Supplementary Material Available: A table of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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Unsaturated Acyl Derivatives of Silicon, Germanium, and Tin from Metalated Enol Ethers[2a]

John A. Soderquist[1a] and Alfred Hassner*[1b]

Contribution from the Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901.

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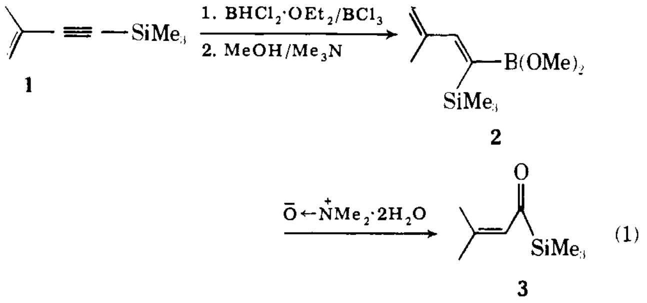
Abstract: The preparation of 1-lithio derivatives of some conjugated vinyl ethers is described. Reaction of these compounds with the chlorotrimethyl derivatives of silicon, germanium, and tin gives the corresponding metallovinyl ethers in 50–80% yield. At least in the case of silicon these reactions proceed with retention of stereochemistry. The silyl compounds undergo $Z \rightleftharpoons E$ photoisomerization. Hydrolysis of the ethers in aqueous acetone gives the corresponding acylmetallanes in 60–75% yield. The metalation and hydrolysis reactions are examined in some detail. The spectral properties of these novel unsaturated acylmetallanes are presented and discussed.

Introduction

Studies in our laboratory have revealed that 1-trimethylsilylacetylenes can be converted to the corresponding α-silaketones (acylsilanes) using a hydroboration/oxidation sequence.[2b] From the enyne **1**, it was possible to prepare the first example of an acrylic α,β-unsaturated acylsilane (**3**) since the oxidation of the vinylboronate (**2**) is accompanied by isomerization of the double bond into conjugation (eq 1). In spite of repeated attempts, we were unable to extend this method to the preparation of the corresponding germanium and tin ketones. Under our conditions, the hydroboration step failed to give the desired adducts, presumably owing to the strong Lewis acid nature of the reactants. Therefore, we chose to investigate other routes to **3**, which could accommodate not only a variety of enone moieties, but also germanium and tin substitution.

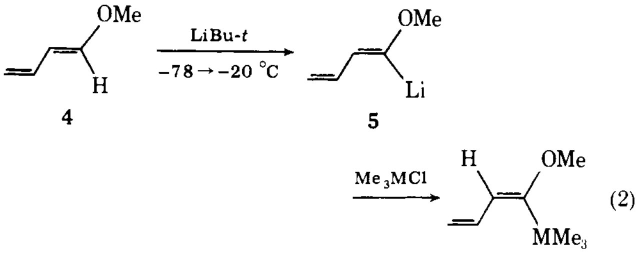


To date, the most convenient and general methods for the preparation of acyl derivatives of silicon and germanium involve the use of masked acyl anion equivalents,[3] including the dithiane method.[4] Unfortunately, this method fails in the hydrolysis step for the tin case.[4]

More recently, Baldwin and co-workers have reported that lithiated 1-methoxybutadiene can be used as a crotonyl anion equivalent.[5] Owing to the exceptionally mild conditions required to hydrolyze vinyl ethers, an approach to α,β-unsaturated acylmetallanes based on such compounds seemed particularly attractive. Therefore, we undertook an investigation of the metalation of several representative vinyl ethers and their conversion to acylmetallanes.

Results and Discussion

Synthesis and Photochemistry of Metalated Enol Ethers. When *trans*-1-methoxy-1,3-butadiene was metalated using 1 equiv of *tert*-butyllithium and the resulting 1-lithiated compound (**5**) was treated with the chlorotrimethyl derivatives of silicon, germanium, and tin, the corresponding adducts (**6**) (eq 2) were isolated in good yields.



6a, M = Si
b, M = Ge
c, M = Sn

Minor amounts (<5%) of *trans*-1 methoxy-5,5-dimethylhex-2-ene (**7**) were formed in each case, apparently arising from the addition of *tert*-butyllithium to **4**.

Photoisomerization of the silylated ether (**6a**) in C_6D_6 (monitored by GC) led to a photostationary 60:40 mixture of

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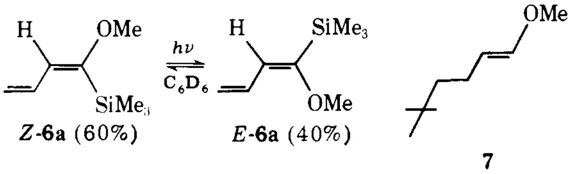
Table I. Products Obtained from the Metalation of *cis*-β-Methoxystyrene under Various Conditions

	solvent	product yields,[a] %				
run	(reaction temp, °C)	*cis*-**12**	*trans*-**12**	**13a**	**11**	total
1	TMEDA (−78)	43	11	9	32	95
2	TMEDA (−78 → 0)	43	9	19	26	97
3	TMEDA (0)	34	16	31	17	98
4	TMEDA (25)	24	24	24	27	99
5	THF (−78 → 0)	42	17	19	12	90
6	THF (0)	37	18	28	14	97

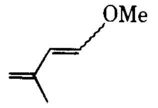
[a] Yields were determined by GC analysis using dodecane as an internal standard. Approximately 10% of α-methoxystyrene was present in the starting material and yields are corrected for this impurity. An additional minor product with a similar retention time to that of this impurity was observed in the THF reactions.

E and *Z* isomers (eq 3). In *E*-**6a** the 2-vinyl proton trans to the methoxy group was found ca. 0.20 ppm upfield from the corresponding proton in the cis isomer.[6] Further, using europium shift reagent, we were able to preferentially shift downfield the signals attributable to *E*-**6a** since the absorbances due to *Z*-**6a** were unaffected by this reagent. This allowed us to perform a variety of decoupling experiments to verify the proton assignments for *E*-**6a** in the mixture and clearly established that **4** was converted to **6** with clean retention of stereochemistry.

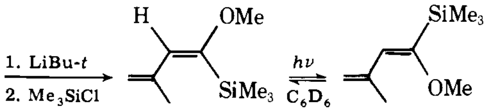


Z-**6a** (60%) *E*-**6a** (40%) **7** (3)

The silylation of the analogous isoprenyl system (**8**), prepared as a ca. 25:75 mixture of cis and trans isomers using the method of Mironov and co-workers,[7] gave a single silylated ether (*Z*-**9a**) in 69% yield by GC (eq 4).



