

**REACTIVITY OF ALLYLIC AND VINYLIC SILANES, GERMANES,
STANNANES AND PLUMBANES TOWARD $S_{H2'}$ OR S_{H2} SUBSTITUTION
BY CARBON- OR HETEROATOM-CENTERED FREE RADICALS ***

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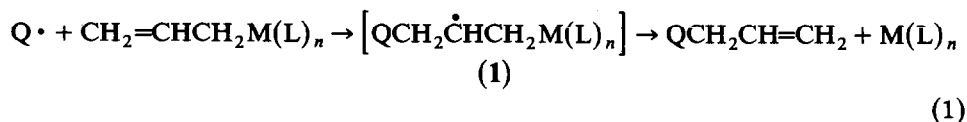
Summary

Compounds of the type $CH_2=CHCH_2MR_3$ and (*E*)- $PhCH=CHMR_3$ ($M = Si, Ge, Sn, Pb$) were allowed to react with a series of heteroatom-centered radicals ($PhY\cdot$, $Y = S, Se, Te$, derived from $PhYYPh$) and carbon-centered radicals ($(CH_3)_2CH\cdot$ derived from $(CH_3)_2CHHgCl$). We report that alkenylplumbanes and, under forcing conditions, alkenylgermanes undergo S_{H2} or $S_{H2'}$ substitution of the metal by chain mechanisms analogous to those previously reported for alkenylstannanes. Alkenylsilanes are unreactive.

Based solely upon product yields, the following trends were observed: The reactivity of the alkenylmetals follow the order metal = $Pb > Sn > Ge (> Si)$. The allylmetals were more reactive than the β -metallostyrenes toward the reactants employed in this study. The chalcogen series $PhYYPh$ exhibits the reactivity order $Y = S > Se > Te$.

Introduction

The free-radical substitution of allylstannanes by an addition–elimination ($S_{H2'}$) sequence has been recognized for more than a decade [1–7] (eq. 1). Similar reactions have been observed for allylcobalt [12,13], allylrhodium [14], and allyliridium [14]

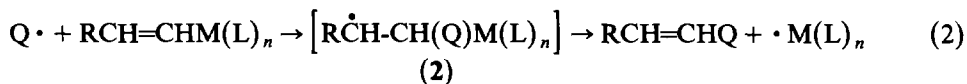


($Q =$ a carbon- or heteroatom-centred radical)

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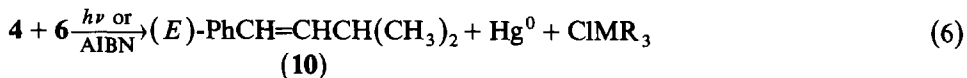
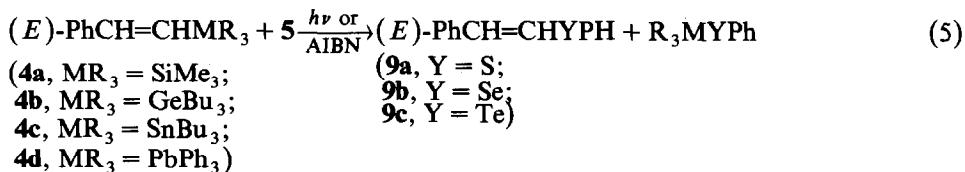
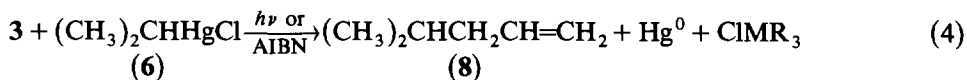
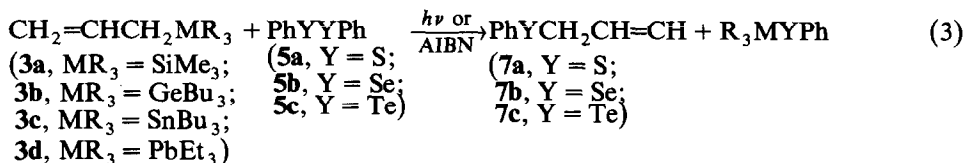
complexes. Recently, the reactivity of allylstannanes has found application in organic synthesis [2-4].

