Table I. Values of g_{av} for Some of the Radicals Discussed in the Text[a]

Radical	$H_2\dot{C}CH_2C(Me)_3$	$H_2\dot{C}CH_2Si(Me)_3$	$H_2\dot{C}CH_2Ge(Me)_3$	$H_2\dot{C}CH_2Sn(Me)_3$		
g_{av}	2.00268	2.00265	2.00255	2.00205		
Radical	$Me\dot{C}HCH_2AsO_3H^b$	$H_2\dot{C}C(OH)MePO(OMe)_2{}^c$	$HOCH_2\dot{C}HCH_2SO_3{}^-$	$H_2\dot{C}CH(Me)PPh_3{}^{+\,b}$		
g_{av}	2.0073	2.00273	2.0026^d	2.003		
Radical	$H_2\dot{C}CH_2AsEt_3$	Me_3Si	Me_3Ge	H_3Sn^e	Bu_3Sn^f	
g_{av}	~2.01^b	2.0031	2.0100	2.018	2.007	
Radical	$PH_3{}^{+\,b}$	$PEt_3{}^{+\,b}$	$AsEt_3{}^{+\,b}$	$SO_3{}^{-\,g}$	$PO_3{}^{2-\,h}$	$AsO_3{}^{2-\,i}$
g_{av}	~2.007	~2.007	~2.01	2.0036	2.001	1.997

[a] Data from ref 3 unless otherwise stated. [b] Reference 2. [c] Reference 10. [d] Reference 11. [e] Reference 4. [f] Unpublished results. [g] G. W. Chantry, A. Horsfield, J. R. Morton, and D. H. Whiffen, Mol. Phys., 5, 233 (1962). [h] A. Horsfield, J. R. Morton, and D. H. Whiffen, ibid., 4, 475 (1961). [i] Reference 8.

allow for the effect of hyperconjugation delocalization, we need $\rho\sigma$, which is ca. 15.7%,[2] and g_{av} for the β-group radical, $HAsO_3$. For the radical $AsO_3{}^{2-}$, g_{av} is reported to be 2.005 in one environment,[7] and 1.997 in another,[8,9] and our unpublished results for this radical favor the latter value. Thus, the $\rho\sigma$ correction makes the g shift even more positive, whereas any delocalization into the outer d manifold for arsenic must require a negative shift.

(ii) Similarly, for the radical $H_2\dot{C}C(OH)MePO-(OMe)_2$, g_{av} = 2.00273,[10] while those for $PO_3{}^{2-}$ and related radicals are usually slightly less than 2.000. Thus again, the g_d value is positive rather than negative.

(iii) The radical $HOCH_2\dot{C}HCH_2SO_3{}^-$ has g_{av} = 2.0026,[11] while that for $SO_3{}^{2-}$ is generally reported to be ca. 2.00345.

Our results for many other radicals in this class are generally insufficiently accurate to enable us to deduce g values to better than ca. ±0.002, but, in all cases, values close to that of the free spin were found, which leads us to conclude that d-orbital participation is of trivial significance (compare data in Table I).

Finally, one can estimate the extent of delocalization with fair accuracy from the values of the isotropic coupling to the α protons. For the tin compound mainly considered herein, Kawamura[1] and Kochi find $a(\alpha\ H)$ = 19.69 G, whereas the corresponding carbon compound had $a(\alpha\ H)$ = 22.06 G. This gives a 10.7% total delocalization of the spin. Since it is agreed that the σ delocalization corresponds to ca. 13% delocalization,[3] one must surely conclude that there is no other major delocalization mechanism.

Our results for many similar radicals[2] give good agreement between the delocalization estimated for the α-proton coupling and that estimated for the metal coupling.