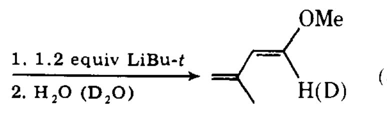
8 (cis/trans = 25/75)



Z-**9a** (60%) *E*-**9a** (40%) (4)

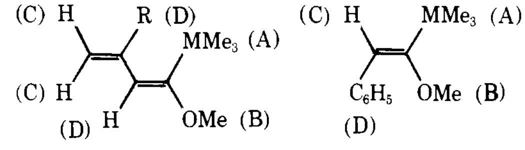
As for *Z*-**6a**, the photoisomerization of *Z*-**9a** was carried out in C_6D_6 to give a 60:40 mixture of *Z* and *E* isomers and the stereochemical assignment was carried out by NMR. The results indicate that the *Z* product was formed by the metalation/silylation of *trans*-**8**; however, the fate of *cis*-**8** on treatment with *tert*-butyllithium was less clear since it neither remained unreacted nor was converted to *E*-**9a**. That *t*-BuLi does not cause cis–trans isomerization of **8** is apparent from the unchanged cis/trans ratio of 25/75 of the 10% unreacted **8** when 0.9 equiv of *tert*-butyllithium was employed. Treatment of **8** with 1.2 equiv of *tert*-butyllithium, followed by quenching with water or D_2O, gave pure *trans*-**8** or 1-deuterated *E*-**8** (>98% isomeric purity) in 50 and 45% yield, respectively. Through our data, it is not possible to rule out the equilibration of the *Z*-lithiated derivative of **8** to give only the *E* isomer. However, the 69% yield of *Z*-**9a** from **8** is essentially the same as the amount of the trans isomer (75%) present in this material. The fact that this type of equilibration does not occur in related systems[8] (vide infra) suggests that the *Z*-lithiated compound derived from *cis*-**8**, if formed, is unstable and its decomposition products do not contribute to the yield of the *Z*-**9a** or related products. With an excess of the *E*-lithio ether reagent (**10**), good yields of the corresponding silicon, germanium, and tin compounds (*Z*-**9**) are formed (eq 6).

8 (cis/trans = 25/75)



(cis/trans < 50%) (5)

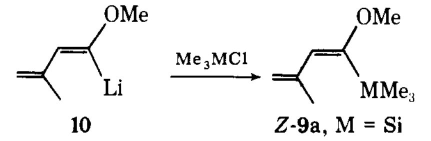
Table II. NMR Parameters for the Methoxyvinyl Derivatives of Silicon, Germanium and Tin



6,**9** **13**

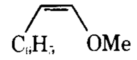
compd	chemical shifts,[a] ppm			
	A	B	C	D
6a	0.17	3.52	4.7–5.1 (8)	5.75–6.80 (10)
6b	0.33	3.50	4.6–5.0 (8)	5.62–6.60 (8)
6c	0.26	3.56	4.44–5.2 (m)	5.8–6.7 (m)
9a	0.10	3.41	4.64	5.48 (1.63)
9b	0.40	3.59	4.76	5.56 (1.92)
9c	0.17	3.53	4.65	5.66 (1.82)
13a	0.37	3.71	5.77	7.0–7.7
13b	0.50	3.77	5.55	7.0–7.7
13c	0.39[b]	3.76	5.31[c]	7.0–7.7

[a] Measured in CCl_4 solution. For **6**, the numbers in parentheses are the number of lines observed for this absorbance. For **9**, the chemical shift of the 3-Me protons are given in parentheses. For **6**, the apparent coupling constants $J_{23} = 10.6$, $J_{34} = 15.6$, $J_{34'} = 9.2$, and $J_{44'} = 2.0$ Hz are observed. For **6**, the relative areas are 9 (A):3 (B):2 (C):2 (D). For **9**, relative areas are 9 (A):3 (B):2 (C):1 (D):3 (3-CH_3). All absorbances appear as singlets, the C and D peaks being broad. Irradiation of any of these broad peaks with rf power sharpens the others, indicating long-range (four-bond) coupling. For **13** the relative areas of A:B:C:D were 9:3:1:5. [b] $J_{Sn-CH_3} \sim 55$ Hz. [c] $J_{Sn-ViH} \sim 39$ Hz.

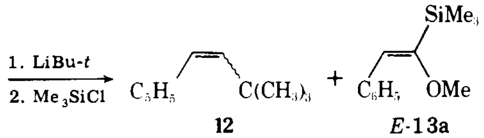


10 *Z*-**9a**, M = Si (6)
b, M = Ge
c, M = Sn

The metalation of *cis*-β-methoxystyrene (**11**) and reaction with chlorotrimethylsilane was carried out at several reaction temperatures using either THF or *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) solvent. The product mixtures contained *cis*- and *trans*-β-*tert*-butylstyrene (**12**), the *E*-silylated ether (**13a**), as well as unreacted starting material (see eq 7 and Table I). The total yield of **12**, unlike that of **13**, is largely independent of reaction conditions. Quenching of the reaction mixture with D_2O (entry 2, Table II) gave a 17% yield of the *Z*-β-deuterated **11** in good agreement with the corresponding yield of *E*-**13a**. Hence, it is likely that complete re-



11



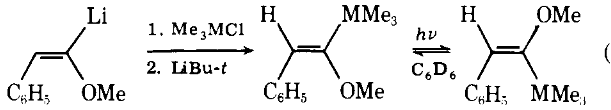
12 *E*-**13a** (7)

Table III. Mass Spectral Data for the α-Methoxyvinyl Derivatives of Silicon, Germanium, and Tin[a,b]

compd	*m/e* (% base)
6a	156 (23), 141 (22), 89 (100), 73 (100), 59 (32)
6b	202 (42), 187 (42), 135 (52), 119 (100), 105 (42), 89 (20), 71 (54),[c] 57 (61)[c]
6c	248 (31), 233 (100), 181 (26), 165 (28), 150 (31), 135 (21), 83 (42)[c]
9a	170 (56), 155 (57), 138 (14), 125 (9), 123 (7), 97 (17), 89 (100), 75 (22), 73 (100), 59 (20)
9b	216 (35), 201 (61), 169 (12), 135 (35), 119 (36), 105 (24), 97 (100),[c] 89 (11)
9c	262 (9), 247 (100), 181 (14), 165 (27), 151 (20), 135 (14), 97 (75)[c]
13a	206 (100), 191 (6), 163 (17), 135 (8), 121 (4), 89 (86), 73 (86)
13b	252 (100), 237 (46), 135 (74), 119 (36), 105 (17)
13c	298 (32), 283 (100), 181 (32), 165 (16), 150 (26), 135 (13)

[a] Recorded using a Du Pont Model 21-491B mass spectrometer. [b] For the germanium and tin compounds only the uncorrected peaks attributable to the ^{74}Ge or ^{120}Sn isotopes are listed from each set observed. [c] These peaks do not contain the metalloid as evidenced by the isotopic distribution.

action of the lithiated styrene (**18**) with chlorotrimethylsilane is occurring. Therefore, from the yields of **13**, it was possible to calculate the molarity of the corresponding lithium reagent (**18**). Addition of the stoichiometric amounts of the chlorotrimethyl derivatives of silicon, germanium, or tin completely discharged the purple color[9] of the solution containing **18** and gave good yields of the desired *E* ethers (**13**) (eq 8).



(8)

18

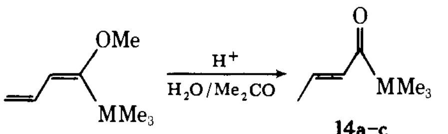
E-**13**

Z-**13a**, M = Si
b, M = Ge
c, M = Sn

13a (M = Si) was photoisomerized to a ca. 50:50 mixture of *E* and *Z* isomers in C_6D_6 solvent. The α vinylic proton in *E*-**13a** at 6.07 ppm shifted downfield to 6.51 ppm in the *Z* photoproduct in agreement with a change from a trans to a cis relationship to the methoxy group.

