to destroy excess potassium permanganate. The manganese salts were removed by filtration and washed with hot water. The aqueous solution was cooled and acidified to pH 1 with concentrated HCl, and the white plates of (IV) (21.5 g, 72%) were collected by filtration and dried in vacuum. A sample of (IV) melted at 121–123°. The mass spectroscopic isotopic composition of a typical sample of (IV) was: 5% d_0; 22% d_1; 73% d_2.

Benzoyl-2,5-d_2 chloride (V)

To 100 g of thionyl chloride was added 15.0 g (0.121 mole) of benzoic-2,5-d_2 acid (IV). The mixture was stirred at 40–44° for 15 h. Distillation through a short path still yielded 15.9 g (92%) of (V), b.p. 131° (110 mm) [lit.[20] b.p. 92.5° (25 mm)].

Chlorobenzene-2,5-d_2 (VI)

Benzoyl-2,5-d_2 chloride (V) was decarbonylated to give (VI) using published procedures[21]. It was our experience that traces of impurities in the benzoyl-2,5-d_2 chloride usually poisoned the catalyst in the early stages of the first attempt at decarbonylation. When this poisoning occurred (as judged by cessation of carbon monoxide evolution, or by an inability to initiate the reaction), the benzoyl chloride was distilled from the catalyst, fresh catalyst added, and the decarbonylation again attempted. Frequently three or four cycles of distillation were necessary before the reaction proceeded smoothly.

Iodobenzene-2,5-d_2 (VII)

A solution of phenyl-2,5-d_2-magnesium chloride in tetrahydrofuran[22], prepared from 5.0 g (0.044 mol) of (VI), was added with stirring to a cold solution of 11.4 g (0.045 mole) of iodine in 20 ml of tetrahydrofuran. The reaction mixture was refluxed for 0.5 h, and filtered, and the inorganic material was washed with ether. The THF/ether solution was extracted with two 25-ml portions of saturated aqueous sodium thiosulfate followed by two 25-ml portions of water. The organic phase was dried, concentrated, and distilled to yield 5.5 g (61%) of (VII), b.p. 117–120° (97 mm) [lit.[23] b.p. 188.4° (768 mm)].

Benzoyl-2,5-d_2 peroxide

To a solution of 7.35 g (0.0943 mole) of sodium peroxide in 73.5 ml of water cooled in a methanol/ice bath was added slowly the benzoyl-2,5-d_2 chloride (V) prepared from 15.2 g (0.122 mole) of (IV). The mixture was stirred for 0.5 h, and the peroxide was collected on a filter. Recrystallization from chloroform/methanol (1/2) gave 6.14 g (41 %) of benzoyl-2,5-d_2 peroxide, m.p. 104–104.5° (lit.[24] m.p. 106°).

Iodobenzene-2,5-d_2 (VII)

A solution of 6.35 g (0.025 mole) of iodine and 6.14 g (0.025 mole) of benzene-2,5-d_2 peroxide in 94 ml of carbon tetrachloride was refluxed for 48 h[25]. The solution was dried, concentrated, and distilled to give 6.63 g (64 %) of (VII), b.p. 54° (6 mm), [lit.[23] b.p. 188.4° (768 mm)].

Phenyl-2,5-d_2-triethylsilane (VIII)

A tetrahydrofuran solution of phenyl-2,5-d_2-magnesium iodide, prepared from 12.5 g (0.0607 mole) of (VII) and 9.0 g (0.060 mole) of chlorotriethylsilane were sealed in a tube under nitrogen. The tube was heated on a steam bath for 36 h, then opened, and the contents poured into an ice/water mixture. Conventional workup, followed by distillation through a 30-cm Nester–Faust annular Teflon spinning band column yielded 3.95 g (31 %) of (VIII), b.p. 50–65° (0.45–0.65 mm) [lit.[26] b.p. 238.2–238.4° (763.1 mm)].