Free-radical (S_H2) substitution of vinylmetallic compounds (eq. 2) has been recently reported for vinylmercurials [15] and vinylstannanes [8,9,15]. Baldwin has demonstrated that vinylic stannanes hold promise as vinyl-transfer reagents in natural product synthesis [10,11].



The mechanisms by which allyl- and vinyl-metals undergo free-radical substitution of the metal bear a close formal resemblance (eq. 1 and 2). Both proceed via an intermediate carbon-centered radical bearing a β -metallo substituent (structures 1 and 2). It has been suggested that such species enjoy a hyperconjugative stabilization similar to that of related β -metallo carbocations [16-19]. Russell has recently reported that the free-radical substitution of vinylmercury or vinyltin compounds can proceed with partial retention of stereochemistry in select cases [9]. This suggests a very short lifetime for structures such as 2, at least with $M = Hg$ or Sn .

In this paper we report the effect of systematic variation of the metal and of the attacking radical upon the free-radical substitutions of allylic and vinylic compounds of the Group IV metals. Thus compounds of type 3 and 4 were subjected to reactions with thiyl, selenyl, telluryl, and alkyl radicals. These radicals were generated under conditions conducive toward chain reactions from 5 or 6 [7,8,15]. The expected substitution products from allylmetals (3) are 7 and 8 (eq. 3 and 4). From the vinylmetals (4), the expected products are 9 and 10 (eq. 5 and 6).



Experimental

The 1H NMR spectra were recorded with either a Varian EM 360 or Bruker WH-90 instrument. ^{13}C NMR spectra were recorded at 22.6 MHz on the Bruker WH-90. GLC was performed on a GOW MAC Series 550 Gas Chromatograph (thermal detection) equipped with a $5' \times 1/4''$ 3% SE30/Chromosorb W packed

column. GC-Mass spectrometry was performed with an HP 5993-B equipped with a $6' \times 1/4''$ glass column packed with 5% OV-17/Chromosorb W.

Preparation of starting materials

Allyltrimethylsilane (**3a**) and allyltributylstannane (**3c**) were obtained commercially. Allyltributylgermane (**3b**) [20] and allyltriethylplumbane (**3d**) [21] have been reported in the literature and were prepared by treatment of allylmagnesium chloride with chlorotributylgermane or chlorotriethylplumbane in ether. The [(*E*)-2-phenylethenyl]triorganometals **4a** [22], **4b** [23], **4c** [24], and **4d** [25] have all been previously characterized and were prepared by reaction of the appropriate triorganometal chloride (Me_3SiCl , Bu_3GeCl , Bu_3SnCl , or Ph_3PbCl) with (2-phenylethenyl)magnesium bromide in ethyl ether or THF. Compounds **3a**–**3d** and **4a**–**4d** all afforded acceptable ^1H NMR spectra. The β -metallostyrenes **4a**–**4d** were all > 90% *trans* isomers.

Efforts to prepare [(*E*)-2-phenylethenyl]triethyl lead or [(*E*)-2-phenylethenyl]tributyllead by the reactions of (2-phenylethenyl)magnesium bromide with triethyllead chloride or tributyllead chloride in THF or diethyl ether failed. Instead, unstable oils were obtained which deposited metallic lead and oxides of lead.

The diphenyl disulphide (**5a**) and diphenyl diselenide (**5b**) were obtained commercially. Diphenyl ditelluride (**5c**) was prepared according to the literature [26]. Isopropylmercury chloride (**6**) was also prepared by a literature procedure [27].

Preparation of authentic substitution products

Authentic samples of **7a**–**7c** were prepared by treatment of PhSSPh, PhSeSePh, or PhTeTePh with allylmagnesium chloride in diethyl ether. Compound **8**, 4-methyl-1-pentene, was commercially obtained. Compounds **9a**–**9c** were prepared by reactions of [(*E*)-2-phenylethenyl]mercury bromide with PhSSPh, PhSeSePh, or PhTeTePh (using a 275 watt sunlamp for initiation) [15]. Compounds **9a**–**9c** prepared in this manner were $\geq 90\%$ *E*. Compound **10**, 3-methyl-1-phenyl-1-butene (> 90% *E*) was prepared by a literature procedure [28].