New absorbances attributable to *Z*-**13a** were observed in this mixture for all protons. The spectral properties of the metalloidal enol ethers (**6**, **9**, and **13**) are given in Tables II and III.

Hydrolysis of Metalloidal Enol Ethers to Acyl Metallanes. The acid-catalyzed hydrolyses of the metalloidal vinyl ethers to acyl metallanes **14**, **16**, and **17** were carried out in acetone–water (4:1) solution. For the butadienyl systems (**6**), hydrolysis gives the *trans*-crotonyl compounds in good yield (eq 9). In deuterated solvents, the product is found to contain



(9)

6

14a–c

a single deuteron located in the 4 position. Other butadienyl ethers have exhibited similar behavior.[10] Under these conditons, all of the ethers **6** exhibit smooth first-order kinetics as shown in Figure 1. These data give rate constants of 6.2, 10, and 18 × 10^{-4} s^{-1} at 33 °C for the silicon (**6a**), germanium (**6b**), and tin (**6c**) compounds, respectively. This rate ordering (Si < Ge < Sn) appears to be quite general for such metalloidal systems.[10]

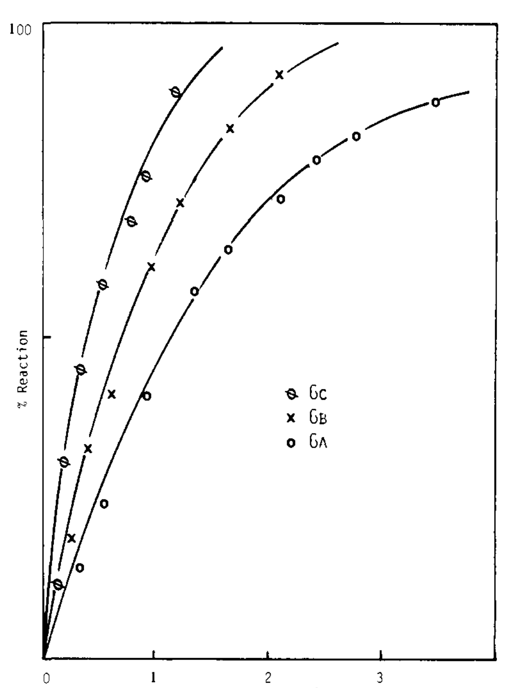
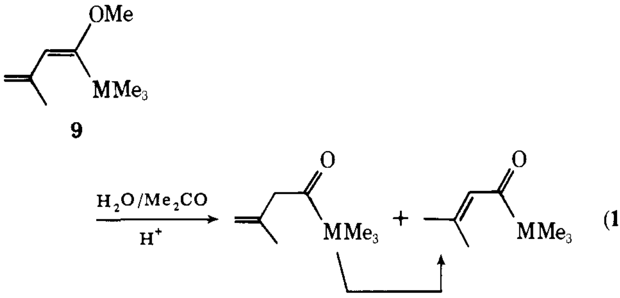


Figure 1. Comparative rate of hydrolysis of **6** in acetone-d_6/D_2O (4:1) using DBr (0.20 M) catalysis at 33 °C.

Unlike for the butadienyl ethers (**6**), the hydrolyses of the isoprenyl ethers (**9**) did not lead to the exclusive formation of the conjugated enones (**16**) (eq 10). After disappearance of the



(10)

15

16a–c

starting ethers (**9**), the ratios of **15**:**16** were 10:90, 15:85, and 40:60 for the silicon, germanium, and tin compounds, respectively. By contrast, we found the hydrolysis of the parent ether system (**8**) to give only the conjugated product, β-methylcrotonaldehyde.[12] These facts suggest that the formation of the nonconjugated product (**15**) is due to steric interaction of the metalloidal group with the C_3 methyl group in **9**, limiting the conjugative interaction of the vinyl moieties and giving rise to a competitive protonation at C_2. Furthermore, in deuterated solvents, **9a** (M = Si) undergoes hydrolysis six times faster than the butadienyl compound (**6a**) (see Figure 2).

By NMR, all of the protons in the methylcrotonyl moiety were found to exchange with deuterated solvents under the reaction conditions. Therefore, using longer reaction times (i.e., 20 h), clean formation of the conjugated products (**16**) was observed in the silicon and germanium cases. However, the tin compound (**16c**) was evidently too unstable to survive an isomerization of the type **15** → **16** since reaction mixtures containing this compound were found to decolorize after 3–4 h. Therefore, we chose to investigate the isomerization of **15c** under basic conditions. Indeed, using 1 molar equiv of pyridine in benzene solution, clean formation of the desired conjugated ketone (**16c**) was observed after 1 h at reflux temperature.

The hydrolyses of the β-methoxystyryl ethers (**13**) were found to proceed slower than for the dienyl ethers (see Figure

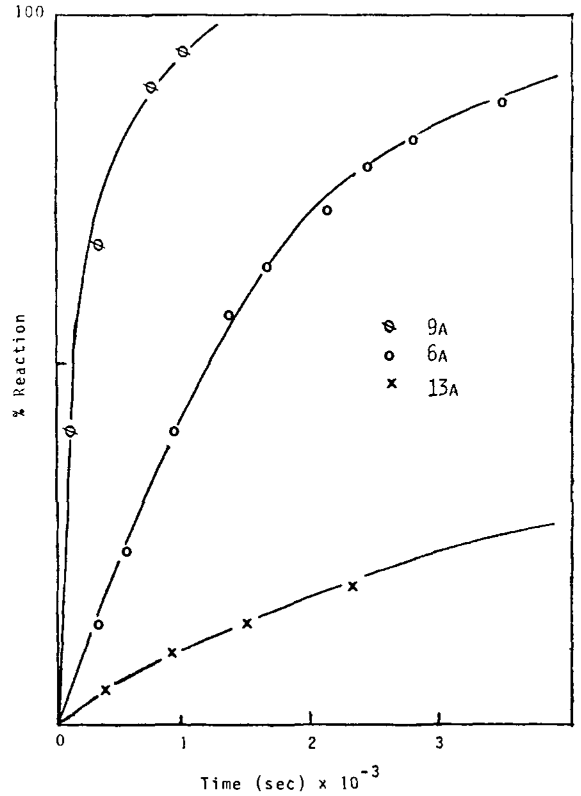
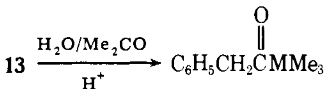


Figure 2. Comparative rate of hydrolysis of silyl vinyl ethers in acetone-d_6/D_2O (4:1) using DBr (0.20 M) catalysis at 33 °C.

