

Deoxymetalation Reactions. The Mechanism of Deoxystannylation<sup>1,2</sup>

DENNIS D. DAVIS AND CHARLES E. GRAY

Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88001

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$\beta$ -Triphenylstannyl and  $\beta$ -triphenylplumbyl alcohols prepared from the corresponding epoxides and the triphenylmetal-alkali metal derivatives readily undergo an acid-catalyzed deoxymetalation reaction in acetic acid-perchloric acid and methanol-perchloric acid mixtures. The reaction was followed manometrically and found to be first order in organometallic reagent and to show proportionality to the Hammett acidity function in both solvent systems. Additionally, dependence on water concentration was noted in acetic acid. By study of the acidity function, activation parameters, and stereochemistry and by comparison with similar reactions, a mechanism is proposed which involves a concerted elimination of water and a hydrated triphenylmetal cation.

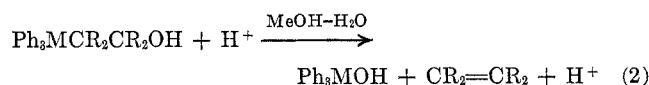
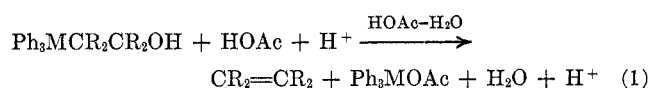
In contrast to the well-studied deoxymercuration<sup>3</sup> reaction, deoxymetalation reactions involving group IV metals and metalloids have received little attention. Early observations by Whitmore, Sommer, and co-workers<sup>4</sup> indicated that substituted organosilanes of the general type  $R_3SiCH_2CH(R')X$  ( $X$  = halogen or hydroxyl,  $R'$  = H or alkyl) react rapidly with acid, base, and a variety of other reagents to generate the corresponding alkene and  $R_3SiX$ . Later studies by Sommer and Miller<sup>5</sup> have shown that the rate of deoxysilylation of 2-(trimethylsilyl)ethanol is proportional to the Hammett acidity function and that effects of substituents on the silicon correlate to the Taft equation with a  $\rho^*$  of  $-1.85$ . The similarly substituted organolead compound, 3-chloro-1-(triphenylplumbyl)propan-2-ol, reacts rapidly with HCl to yield the elimination product, allyl chloride.<sup>6</sup>

Although there may be some debate concerning the fine points of the deoxymercuration reaction, the generally accepted mechanism is similar to that proposed by Kreevoy and Kowitz,<sup>3a</sup> which involves a metal-bridged ionic intermediate. Because of the apparent overall similarity of the deoxymetalation reactions of the group IV elements and the deoxymercuration reaction, we have investigated the mechanism of deoxymetalation of group IV organometallic compounds with a hope toward further elucidating the nature of the intermediates and transition states involved in these reactions.

## Results

The  $\beta$ -hydroxyalkyl triphenyl metal compounds are readily accessible through the reaction of triphenyl metal-alkali metal compounds with epoxides.<sup>7</sup> The alkali metal organometallic derivatives were prepared in a variety of ways depending upon the group IV ele-

ment.<sup>8</sup> The epoxide opening occurs smoothly at room temperature in a tetrahydrofuran or ethylene glycol dimethyl ether solution in 1-2 hr. The final organometallic products are air- and water-stable crystalline solids; however, in either aqueous methanol or aqueous acetic acid solution containing a catalytic amount of perchloric acid the organotin and organolead compounds undergo a rapid elimination reaction to yield the alkene (95-100%) and a triphenyl metal salt (90-93%).



The organometallic salts and alkenes were isolated and identified by comparison with known samples. The water produced was not identified directly, but is required by the stoichiometry and its formation was indirectly confirmed during the kinetic studies in acetic acid.

**Kinetics.**—The kinetics of the elimination reactions were followed by monitoring the evolution of the alkene manometrically. The solutions were previously saturated with the product alkene to prevent difficulties owing to solubility of the alkene in the solvent. Good pseudo-first-order kinetics were obtained in all reactions carried out as above. If the solutions were not saturated prior to the start of the run, deviations from linearity were particularly noticeable in the initial portions of the run and the expected volume of gas was not evolved. The overall rate in the nonsaturated solutions is not significantly different from that in the alkene-saturated solutions; thus there appears to be no effect on the rate owing to the presence of product alkene.

**Dependence of Rate on Acidity.**—At 25.0° in methanol containing 9-27 vol. % water and with perchloric and hydrochloric acid concentrations in the 0.003-0.2  $M$ , range good pseudo-first-order kinetics were obtained. Acidity-function studies on the rate of elimination from 2-(triphenylstannyl)ethanol were carried out in 82% aqueous methanol.  $H_0$  data is available for 91% aqueous methanol;<sup>9</sup> however, in our system the rates were too fast to measure at higher acid concentrations in this medium.  $H_0$  data for HCl in 91 and 73% aqueous methanol are parallel functions,<sup>9</sup> and it is assumed

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(2) Portions of this work appeared as a communication: D. D. Davis and C. E. Gray, *J. Organometal. Chem.*, **18**, 1 (1969).

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(4) (a) L. H. Sommer and F. C. Whitmore, *J. Amer. Chem. Soc.*, **68**, 485 (1946). (b) L. H. Sommer, G. M. Goldberg, E. Dorfman, and F. C. Whitmore, *ibid.*, **68**, 1083 (1946). (c) L. H. Sommer, D. L. Bailey, and F. C. Whitmore, *ibid.*, **70**, 2869 (1948). (d) J. Gold, L. H. Sommer, and F. C. Whitmore, *ibid.*, **70**, 2874 (1948).