Reactions of 3 or 4 with 5 or 6

Approximately 100 mg of the alkenylmetal (**3** or **4**) and a slight excess of PhYYPh (**5**) or $(\text{CH}_3)_2\text{CHHgCl}$ (**6**) were dissolved in 0.5 ml of benzene or benzene- d_6 in a small Pyrex flask or a 5 mm Pyrex NMR tube. The solution was deoxygenated with a stream of nitrogen. For reactions where thermal initiation was required, 10 mole percent (based upon alkenylmetal) of azobis[isobutyronitrile] (AIBN) was added, the flask or NMR tube was sealed under nitrogen with a septum, and the contents of the flask (or tube) were heated to 70°C in an oil bath. For reactions employing photoinitiation, the flask or NMR tube was positioned approximately 25 cm from a 275 watt sunlamp at ambient temperature. Reaction progress was monitored by ^1H NMR or GLC and yields were determined by addition of suitable integration standards. Products were verified by ^1H NMR and GCMS comparison with authentic samples.

Results and discussion

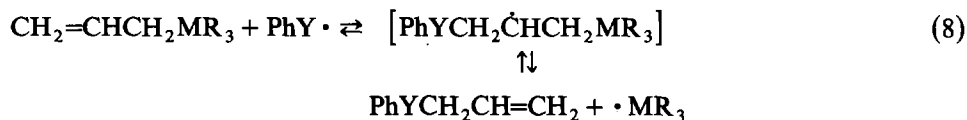
Table 1 shows the results of substitution reactions of the allylmetals **3a**–**3d**. The order of reactivity by metal is $\text{Pb} > \text{Sn} > \text{Ge} > \text{Si}$. This ordering is reflected both by

TABLE 1
SUBSTITUTION REACTIONS OF ALLYLMETALS (3a-3d)

Experiment	Allylmetal	Substitution reagent	Initiation (time) ^a	Expected product	Yield (%) ^b
1	3a	PhSSPh	A (12 h)	7a	< 2 ^c
2	3a	PhSeSePh	A (12 h)	7b	< 2 ^c
3	3a	PhTeTePh	A (12 h)	7c	< 2 ^c
4	3a	(CH ₃) ₂ CHHgCl	A (12 h)	8	< 2 ^c
			or		
			B (12 h)		
5	3b	PhSSPh	A (12 h)	7a	< 2 ^c
6	3b	PhSeSePh	A (12 h)	7b	< 2 ^c
7	3b	PhTeTePh	A (12 h)	7c	< 2 ^c
8	3b	(CH ₃) ₂ CHHgCl	A (29 h)	8	12
9	3c	PhSSPh	A (4 h)	7a	63
10	3c	PhSeSePh	A (4 h)	7b	56
11	3c	PhTeTePh	A (12 h)	7c	< 2 ^c
12	3c	(CH ₃) ₂ CHHgCl	A (29 h)	8	32
13	3c	(CH ₃) ₂ CHHgCl	A (5 h)	8	22
14	3d	PhSSPh	A (1.5 h)	7a	34
15	3d	PhSeSePh	A (1.5 h)	7b	62
16	3d	PhTeTePh	A (1.5 h)	7c	62
17	3d	(CH ₃) ₂ CHHgCl	A (4 h)	8	30

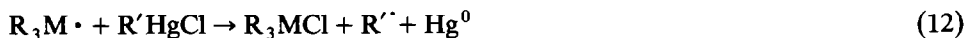
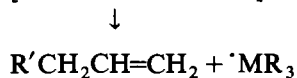
^a A = photoinitiation (275 watt sunlamp) at ambient temperature. B = thermal initiation at 70 °C with 10 mol percent (based upon 3) of AIBN. ^b Yield determined by ¹H NMR or GLC by reference to a suitable integration standard. These yields should not be considered optimized; in some cases starting material was not completely consumed. ^c Nearly all (> 90%) of the starting allylmetal remained after the reaction period was complete.

the qualitative reaction rates and by the appearance or absence of anticipated substitution products. The reactions of allyltributyltin with PhSSPh and PhSeSePh have been reported previously [7]. The mechanism for these reactions was proposed to follow the free-radical chain sequence of eq. 7-9.