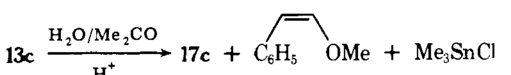
2). For **13a** a first-order rate constant of $9.6 \times 10^{-5}\ s^{-1}$ was obtained in deuterated solvents under the same conditions where **6a** had a rate constant of $6.2 \times 10^{-4}\ s^{-1}$ and **9a** a value of $3.7 \times 10^{-3}\ s^{-1}$. This is consistent with the rate-retarding influence of the phenyl group β to the methoxy moiety.[13] For the silicon and germanium compounds, smooth conversion of the enol ethers to the corresponding ketones (**17**) was observed (eq 11).



$$\mathbf{13} \xrightarrow[H^+]{H_2O/Me_2CO} C_6H_5CH_2\overset{\overset{\displaystyle O}{\|}}{C}MMe_3 \qquad (11)$$

17a, M = Si
b, M = Ge
c, M = Sn

The tin compound (**13c**) also gives the desired ketone (**17c**) in major amounts (72%). However, products of destannylation are also obtained in minor amounts (28%) (eq 12). The formation of only cis ether (**11**) from **13c** indicates that the destannylation occurs with clean retention of configuration. This phenomenon has been observed for desilylation of β-silylstyrenes as well as a number of related processes.[14]


(12)

11

Spectra. The spectral properties of the acyl derivatives are given in Tables IV–VI. These acylmetallanes all have infrared absorbances attributable to the carbonyl moiety which are shifted by 30–50 cm^{-1} from the all-carbon counterparts,[16] a phenomenon quite general for acylmetallanes.[1] The double-bond moiety in **6** or **9** is similarly influenced by the metalloidal substitution (see Table VI). The cortonylmetallanes (**14**) give two carbonyl stretching absorbances attributable[16] to the s-trans (1642–1648 cm^{-1}) and the s-cis conformation (1652–1660 cm^{-1}) with a preference for the s-trans conformation. The carbonyl stretching frequency of the β-methylcrotonylmetallanes (**16**) is found as one band in the 1640–1645-cm^{-1} region, which indicates that, as in the carbon system, the s-trans conformation comprises most of the equilibrium mixture.

Table IV. Mass Spectral Data for the Acylmetallanes

compd	m/e (% base)
14a	142 (7), 127 (15), 99 (14), 73 (100), 59 (11)
14b	188 (17), 173 (10), 145 (7), 119 (100), 105 (5), 89 (9)
14c	234 (5), 219 (3), 191 (1), 165 (70), 150 (4), 135 (5), 69 (100)[a]
16a[b]	156 (41), 141 (27), 113 (21), 101 (5), 83 (13), 73 (100)
16b	202 (20), 187 (5), 159 (14), 119 (70), 105 (4), 89 (5), 83 (100)[a]
16c[c]	248 (6), 233 (4), 220 (6), 205 (14), 165 (74), 150 (9), 135 (20), 83 (100)[a]
17a[b]	192 (1), 177 (2), 164 (18), 149 (6), 121 (4), 101 (17), 91 (3), 75 (9), 74 (6), 73 (100)
17b	238 (0), 210 (25), 197 (7), 147 (5), 119 (100), 91 (11)[a]

[a] Peak does not contain metalloid. [b] For **16a**, metastable ions were observed at *m/e* 127.4. For **17a**, metastable ions were observed at *m/e* 98.3, 32.5, and 27.8. [c] Ca. 60:40 mixture of isomers (**16c:15c**).

The ultraviolet data for the crotonylmetallanes (**14**) show a n → π^* absorbance[15] in the 415–430-nm region while the β-methylcrotonyl derivatives have this absorbance in the 430–450-nm region in nonpolar solvents. In similar carbon systems, this absorbance is found at ca. 330 nm and is known to be solvent[16] as well as substituent[17] dependent. Hence, the effect exhibited by the metalloidal atom in these α-metalla-α',β'-enones compared to substitution by a *tert*-butyl group is to shift the n → π^* band to ca. 100 nm longer wavelength (comparable to the aliphatic systems[1] ($Me_3C(CO)Me$, λ_{max} 278 nm vs. $Me_3Si(CO)Me$, λ_{max} 372 nm). For **14a**, the λ_{max} for this transition has values of 430 nm in the vapor phase, 439 nm in C_6H_{12}, and 421 nm in 95% ethanol, a similar ordering as for mesityl oxide.[19]

The influence of the metalloid on the $\pi \rightarrow \pi^*$ transition, i.e., 224 nm (ϵ 10 300) for **14a** in cyclohexane vs. 220 nm (ϵ 10 800) for *trans*-3-hexen-2-one in EtOH, is small (ca. 10 nm after correction for solvent). The powerful influence of the adjacent metalloid seems restricted to the n → π^* transition in ketones, having little effect on $\pi \rightarrow \pi^*$ transitions.

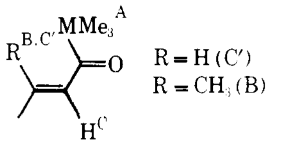
Experimental Section

Chlorotrimethylsilane (Aldrich) was distilled from calcium hydride prior to use. Chlorotrimethylgermane (Laramie) and chlorotrimethyltin (Alfa) were used without purification. The ethers (i.e., **4** (Aldrich), **8**[7], and **11** (Aldrich)) were distilled from lithium aluminum hydride to remove aldehyde impurities. The latter compound was found to contain ca. 10% α-methoxystyrene, which did not interfere with the metalation procedure. However, it could be removed from **11** by the partial hydrolysis of the commercial material following by distillation from $LiAlH_4$. Solutions of *tert*-butyllithium in pentane (Alfa) were used directly after analysis for active organolithium.

All reactions were carried out under an inert gas atmosphere. The metalation procedures were carried out in oven-dried glassware. The hydrolysis reactions were carried out with a minimum of exposure to light. Analyses were performed on an HP-5750 research chromatograph using 5 ft × 1/4 in. 10% Carbowax on silylated Chromosorb W temperature programmed from 50 °C to 10 °C/min unless otherwise stated. Nuclear magnetic resonance spectra were obtained using a Varian EM-360 equipped with a lock-decoupler.

***cis*- and *trans*-1-Methoxy-3-methyl-1,3-butadiene (8).** This compound was prepared from 1,1,3-trimethoxy-3-methylbutane in 40–60% yields using the $MgHPO_4{\cdot}Na_2SiO_3$ catalyst as described by Mironov et al.[7] Typically ca. 50 g of this material was slowly introduced into the combustion tube (350–400 °C) against a pressure of 25 Torr over 1 h. The pyrolysate was collected in a cold trap (−78 °C)

Table V. NMR Data for the Acylmetallanes



compd	chemical shifts,[b,c] ppm A	B, B′	C, C′
14a	0.32	—, 2.00	6.10, 6.77
14b	0.35	—, 1.95	6.02, 6.62
14c	0.28	—, 2.00	5.94, 6.39
16a	0.25	1.98, 2.18	6.56, —
16b	0.30	1.85, 2.04	6.32, —
16c	0.23	1.87, 2.04	6.40, —
17a[d]	0.12	3.77	7.23
17b[d]	0.21	3.73	7.13
17c[d]	0.10	3.80	7.30

[a] Data recorded on CCl_4 solution. [b] Assignments based on carbon system.[17] [c] For the compounds **14** (R = H), the following coupling constants were measured: $J_{CC'} = 16.0$, $J_{B'C'} = 6.4$, $J_{B'C} = 1.1$ Hz. For **16** the J values were ≤ 1.0 Hz and could not be resolved. For **14** treatment with Eu(fod)$_3$ showed the following order of $\Delta\delta$: C > C′ $\sim$ A > B′. All couplings were confirmed by double-resonance experiments. [d] For **17**, A, B, and C are in a 9:2:5 ratio. A and B are singlets and C is a multiplet.

which contained K_2CO_3 (1 g). After washing with water (2 × equal volume), the dried (K_2CO_3) ether was distilled (bp 112-117 °C (750 Torr)) (lit. 115-116 °C). By NMR, the distillate contained the cis and trans compounds in a ratio of 25:75 with a trace (<2%) of β-methylcrotonaldehyde (δ 9.85 (d), J = 8 Hz).