It is interesting to note that a very similar criticism can be made of the arguments presented by Mackey and Wood,[12] as modified by Kawamura[1] and Kochi,[3] upon which much of this work[3] was based. These workers found very small negative shifts in g_{av} for the series $H_2\dot{C}CMe_3$, $H_2\dot{C}SiMe_3$, $H_2\dot{C}GeMe_3$, and $H_2\dot{C}-SnMe_3$ and hence argued in favor of d-orbital partici-

pation. While their value of ca. 1% was too small to affect the α-proton coupling constants appreciably, the revised value[3] of ca. 10% is; since, in fact, the α-proton coupling constants are almost invariant through the series, it is unlikely that such a large delocalization is occurring. Furthermore, g_{av} values for isostructural radicals derived from group V elements, such as $R_2\dot{C}PR_3{}^+$ and $R_2\dot{C}AsR_3{}^+$, are in fact clearly greater than that of the corresponding carbon radicals,[13] which again seems to nullify the argument.

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The Formation of Tin–Group III Metal–Metal Bonded Derivatives and Their Nuclear Magnetic Resonance Spectra

Sir:

The formation of mixed metal–metal bonded compounds has been of interest for many years because of the information which may be gained from study of the bonding interactions and varied chemical reactivity of these species. Major efforts have been placed on obtaining metal group III derivatives but these have failed to yield significant results for other than boron derivatives. We now wish to report preliminary data on the formation of Sn–Al, Sn–Ga, Sn–In, and Sn–Tl bonded derivatives. Data on the Sn–^{1}H coupling across these metals as well as Tl–^{1}H coupling in these species are also included.

$Li[Sn(CH_3)_3]$ was prepared by reaction of $Sn_2(CH_3)_6$ (0.25 ml) with lithium metal in 4 ml of dimethoxy-ethane (DME) at −10 to −5° for 4 hr. At 0° J_{SnCH} = 10.0 Hz and δ 1.925 ppm above cyclopentane for this compound. Wells and Brown[1] reported J_{SnCH} = 5.2 Hz when the compound was prepared in THF, as described by Tamborski, et al.[2] These results and those in Table I show that J_{Sn-H} in $LiSn(CH_3)_3$ varies substantially both as a function of solvent and temperature due to ion pair and complex formation and will be discussed elsewhere.[3]

The $Li[B(CH_3)_4]$ was obtained from the reaction of $LiCH_3$ and $B(CH_3)_3$ in ethyl ether[4] while $Li[Al(CH_3)_4]$

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Table I. Nuclear Magnetic Resonance Parameters for $Li[Sn(CH_3)_3R]$ and Related Species

	$Li(CH_3)_3SnM(CH_3)_3$[a,b]						Tin species[a,c]			
M	δ_{MCH_3}	J_{SnMCH}[c,d]	J_{TlCH}	δ_{SnCH_3}	J_{SnCH}	J_{TlSnCH}		δ	$J_{^{119}Sn}$	$J_{^{119}SnSnCH}$
B							$Sn_2(CH_3)_6$[e]	1.30	+48.9	−16.0
Al	2.55	29.6		1.85	17.2		$Sn(CH_3)_4$[f]	1.45	+53.6	
Ga	2.28	34		1.83	20.2		$LiSn(CH_3)_3$[g]	1.91	8.6	
In	2.33	21		1.74	22.0		$LiSn[Sn(CH_3)_3]_3$[g]	1.52	34.5	Not obsd
Tl	1.73	17.2	223.1	1.68	24.5	31.8				

[a] All data are for DME solutions. Chemical shifts are reported relative to internal cyclopentane in ppm ($\delta = \delta_{TMS} + 1.513$), coupling constants are in Hz. [b] −60°. [c] Ambient temperature. [d] Separate ^{117}Sn and ^{119}Sn satellites could not be distinguished due to the relative size of coupling constants and the slightly broadened resonance lines. [e] Reference 12. [f] W. McFarlane, *J. Chem. Soc. A*, 528 (1967). [g] Reference 1. J_{SnCH} is a function of solvent and temperature; $J_{Sn-SnCH}$ has been observed for $LiSn[Sn(CH_3)_3]_3 \cdot 3THF$ in benzene solution ($J = 2.3$ Hz) but could not be observed in THF solvent.