Phenyl-2,5-d_2-triethylgermane (IX)

To an ether solution of phenyl-2,5-d_2-magnesium iodide prepared from 3.65 g (0.0175 mole) of (VII) was added with stirring an ethereal solution of 5.0 g (0.0174 mole) of triethylgermanium iodide. The mixture was allowed to reflux for 3 h, then worked up by conventional techniques to yield 1.30 g (31 %) of (IX), b.p. 60° (0.8 mm) [lit.[27] b.p. 117–118° (13.5 mm)].

Phenyl-2,5-d_2-triethyltin (X)

The procedure used to synthesize (IX) was used for the preparation of (X) from (VII) (3.75 g, 0.0183 mole) and 5.3 g (0.0183 mole) of triethyltin bromide. This method gave 1.18 g (23 %) of (III), b.p. 80° (1.5 mm) [lit.[28] b.p. 134° (17 mm)].

Phenyl-2,5-d_2-triethyllead (XI)

An ether solution of phenyl-2,5-d_2-lithium was prepared from 3.1 g (0.015 mole) of (VII) under a helium atmosphere. To the solution was added slowly 5.0 g (0.015 mole) of triethyllead chloride. The mixture was refluxed for 9 h and then worked up to yield (XI) (2.9 g, 52 %) b.p. 65–70° (0.15 mm) [lit.[29] b.p. 127–131° (7 mm)].

α,α,α-Trichlorotoluene-2,5-d_2 (XII)

Chlorine gas was bubbled through a solution of 3.5 g (0.037 mole) of toluene-2,5-d_2 (III) in 100 ml of carbon tetrachloride while the solution was irradiated with UV light from a chromatographic hand scanner. Solvent was added periodically to replace that lost by evaporation. After 45 h the solvent was removed, and the remaining viscous liquid was distilled through a short path still. Compound (XII) (1.2 g, 16 %) was collected, b.p. 122–125° (33–35 mm) [lit.[30] b.p. 110.7° (23 mm)].

Phenyl-2,5-d_2-trichlorosilane (XIII)

A solution of phenyl-2,5-d_2-magnesium chloride in tetrahydrofuran, prepared from 5.0 g (0.44 mole) of (VI), was added over a period of 1 h to a well-stirred solution of 8.3 g (0.49 mole) of silicon tetrachloride in 45 ml of heptane while maintaining the temperature at 45–47°. The reaction mixture was refluxed for 2 h, then worked up to yield (XIII) (1.9 g, 20 %), b.p. 130–133° (88 mm) [lit.[31] b.p. 54–57° (0.4 mm)].

Phenyl-2,5-d_2-trichlorogermane (XV)

A Pyrex ignition tube was charged with 5.0 g (0.024 mole) of (VII), 5.85 g (0.027 mole) of germanium tetrachloride, and 5 g of copper-bronze powder. The tube was cooled in an ice/methanol bath, sealed, and then heated at 200° for 16 h. The tube was cooled and opened, and its contents taken up in isopentane and filtered. Removal of the solvent followed by distillation through a short path column gave 1.5 g (24 %) of (XV), b.p. 123–124.5° (23 mm) [lit.[32] b.p. 115° (19 mm)].

Phenyl-2,5-d_2-trichlorostannane (XIV)

The procedure to synthesize (XIII) was used for the preparation of (XIV) from 5.0 g (0.044 mole) of (VI) and 12.75 g (0.049 mole) of stannic chloride. This method gave 1.0 g (7.5 %) of (XIV), b.p. 68–69° (0.23 mm) [lit.[33] b.p. 128° (15 mm)].

NMR spectra

NMR spectra were obtained at ambient temperature using Varian A-60 or HA-100 spectrometers, equipped with an NMR Specialities HD-60A heteronuclear spin decoupler. Peak positions in spectra from the A-60 spectrometer were the average of 3–5 upfield and downfield sweeps, and were referenced with respect to internal TMS audiosidebands generated using a Krohn–Hite Model 450 pushbutton oscillator. The frequency of this oscillator was checked periodically using a Hewlett–Packard Model 524 electronic counter. Peak positions in spectra from the HA-100 spectrometer were referenced directly to the TMS lock signal, using frequency-sweep mode. Analyses of spectra to obtain coupling constants and chemical shifts were carried out using the iterative programs LAOCN3, NMRIT, and NMREN[34]. Results are summarized in Table 1.

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