NMR (CCl_4): cis-*d* (25% of mixture) δ 1.96 (bs, 3 H), 3.60 (s, 3 H), 4.6-4.8 (m, 3 H), 5.72 (d, 1 H), J = 7.2 Hz.

trans-*d* (75% of mixture): δ 1.81 (bs, 3 H), 3.57 (s, 3 H), 4.6-4.8 (m, 2 H), 5.51 (d, 1 H), J = 12.8 Hz, 6.52 (d, 1 H), J = 12.8 Hz.

Since this mixture was not separated, the values given in the δ 4.6-4.8 region are calculated and not measured directly. The presence of the upfield proton which couples with the δ 5.51 ppm doublet in cis-*d* was verified by a double-resonance experiment. All J's are apparent values.

Distillation of this material from $LiAlH_4$ removed the aldehyde impurity.

Lithiation of the Vinyl Ethers Using THF Solvent. To a cold (−78 °C), stirred solution of the appropriate vinyl ether (i.e., **4** or **8**) (2.5 M) in THF, 1 molar equiv of *tert*-butyllithium (1.6 M) in pentane was added dropwise. After the addition was complete, the reaction mixture was allowed to warm to ca. −20 °C over 30 min. After ca. 30 min at this temperature, the mixture was used for subsequent reactions.

(*Z*)-1-Methoxy-1-trimethylsilyl-1,3-butadiene (6a). Chlorotrimethylsilane (2.7 g, 25 mmol) in pentane (ca. 10 mL) was stirred and cooled (−78 °C) while **5** (ca. 50 mL) was added using a syringe. Addition of **5** was ceased when the color was no longer discharged upon addition. The mixture was carefully poured into a separatory funnel which contained saturated ammonium chloride solution (ca. 50 mL). The organic layer was dried (K_2CO_3), filtered, and distilled to give 2.3 g (59%) of **6a** (bp 156-158 °C (740 Torr)).

Anal. Calcd for $C_8H_{16}OSi$: C, 61.47; H, 10.32. Found: C, 61.33; H, 10.34.

(*Z*)-1-Methoxy-1-trimethylgermyl-1,3-butadiene (6b) was prepared as for **6a** from chlorotrimethylgermane (5.0 g, 33 mmol) in pentane (10 mL) and an excess of **5** to give 3.5 g (53%) of **6b** (bp 168-170 °C (740 Torr)).

Anal. Calcd for $C_6H_{16}OGe$: C, 47.85; H, 8.03. Found: C, 48.00; H, 8.08.

(*Z*)-1-Methoxy-1-trimethylstannyl-1,3-butadiene (6c) was prepared as for **6a** from chlorotrimethyltin (9.8 g, 49 mmol) in THF (25 mL) and an excess of **5** to give 9.0 g (74%) of **6c** (bp 86-90 °C (15 Torr)).

Anal. Calcd for $C_6H_{16}OSn$: C, 38.92; H, 6.53. Found: C, 39.00; H, 6.57.

(*Z*)-1-Methoxy-3-methyl-1-trimethylsilyl-1,3-butadiene (9a) was prepared as for **6a** from chlorotrimethylsilane (2.2 g, 25 mmol) and an excess of **10** to give 3.5 g (82%) of **9a** (bp 69-72 °C (16 Torr)).

Table VI. Selected Infrared and Ultraviolet Absorbances for the Acylmetallanes[a,b]

compd	C=O[c]	C=C[c]	λ_{max} (ϵ)[d]
14a	1652, 1642	1590	424 (98), 224.5 (10 300)
14b	1652, 1644	1612	416.3 (109). 258 (11 300)
14c	1660, 1648	1600	432, 258
16a	1640	1576	439 (120), 249 (12 700)
16b[e]	1645	1595	432 (140)
16c[e]	1640	1590	453
17a	1635		376.5 (113)
17b	1660		365.5 (124)
17c	1656		379

[a] Additional data given in Experimental Section. Neat liquids were used for IR measurements and cyclohexane solutions for UV spectra. [b] However, all measurements on the tin compounds were CCl_4. [c] In cm^{-1}. [d] In nm. [e] Short-wavelength absorbances were not determined for these compounds.

Anal. Calcd for $C_9H_{18}OSi$: C, 63.46; H, 10.65. Found: C, 63.49; H, 10.66.

(*Z*)-1-Methoxy-3-methyl-1-trimethylgermyl-1,3-butadiene (9b) was prepared as for **6a** from chlorotrimethylgermane (3.8 g, 25 mmol) and an excess of **10** to give 3.0 g (56%) of **9b** (bp 76-78 °C (15 Torr)).

Anal. Calcd for $C_9H_{18}OGe$: C, 50.32; H, 8.44. Found: C, 50.11; H, 8.46.

(*Z*)-1-Methoxy-3-methyl-1-trimethylstannyl-1,3-butadiene (9c) was prepared as for **6a** from chlorotrimethylstannane (10 g, 50 mmol) in THF (25 mL) and an excess of **10** to give 7.8 g (60%) of **9c** (bp 92-96 °C (15 Torr)).

Anal. Calcd for $C_9H_{18}OSn$: C, 38.92; H, 6.53. Found: C, 39.15; H, 6.61.

(*E*)-1-Deuterio-1-methoxy-3-methyl-1,3-butadiene (8-*d*) was prepared from **8** (0.25 g, 2.6 mmol) in THF (1.0 mL) and *tert*-butyllithium (3.1 mmol) in pentane. After the mixture was quenched with D_2O (1.0 mL), tetradecane standard was added, and the dried (K_2CO_3) reaction mixture was analyzed by GC. The yield of **8**-*d* was 45% with the *Z*:*E* ratio $\sim$2:98. A sample of this product was isolated by preparative GC. Complete absence of absorbances in the 6-7-ppm region indicated that the 1 position in **8**-*d* was completely deuterated.

8-*d*: NMR (CCl_4) δ 1.80 (m, 3 H), 3.55 (s, 3 H), 4.70 (m, 2 H), 5.60 (m, 1 H) ppm.

The protonation and silylation studies were similarly performed.