The chain propagation steps 8 and 9 include the addition of the chalcogen radical to the allylmetal followed by elimination of a metal-centered radical, which perpetuates the chain by S_H2 displacement of a chalcogen radical from PhYYPh. This mechanism has been supported by the observation of allylic transposition in the reaction of crotyltin derivatives and of chain inhibition by small amounts of galvinoxyl, a radical scavenger [7]. We believe that all of the reactions in Table 1 can be represented by eq. 7-9 or, where the substitution reagent is isopropylmercury chloride, by eq. 10-12. For a discussion alkylmercurials as a source of alkyl radicals

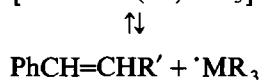
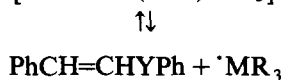
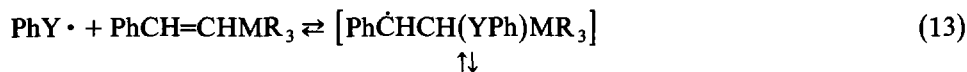
see reference [8]. No products were observed in any of the reactions in Table 1



without photoinitiation or thermal initiation with AIBN. Further, we observed that the facile substitution reactions of allyltriethyllead (**3d**) were inhibited for long periods by the presence of 10 mole percent (based upon **3d**) of galvinoxyl. In addition, metallic mercury was a reaction product in experiments 8, 12, 13, and 17.

The reactions of the allylplumbane **3d** were qualitatively much more rapid than those of allyltributylstannane, **3c**. Further, **3d** reacted readily with PhTeTePh whereas **3c** was completely unreactive. Allyltributylgermane, **3b**, was far less reactive than **3c** or **3d**. Indeed, no reaction was observed between **3b** and the chalcogen series PhYYPh, but a sluggish reaction with isopropylmercury chloride was demonstrated (experiments 5-8, Table 1). Under no conditions could allyltrimethylsilane be induced to react with PhYYPh or with $(CH_3)_2CHHgCl$. For all cases in which no products (<2%) were observed (experiments 1-7, 11) nearly all of the starting allylmetal was recovered after extensive reaction periods. Furthermore, in these experiments there was no evidence of significant reaction or decomposition of the substitution reagents **5a-5c** or **6**.

The free-radical substitution reactions of [(*E*)-2-phenylethenyl]metals **4a-4d** are summarized in Table 2. The free-radical addition-elimination mechanism for the substitution reactions of vinylic tin and mercury compounds has been studied previously in detail [8,15]. Equations 13 and 9 are the accepted propagation steps when the substitution reagent is PhYYPh. Equations 14 and 12 pertain to propagation of chain reactions with isopropylmercury chloride.



These mechanisms are supported [8,15] by the observations of inhibition by small amounts of radical scavengers, and of the requirement of photoinitiation or thermal (AIBN) initiation. We believe that the free radical chain mechanism satisfactorily explains the reactions described in Table 2. In no instance was product formed without sunlamp irradiation or thermal (AIBN) initiation.

The reactivity of the vinylmetals, as with the allylmetals, follows the trend $Pb > Sn > Ge > Si$. Qualitatively, the reaction of PhSSPh with styrenyllead **4d** is much more facile than with the styrenyltin **4c**. In contrast to the tin compound, which is unreactive toward PhSeSePh, the vinyllead compound reacted readily,

TABLE 2
 SUBSTITUTION REACTIONS OF VINYLMETALS (4a-4d)