and $Li[Ga(CH_3)_4]$ were prepared by reaction of Li and the corresponding metal alkyl in ether as described by Mach.[5] It was also possible to make use of the latter method to produce and isolate $Li[Tl(CH_3)_4]$ reported for the first time here. Due to the light sensitivity of the thallium compounds, especially in solution, this reaction was run in the dark, usually at 0°. From the ether solution a 70% yield of $Li[Tl(CH_3)_4]$ was obtained. *Anal.* Calcd for $Li[Tl(CH_3)_4]$: Li, 2,56; Tl, 75.4; C, 17.8; H, 4.46. Found: Li, 2.70; Tl, 75.31; C, 18.1; H, 5.07. A DME solution of $Li[Tl(CH_3)_4]$ gave rise to a doublet in the nmr spectrum centered at 2.01 ppm above cyclopentane with $J_{^{205}TlCH} = 224.1$ Hz at ambient temperature.

Reactions between group III alkyl and $Li[Sn(CH_3)_3]$ in DME were carried out by distillation of the group III alkyl into a frozen 0.6 *M* solution of the tin species contained in an nmr tube so that approximately equimolar amounts of tin and the group III metal alkyl were present. The nmr tube was sealed off and removed from the vacuum line and stored in liquid nitrogen until put in the nmr at −60° with minimal warming.

The starting materials, $Sn_2(CH_3)_6$ and $[Al(CH_3)_2]_2$, were obtained from commercial sources and distilled before use while $B(CH_3)_3$,[6] $Ga(CH_3)_3$,[7] $In(CH_3)_3$,[8] and $Tl(CH_3)_3$[9] were prepared by procedures outlined in the literature. The purities of all compounds used were determined from their nmr spectra.

All manipulations were performed using standard high-vacuum techniques or under an argon atmosphere dried by sodium–potassium alloy. Solvents were dried over Na–K, distilled, and stored on the vacuum line. Nmr samples were run on a Varian A-60A with standard variable temperature accessories or on a JEOL 4-H100 spectrometer. Temperatures were calibrated by the method of Van Geet.[10]

The results of these investigations provide evidence for the formation of $Li[(CH_3)_3SnM(CH_3)_3]$ derivatives for M = Al, Ga, In, Tl, but not for M = B. When $Li[Sn(CH_3)_3]$ and $M(CH_3)_3$ in DME were mixed at reduced temperatures, the initial spectrum obtained at low temperature with $Al(CH_3)_3$, $Ga(CH_3)_3$, or $In(CH_3)_3$ gives rise to two major peaks of equal intensity in the nmr spectrum. In each case both species showed tin satellites as seen in Figure 1. No $Li[M(CH_3)_4]$ was formed as indicated by comparison of the spectra with those of separately produced $Li[M(CH_3)_4]$. The addition of $Tl(CH_3)_3$ to $Li[Sn(CH_3)_3]$ led to the formation of several products. Three of these contain Tl–Sn bonds as indicated by the presence of three sets of doublets in the methyl tin region with J_{TlSnCH} = 32, 39, and 44 Hz. The two major products of the reaction, however, were $Li[Tl(CH_3)_4]$ and $Li[(CH_3)_3SnTl(CH_3)_3]$.

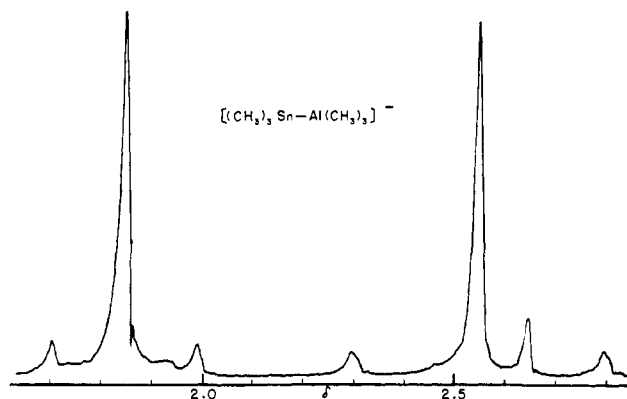
$[(CH_3)_3Sn-Al(CH_3)_3]^-$
2.0
δ
2.5

Figure 1. The 60-MHz nmr spectrum at −60° of a DME solution of $Li[(CH_3)_3SnAl(CH_3)_3]$ showing tin–proton coupling. The upfield lines are assigned to the $Al(CH_3)_3$ moiety and the downfield lines to the $Sn(CH_3)_3$ moiety.