Lithiation of *cis*-β-Methoxystyrene (11). To a cold (−78 °C) mixture of **11** (50 g, 0.37 mol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (86 g, 0.74 mol) was added *tert*-butyllithium (161 mL, 2.3 M, 0.37 mol) dropwise over 30 min. After the addition was complete, a portion (10 mL) of the mixture was withdrawn and quenched with cold (0 °C) D_2O (10 mL). After treatment with saturated ammonium chloride (10 mL), the organic layer was washed with water (3 × 10 mL), followed by cold (0 °C) 1.0 M HCl (10 mL). The dried (K_2CO_3) organic layer was concentrated and distilled to give 1.0 g of a mixture (bp 47-50 °C (1.2 Torr)). Gas chromatographic analysis (10% Carbowax) of this mixture revealed three components. The first two were found to be *cis*- and *trans*-β-*tert*-butylstyrenes (**12**) in a ca. 9:1 ratio. The third, which composed roughly half the mixture, was found to be a mixture of β-deuterated and nondeuterated **11**.

The NMR spectrum of this mixture exhibited signals at δ 3.71 (s), 5.05 (d, J = 7.0 Hz), 5.95 (d, J = 7.0 Hz), and 6.9-7.55 (m) ppm. However, an additional peak at δ 5.05 ppm (between the doublet) was observed. This absorbance was taken as the α proton in (*Z*)-β-deuterio-β-methoxystyrene. Integration of the doublet at 5.95 ppm vs. the 5.05-ppm region gave a ratio of 2:3. Since the 3.71 to 6.9-7.55 to 5.05 ppm regions gave areas of 3:5:1, it was concluded that the ratio of deuterated β-methoxystyrene to the nondeuterated starting material was 1:2. Hence the original reaction mixture was calculated to contain ca. 17% of deuterated material.

The lithiation of **11** was carried out on a 5-10-mmol scale using dodecane as an internal GC standard. The order of elution on a 10% Carbowax column was $C_{12}H_{26}$, *cis*-**12**, *trans*-**12**, α-methoxystyrene, **11**, **13a**. These results are tabulated in Table I.

(*E*)-1-Methoxy-2-phenyl-1-trimethylsilylethene (13a). Chlorotrimethylsilane (2.2 g, 20 mol) in pentane (10 mL) was stirred and cooled (−78 °C) while a solution of **14** (100 mL) was added using a syringe.

After the addition was complete, water (20 mL) was carefully added, followed by saturated ammonium chloride solution (50 mL). After separation, the organic layer was washed with water (3 × 50 mL) followed by saturated ammonium chloride solution (50 mL). The dried solution (K_2CO_3) was concentrated and distilled to give an initial forerun (bp 40–70 °C (1.2 Torr)) which was not weighed, but rather combined with that obtained in subsequent preparation, which gave 37.4 g (total) of a mixture of **11** (45%), *cis*-**12** (45%), and *trans*-**12** (10%).

The product, **13a** (3.3 g, 80% based on TMSCl), was collected at 85 °C (1.2 Torr).

Anal. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79. Found: C, 69.98; H, 8.83.

(*E*)-1-Methoxy-2-phenyl-1-trimethylgermylethane (13b). This compound was prepared from chlorotrimethylgermane (3.1 g, 20 mmol) exactly as described for **13a.** Distillation gave 3.0 g (60%) of **13b** (bp 94–95 °C (1.2 Torr)).

Anal. Calcd for $C_{12}H_{18}OGe$: C, 57.45; H, 7.23. Found: C, 57.69; H, 7.32.

(*E*)-1-Methoxy-2-phenyl-1-trimethylstannylethane (13c). This compound was prepared from chlorotrimethyltin (4.0 g, 20 mmol) exactly as described for **13a.** Distillation gave 3.2 g (54%) of **13c** (bp 102–104 °C (1.2 Torr)).

Anal. Calcd for $C_{12}H_{18}OSn$: C, 48.64; H, 6.12. Found: C, 48.54; H, 6.12.

Photoisomerization of (Methoxyvinyl)silanes. Solutions of the appropriate ethers in an inert gas atmosphere were irradiated in benzene-d_6 solvent using a 450-W mercury lamp whose light was filtered through Pyrex glass (ca. 0.5 cm). The isomerizations were monitored by gas chromatography (6 ft × 1/4 in. 10% QF-1 on silylated Chromosorb W).

For **6a,** irradiation for 4 h gave a 60:40 *Z*:*E* mixture. The *E* isomer had the longer retention time.

NMR (**6a,** C_6D_6): δ 0.40 (s, OH), 3.34 (s, 3 H), 4.96 (dd, 1 H), J = 9.2, 2.0 Hz, 5.18 (dd, 1 H), J = 15.6, 2.0 Hz, *6.08* (d, 1 H), J = 10.6 Hz, 6.95 (ddd, 1 H), J = 15.6, 10.6, 9.2 Hz.

Although the spectrum of the mixture of *Z*-**6a** (60%) and *E*-**6a** (40%) was too complicated for a complete analysis, the photoproduct, *E*-**6a,** gave new absorbances at 0.23 (s, 9 H), 3.54 (s, 3 H), and *5.88 (d, 1 H)* (J = 10.2 Hz) ppm that were in an area ratio (40:60) with the corresponding peaks in *Z*-**6a.** Other regions stayed constant in area throughout the irradiation, but these regions were not interpretable. Treatment of a mixture of *Z*-**6a** and *E*-**6a** with Eu(fod)$_3$ revealed that *Z*-**6a** was very insensitive to this reagent, whereas *E*-**6a** showed large shifts. It was possible therefore to confirm the coupling constant (J = 10.2 Hz) for the 2-H since this proton could be shifted to a region (~6.35 ppm) where other absorbances were absent. Irradiation of the multiplet (3-H) in *E*-**6a** when δ ~8 ppm gave collapse of this doublet (2-H) to a singlet. When the methoxy protons in *E*-**6a** had been shifted to δ ~5 ppm, the Me_3Si absorbance could be found at ca. 0.12 ppm downfield from the corresponding Me_3Si peak in *Z*-**6a.** The protons in *Z*-**6a** underwent no detectable shift during this experiment.

After 21 h of irradiation as for **6a,** a 60:40 mixture of *Z*-**9a** to *E*-**9a** was obtained. These compounds were not separated, but from the change in the NMR spectrum (*Z*-**9a:** δ 0.38 (s, 9 H), 1.85 (bs, 3 H), 3.32 (s, 3 H), 4.93 (m, 2 H), 5.68 (bs, 1 H)) with time the amount of *E* isomer could be calculated. New peaks at δ 0.21, 2.19, 3.44, and 5.41 ppm were observed with relative areas of 9:3:3:1. The area of the 4.93-ppm absorbance remained constant with time.

Photoisomerization of **13a** in benzene-d_6 gave an apparent 50:50 mixture of two compounds after 8 h of irradiation. The spectrum of *E*-**13a** (δ 0.37 (s, 9 H), 3.62 (s, 3 H), 6.07 (s, 1 H), 7.32, 7.95 (m, 5 H) ppm) changed with time such that new peaks (calculated to be in the same ratio of peak areas as *E*-**13a**) appeared at 0.30 (s), 3.54 (s), 6.51 (s), and 7.24 (bs) ppm, respectively. The separation of the multiplets at 7.32 (3 H) and 7.95 (2 H) ppm for *E*-**13a** from the 7.24-ppm absorbance in *Z*-**13a** allows calculation of the relative areas.