Experiment	Vinylmetal	Substitution reagent	Initiation (time) ^a	Expected product	Yield (%) ^b
1	4a	PhSSPh	A (12 h) or B (12 h)	9a	< 2 ^c
2	4a	PhSeSePh	A (12 h)	9b	< 2 ^c
3	4a	PhTeTePh	A (12 h)	9c	< 2 ^c
4	4a	(CH ₃) ₂ CHHgCl	A (12 h) or B (12 h)	10	< 2 ^c
5	4b	PhSSPh	A (12 h)	9a	< 2 ^c
6	4b	PhSeSePh	A (12 h)	9b	< 2 ^c
7	4b	PhTeTePh	A (12 h)	9c	< 2 ^c
8	4b	(CH ₃) ₂ CHHgCl	A (12 h) or B (12 h)	10	< 2 ^c
9	4c	PhSSPh	B (20 h)	9a	95
10	4c	PhSeSePh	A (12 h) or B (12 h)	9b	< 2 ^c
11	4c	PhTeTePh	A (12 h) or B (12 h)	9c	< 2 ^c
12	4c	(CH ₃) ₂ CHHgCl	B (12 h)	10	90
13	4d	PhSSPh	A (3 h)	9a	95
14	4d	PhSeSePh	A (5 h)	9b	38
15	4d	PhTeTePh	A (12 h) or B (12 h)	9c	< 2 ^c
16	4d	(CH ₃) ₂ CHHgCl	B (12 h)	10	< 2

^a See footnote *a* in Table 1. ^b See footnote *b* in Table 1. The products were always predominately (> 80%) *trans* by ¹H NMR. ^c Nearly all (> 90%) of the starting vinylmetal remained at the end of the reaction period.

albeit in only 38% yield (experiments 10 and 14). The complete disappearance of starting materials in experiment 14 indicates a competing side reaction between 4d and phenyl diselenide. A reaction producing voluminous precipitate occurred between 4d and isopropylmercury chloride, but very little (< 2%) of the expected product was detected (experiment 16). We speculate that the phenyl ligands may exert a deleterious influence upon the reactivity of 4d toward the highly reactive isopropyl radical.

Tables 1 and 2 reveal similar reactivity patterns for allyl- and vinyl-metals towards the chalcogen series PhYYPh and isopropylmercury chloride. In both series the reactivity by metal increases according to the order Si < Ge < Sn < Pb and the reactivity of the chalcogen series PhYYPh increases according to the order Y = Te < Se < S. This is not particularly surprising in view of the similar mechanisms governing the substitution reactions (see equations 7-14). The obvious distinction lies in the site of addition of the incoming free radical (PhY· or (CH₃)₂CH·) to the alkenylmetal: γ -addition to allylmetals and α -addition to vinylmetals. Subtle dif-

ferences in reactivity appear, however. Allyltin **3c** reacts readily with PhSeSePh whereas vinyltin **4c** is completely unreactive. Allylgermane **3b** reacts with isopropylmercury chloride, but vinylgermane **4b** does not. Based upon product yields, the styrenylmetals were less reactive towards PhYYPh or RHgCl than were the allylmetals.

The addition of PhY• to an alkenylmetal, and the subsequent elimination of R₃M• are probably reversible processes [28–30]. This is illustrated in equations 8 and 13. Tables 1 and 2 list a number of alkenylmetal-PhYYPh pairs which are completely unreactive. This may be due to the failure of a mechanistic step to occur at all, or to an unfavorable equilibrium. Elementary thermodynamic considerations provide at least a partial understanding of the reactivity trend for alkenylmetals with PhYYPh. The strengths of carbon–metal bonds follow the order (Si–C) > (Ge–C) > (Sn–C) > (Pb–C) [32]. Thus the addition–elimination sequence in equation 8 or 13 is endothermic by approximately 17 kcal mol⁻¹ for M = Si and Y = S, assuming that the bond dissociation energies for C–Si and C–S bonds are 77 and 65 kcal mol⁻¹, respectively [32,33]. This addition–elimination sequence with PhS• is predicted to be exothermic where M = Sn or Pb, since the bond dissociation energies for C–Sn and C–Pb bonds are about 54 and 40 kcal mol⁻¹, respectively [33].

Acknowledgements

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