Generally the thermal stability of the tin–metal bond in these species in solution decreases in the order Tl > In ⋦ Ga > Al with no boron derivative obtained. Instead a similar reaction with $B(CH_3)_3$ yielded $Li[B(CH_3)_4]$, some $Sn(CH_3)_4$, and $Li\{Sn[Sn(CH_3)_3]_3\}$. The latter compound was previously characterized by Wells and Brown[1] as a product formed in the attempted isolation of $Li[Sn(CH_3)_3]$ from THF solution. It was characterized in this study both from chemical shift and coupling constant.

The aluminum–tin species formed decomposed completely after 1 day at 0° to form $Li[Al(CH_3)_4]$, $Sn(CH_3)_4$, and $Li\{Sn[Sn(CH_3)_3]_3\}$. The gallium–tin and indium–tin species had similar stabilities so that about 75% decomposed over a 2 day period at room temperature to the tetramethylmetalate and tin species as above. Thermal stability of the tetramethylthallate and the thallium–tin derivatives produced are similar to one another, all showing less than 25% decomposition after 3 days in the dark at room temperature. Unlike the preceding metal–tin species decomposition of the thallium–tin species in solution does not appear to lead to a relative increase in the amount of tetramethyl-

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metalate, nor does the decomposition lead to formation of Li{Sn[Sn(CH₃)₃]₃}, but only to Sn(CH₃)₄ and other unidentified products.

Nmr data for these species are reported in Table I. A comparison of these data with those of Shaw and Allred[11] on (CH₃)₃SnM(CH₃)₃ where M = a group IV element shows a similar decrease for δ_{SnCH_3} as M increases in atomic number. This trend was explained on the basis of the change in magnetic anisotropy of the system and a similar explanation may pertain here although the trend may also be accounted for on the basis of the decrease in electronegativity of the metal. The δ_{MCH} observed for the group IV systems[11] showed no trend while in our systems a general decrease in δ was noted as a function of increasing size and increasing electronegativity.

It was also noted here that J_{SnCH} increased regularly with the size of the metal while J_{SnMCH} varied as Al < Ga > In > Tl. No attempt has yet been made to establish the sign of the J_{SnMCH}, but in Sn₂(CH₃)₆ McFarlane[12] has established that the J_{SnSnCH} is negative. The absolute value of J_{TlCH} decreases regularly in the series TlCH₃²⁺, Tl(CH₃)₂⁺, and Tl(CH₃)₃ to the value we observe for Tl(CH₃)₄⁻. The sign of J_{TlCH} is presumed to be negative since Maher and Evans have established that the sign of Tl–H coupling in Tl(CH₃)₃ is negative.[13] No data are available concerning the sign of the long range TlSnCH coupling constant.

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## Transformation of Digitoxigenin to Scillarenin[1]

Sir:

The naturally occurring bufadienolides from toad venoms and plant sources have displayed a variety of medically interesting properties ranging from anesthetic and antineoplastic activities to heart and respiration effects.[2] Two years ago we summarized a total synthesis of the toad venom constituent bufalin (3a) with digitoxigenin (1), 14-dehydrobufalin (2), and resibufogenin (the related 14β,15β-epoxide) serving as relays.[3] We now wish to report a more direct route from 14-dehydrobufalin to bufalin and a total synthesis of the plant bufadienolide scillarenin (6)[4] employing bufalin as relay.

(1) Parts 24 and 83, respectively, in the series Bufadienolides and Steroids and Related Natural Products. For the preceding contribution (Steroids and Related Natural Products 82), refer to P. Brown, F. Bruschweiler, and G. R. Pettit, *Helv. Chim. Acta*, **55**, 531 (1972).