***trans*-2,2-Dimethyl-2-silahex-4-en-3-one (14a).** The silylbutadienyl ether (**5a,** 1.56 g, 100 mmol) was added to the hydrolysis mixture (25 mL of 4:1 acetone–water, which is 0.20 M in HCl). After 4 h at 25 °C, ether (10 mL) and water (10 mL) were added and the layers separated. The aqueous layer was washed with an equal volume of ether. The combined organic mixture was dried ($MgSO_4$) and concentrated. Distillation gave 0.95 g (67%) of **14a** (bp 68–70 °C (12 Torr)).

Anal. Calcd for $C_7H_{14}OSi$: C, 59.10; H, 9.92. Found: C, 59.20; H, 9.96. UV (C_6H_{12}): 442 nm (ϵ 67), 424 (98), 406 (87), 224.5 (10 300).

***trans*-2,2-Dimethyl-2-germahex-4-en-3-one (14b)** was prepared from the germabutadienyl ether, **5b** (1.60 g, 80 mmol), and the hydrolysis solution (20 mL). After 4 h of reaction, workup as for **14a** gave 0.95 g (69%) of **14b** (bp 74–76 °C (12 Torr)). UV (C_6H_{12}): 442 nm (sh) (ϵ 74), 416.3 (109), 403.8 (105), 258 (11 300).

***trans*-2,2-Dimethyl-2-stannahex-4-en-3-one (14c)** was prepared from the stannabutadienyl ether (**5c**) (ca. 150 mg) and the hydrolysis solution (5 mL). After the mixture had stood for 1 h, CCl_4 (2 mL) and water (5 mL) were added to the mixture using a syringe. The aqueous layer was drawn off using a syringe. After two additional water (2 mL) washings, the wet CCl_4 solution was transferred to a second container which contained molecular sieves (3 Å) using a double-ended needle. The dry solution was similarly transferred to a third container and concentrated under a stream of dry argon. The residue provided a mass spectral sample and a CCl_4 solution of same provided other spectral samples. Attempted distillation led to decomposition.

IR (CCl_4): 3040 (w), 3000 (sh), 2880 (m), 2840 (w), 2820 (m), 1660 (m), 1648 (s), 1597 (s), 1450 (s), 1380 (s), 1240 (s), 1203 (m), 1172 (w), 1100 (s), 1015 (s), 975 (m), 830 (bs), 796, 760 (s) cm^{-1}. UV (CCl_4): 432, 258 nm.

***trans*-1-Methoxy-5,5-dimethyl-2-hexene (7)** was isolated from the hydrolyses mixtures obtained from **6** by preparative GC.

NMR (CCl_4): δ 0.95 (s, 9 H), 1.95 (d, 2 H), J = 6 Hz, 3.00 (s, 3 H), 3.53 (d, 2 H), J = 4.8 Hz, 5.43 (m, 2 H) ppm. Decoupling each of the upfield doublets showed that the downfield portion of the 5.43-ppm multiplet (vinylic H at C-3) was coupled with the 1.95-ppm absorbance (CH_2 at C-4) while the upfield portion (vinylic H at C-2) was coupled to the 3.53-ppm absorbance (CH_2 at C-2). A trans coupling constant of 15.5 Hz was determined. A small peak at 3.57 ppm suggested that some cis isomer may be present but this was not confirmed.

2,2,5-Trimethyl-2-silahex-4-en-3-one (16a) was prepared from **9a** (1.67 g, 9.8 mmol) and the hydrolysis solution (25 mL). After 24 h **14a** gave 0.95 g (62%) of **16a** (bp 68–71 °C (10 Torr)).

Anal. Calcd for $C_6H_{16}OSi$: C, 61.48; H, 10.32. Found: C, 61.58; H, 10.34.

UV (C_6H_{12}): 481 nm (sh) (ϵ 57), 462 (116), 439 (120), 249 (12 700).

UV (vapor): 470 nm (sh), 450, 430 (λ_{max}), 418 (sh) (10-cm cell); 234, 223 (1 cm cell) 20 °C.

UV (95% EtOH): 421 nm (ϵ 114).

When the reaction time was reduced to 2 h, complete disappearance of **9a** had occurred. However, peaks appeared at δ 0.28, 1.78, 3.2, 4.7, and 4.9 ppm, suggesting that a minor amount (ca. 10%) of the nonconjugated ketone (**15a**) was formed in the initial hydrolysis.

2,2,5-Trimethyl-2-germahex-4-en-3-one (16b) was prepared from the germylisoprenyl ether, **9b** (2.0 g, 9.3 mmol), and the hydrolysis solution (25 mL). After 20 h, workup as for **14a** gave 1.4 g (75%) of **16b** (bp 83–84 °C (15 Torr)).

Anal. Calcd for $C_8H_{16}OGe$: C, 47.85; H, 8.03. Found: C, 48.02; H, 8.09.

UV (C_6H_{12}): 478 nm (sh) (ϵ 62), 443 (133), 432 (140), 408 (sh) (98), 389 (sh) (54), 363 (sh) (17).

When the reaction time was reduced to 1 h, a sample of the reaction mixture was worked up and **9b** was found to have completely disappeared. Material collected by GC gave an NMR as for **16b** with additional absorbances at δ 0.30 (s, 9 H, corrected for **16b**), 1.66 (bs, 3 H), 3.18 (bs, 2 H), 4.70 (m, 1 H), and 4.87 (m, 1 H) ppm. This data was consistent with a nonconjugated ketone, **15b**, 2,2,5-trimethyl-2-germahex-5-en-3-one, and was found (by NMR) to constitute ca. 15% of the mixture.

2,2,5-Trimethyl-2-stannahex-4-en-3-one (16c) was prepared from the stannylisoprenyl ether (**9c**) (ca. 0.5 g) and the hydrolysis solution (10 mL). After 15 min, ether (5 mL) and water (5 mL) were added using a syringe. The organic layer was withdrawn, dried over K_2CO_3, and concentrated at room temperature under a stream of nitrogen. The residue was dissolved in benzene (ca. 10 mL) and transferred to a reaction flask equipped with a reflux condenser. Pyridine (0.16 g, 2.0 mmol) was added and the mixture was heated at reflux temperature for 1 h. The solvents were removed under a stream of nitrogen to give **9c** which contained <5% of the nonconjugated isomer by NMR and no more than trace amounts of volatile impurities by GC (10% Carbowax).

IR (CCl_4): 2980 (s), 2920 (s), 1647 (s), 1600 (s), 1453 (m), 1388 (m), 1277 (m), 1202 (m), 1007 (m), 715 (s) cm^{-1}.

UV (CCl_4): 453 nm.

After the 10-min hydrolysis procedure, the NMR spectrum of the concentrated mixture revealed absorbances (in addition to those given in Table VI for **16c**) at δ 0.23 (s, 9 H, corrected for **16c**), 1.62 (bs, 3 H), 3.13 (s, 2 H), 4.71 (bs, 1 H), and 5.01 (bs, 1 H) (40% of mixture). These absorbances agree with those expected for the nonconjugated isomer, 2,2,5-trimethyl-2-stannahex-5-en-3-one (**15c**). Additionally, the UV spectrum showed absorbances at 395 and 378 nm attributable to **15c**.

2,2-Dimethyl-4-phenyl-2-silabutan-3-one (17a) was prepared from the silylstyryl ether (**13a**) and the hydrolysis solution (20 mL). After 24 h, workup as for **14a** gave 1.2 g (65%) of **17a** (bp 73-75 °C (1.0 Torr)).

Anal. Calcd for $C_{11}H_{16}OSi$: C, 68.69; H, 8.38. Found: C, 68.86; H, 8.43.

UV (C_6H_{14}): 392 nm (ε 80), 376.5 (113), 367.5 (sh) (103), 259 (sh) (1000), 225 (sh) (6700).

2,2-Dimethyl-4-phenyl-2-germabutan-3-one (17b) was prepared from **13b** (1.5 g, 6.0 mmol) and the hydrolysis solution (15 mL). After 24 h, workup as for **14a** gave 0.85 g (59%) of **17b** (bp 82-85 °C (1.0 Torr)).

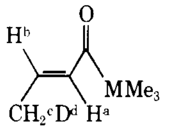
UV (C_6H_{14}): 381 nm (ε 99), 365.5 (124), 354 (sh) (100), 258 (1200), 244 (sh) (2300), 230 (5300), 198 (15 000).

2,2-Dimethyl-4-phenyl-2-stannabutan-3-one (17c) was prepared from **13c** (0.10 g, 3.4 mmol) and the hydrolysis solution (5 mL). After 2 h, workup as for **14c** gave **17c** contaminated with chlorotrimethyltin and **11**. The mole ratio of these components was 56:22:22. Using a 10 °C/min program (initial temperature 50 °C) on a 5 ft × 1/4 in. 10% Carbowax column, elution of Me_3SnCl, **11**, and **17c** was at 85, 145, and 165 °C, respectively. Only very minor amounts of other impurities were observed in this mixture. The infrared spectrum revealed major absorbances at 1656 and 1225 cm^{-1} attributable to **17c**. The UV spectrum exhibited absorbances at 393 and 379 nm with relative intensities of 0.95:1. A shoulder was observed at 367 nm.

Hydrolysis of the α-Methoxybutadienylmetallenes (6) in Deuterated Solvents. A solution (0.5 mL) of acetone-d_6 (80%) and D_2O (20%) containing DBr (0.20 ± 0.02 M (total acid concentration)) was injected into an NMR tube through a septum using a syringe. The solution was allowed to come to thermal equilibrium (33 °C) over 10-15 min. At $t = 0$, a sample of **6** (ca. 0.2 mmol) was injected into the solution and thoroughly mixed. The spectrum was recorded and the resultant peaks were integrated at various time intervals.

6a: NMR ($t = 0$) δ 0.2 (s, 9 H), 3.49 (s, 3 H), 4.66-5.10 (8 lines, 2 H), 5.83-6.81 (10 lines, 2 H).

14a′: NMR ($t = 200$ min) δ 0.26 (s, 9 H), 1.76-2.00 (m, 2 H), 6.10 (m, 1 H), 6.90 (m, 1 H); MeOD (δ 3.27 ppm, 3 H). The coupling constants were verified using double resonance.



$J_{ab} = 17$; $J_{ac} \sim 1$; $J_{bc} \sim 6.5$ Hz; J_{cd} (not determined).

By integration of the 3.49-ppm absorbance in **6a** vs. that in MeOD (3.27 ppm), the points given in Figure 1 were obtained.

6b: NMR ($t = 0$) δ 0.28 (s, 9 H), 3.57 (s, 3 H), 4.75-5.17 (m, 2 H), 5.95-6.90 (m, 2 H).

14b′: NMR ($t = 65$ min) δ 0.33 (s, 9 H), 2.00 (m, 2 H), 6.03 (m, 2 H), 6.85 (m, 2 H); MeOH (3.27).

Essentially the same coupling constants were obtained as for **14a′**. Data were treated as for **6a**.

6c: NMR ($t = 0$) δ 0.21 (s, 9 H), $J_{Sn-Me} = 56$ Hz, 3.54 (s, 3 H), 4.67-5.17 (m, 2 H), 5.97-6.64 (m, 2 H).

14c′: NMR ($t = 30$ min) δ 0.26 (s, 9 H), $J_{Sn-Me} = 54$ Hz, 1.96 (m, 2 H), 5.97 (m, 2 H), 6.73 (m, 2 H); MeOD (δ 3.26). Data as above.

For all compounds the allylic protons (c) were not completely separated from the residual absorbance due to acetone-d_5. The values given are corrected for this absorbance.

From the rate data, first-order rate constants of 6.2, 10, and 18 × 10^{-4} s^{-1} were obtained for **6a, 6b,** and **6c,** respectively. Dividing these values by the 0.20 M acid concentration gives second-order constants of 3.1, 5, and 9 × 10^{-3} M^{-1} s^{-1} for these compounds, respectively. We have verified the first-order dependence of this reaction from semilogarithmic plots.

Hydrolysis of 9a in Deuterated Solvents. Using a similar procedure to that described above for **6,** the hydrolysis of the silylisoprenyl ether, **9a,** was carried on using NMR to follow the reaction. The methoxy protons (δ 3.48 ppm) in **9a** were integrated vs. those in MeOD (δ 3.28 ppm). Values of 0.69 (100 s), 2.0 (300 s), 11 (720 s), and 20 (960 s) were determined for this ratio of areas. A values of $k_{obsd} = 3.7 \times 10^{-3}$ s^{-1} was calculated from this data which gave a second-order constant of ca. 2 × 10^{-2} M^{-1} s^{-1} when divided by 0.20 M DBr. Starting material (δ 0.11, 1.78, 3.48, 4.74, and 5.73) was seen to disappear at ca. 30 min. Peaks attributable to the conjugated ketone, **16a′**, were observed at δ 0.14, 1.83, 2.00, and 6.60 ppm while the nonconjugated isomer showed absorbances at 0.16, 1.62, 4.70, and 4.88 ppm with no peak observed for the α′ proton in the 3-4-ppm region. Other data is given in the text.

Hydrolysis of 13a in Deuterated Solvents. Using a similar procedure to that described for **6**, the hydrolysis of the silylstyryl ether (**11a**) was carried out using NMR to follow the reaction.

13a: NMR ($t = 0$) δ 0.35 (s, 9 H), 3.73 (s, 3 H), 5.82 (s, 1 H), 7.1-7.8 (m, 5 H) ppm.

17a′: NMR ($t = 2$ h) δ 0.15 (s, 9 H), 7.3 (m, 5 H), (3.8, trace absorbance) ppm.

Rate data: % reaction (time, s) 5 (380), 10 (920), 13 (1460), 19 (2295), 38 (4970), 57 (10 010), 86 (24 840).

A value of 9.6 × 10^{-5} s^{-1} was calculated for k_{obsd} from this data which gave a second-order rate constant of 4.8 × 10^{-4} M^{-1} s^{-1} when corrected to 1.00 M acid concentration.

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Supplementary Material Available: IR spectra (4 pages). Ordering information is given on any current masthead page.

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