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(4) An elegant 17-step synthesis of scillarenin starting from 15α-hydroxycortexone has already been achieved: see U. Stache, K.
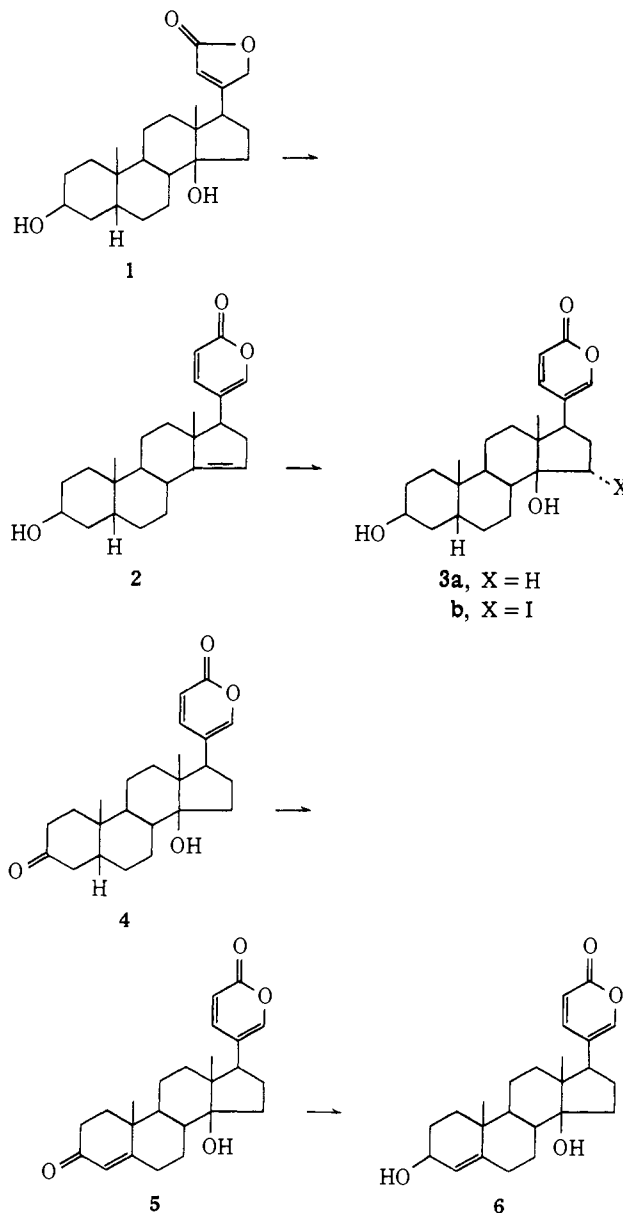
In a typical sequence 14-dehydrobufalin (2, 80 mg)[3] was treated[5] with N-iodosuccinimide in acetone–water (room temperature, 1 day) and the crude iodohydrin (3b, 79 mg) was reduced with Urushibara Ni-A[6] to complete a new synthesis of bufalin (3a, 54 mg, mp 240–243°).[7] Next, bufalin[3] was easily oxidized (chromium trioxide in acetic acid) to bufalone (4, mp 243–245°)[8] which was brominated at C-4 using N-bromosuccinimide in carbon tetrachloride (45 min at reflux). The α-bromo ketone (55% yield) was dehydrohalogenated (refluxing collidine for 6 hr) and scillarenone (5) was

Radscheit, W. Fritsch, W. Haede, H. Kohl, and H. Ruschig, *Justus Liebigs Ann. Chem.*, **750**, 149 (1971).

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(7) Each intermediate was unambiguously characterized as determined by results of infrared, proton magnetic resonance, and mass spectral studies. For a detailed interpretation of bufadienolide mass spectra, refer to P. Brown, Y. Kamano, and G. R. Pettit, *Org. Mass Spectrom.*, **6**, 47, 613 (1972).

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