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that, although the absolute values of  $H_0$  for a given concentration of perchloric acid in 91 and 82% aqueous methanol will differ, the change in the water content will not affect the slope of a correlation line. The  $\log k_1$  value is linearly dependent on  $-H_0$  with a slope of  $0.935 \pm 0.025$  and is nonlinear with respect to acid concentration (Table I).

TABLE I

DEPENDENCE OF RATE ON ACIDITY FUNCTION <sup>a</sup>		
[HClO <sub>4</sub> ]	$H_0^b$	$k_1 \times 10^3, \text{sec}$
0.0983	1.87	0.602
0.210	1.43	1.42
0.307	1.18	2.77
0.371	1.05	3.46

<sup>a</sup> Conditions: 82% aqueous MeOH, 25.0°; [Ph<sub>3</sub>SnCH<sub>2</sub>CH<sub>2</sub>OH] = 0.045. <sup>b</sup>  $H_0$  measurement in 91% aqueous methanol.

The effect of water on the rate was studied in acetic acid-water mixtures containing a constant acid concentration and varying amounts of water.<sup>10</sup> As water concentration is increased from 0.6 to 3.8 *M* at a constant concentration of perchloric acid of 0.006 *M*, the rate is a function not only of  $H_0$  but also of [H<sub>2</sub>O] (Table II). There is no observable reaction in the absence of added mineral acid.

TABLE II  
 $H_0$  AND H<sub>2</sub>O EFFECTS IN HOAc-H<sub>2</sub>O<sup>a</sup>

[H <sub>2</sub> O]	$H_0$	$k_1 \times 10^3, \text{sec}$	$k_1/[\text{H}_2\text{O}]$
3.8	2.5	0.43	0.12
2.94	2.05	0.62	0.21
2.02	1.70	0.99	0.49
1.58	1.45	1.20	0.76
1.08	1.10	1.40	1.30
0.845	0.85	1.60	1.89
0.613	0.70	1.83	2.99

<sup>a</sup> Conditions: 25.0° [HClO<sub>4</sub>] = 0.006 *M*; [Ph<sub>3</sub>SnCH<sub>2</sub>CH<sub>2</sub>OH] = 0.045.

The slope of a plot of  $\log k_1$  vs.  $-H_0$  is  $0.34 \pm 0.14$ . However, if the effect of water is also to increase the rate by directly participating in the reaction as well as altering the acidity of the medium, then a plot of  $\log k_1/[\text{H}_2\text{O}]$  vs.  $-H_0$  should be linear with unit slope. The actual slope of such a plot is  $0.77 \pm 0.13$ . Although there is considerable deviation from unit slope, the rate-accelerating effect of water is clear. Deviations of the slope from unity in low-dielectric media are commonly observed and lay open to question the overall validity of the acidity-function concept in such systems. Other concentration functions of the water, such as activity and molality, give lines of the same slope within experimental error. The inclusion of water as a reactant as suggested by the  $H_0$  correlation is certainly not conclusive. However, further support for this idea is derived from the activation parameters (Table III).

**Salt Effects.**—The inclusion of water as a reactant in the elimination reaction suggests that some nucleophilic assistance at the metal ion is important. The effects of added salts were determined and are shown in Table IV.

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TABLE III  
ACTIVATION PARAMETERS FOR Ph<sub>3</sub>SnCH<sub>2</sub>CH<sub>2</sub>OH<sup>a</sup>

Temp, °C	$k_1 \times 10^3, \text{sec}$	
14.0	2.10	
19.8	3.46	
25.0	5.29	$\Delta H^\ddagger = 13.2 \text{ kcal/mol}$
30.0	7.72	$\Delta S^\ddagger = -19.8 \text{ eu}$
36.0	10.7	

<sup>a</sup> Conditions: 82% MeOH; [HClO<sub>4</sub>] = 0.09.

TABLE IV  
EFFECTS OF ADDED SALTS ON THE RATE OF ELIMINATION OF Ph<sub>3</sub>SnCH<sub>2</sub>CH<sub>2</sub>OH<sup>a</sup>

Salt	[Salt]	$k_1 \times 10^3, \text{sec}$	$k_{\text{rel}}$
None	...	0.602	(1.0)
NaClO <sub>4</sub>	0.25	0.925	1.53
NaI	0.25	0.753	1.25
NaBr	0.25	0.643	1.06
NaCl	0.25	0.593	0.99
NaF	0.25	No react	...

<sup>a</sup> Conditions: 91% MeOH, 25°; [HClO<sub>4</sub>] = 0.0982.

**Stereochemistry.**—The stereochemistry of the acid-catalyzed elimination reaction in acetic acid-water mixtures was determined by using the 3-(triphenylstannyl)butan-2-ols (Table V). These particular compounds were chosen for study because the *threo* and *erythro* alcohols could be prepared from the reaction of triphenylstannylsodium with *cis*- and *trans*-2,3-butylene oxide, respectively.

The gas evolved from the reaction of *threo*-3-(triphenylstannyl)butan-2-ol (prepared from the reaction of triphenylstannylsodium and *cis*-2,3-butylene oxide) with 0.006 *M* perchloric acid in acetic acid-water was collected and analyzed by gas chromatography. *cis*-2-Butene was the only product found; no trace of the *trans* isomer was evident. Identical results were obtained in aqueous methanol solvent.

The *erythro*-3-(triphenylstannyl)butan-2-ol, prepared from *trans*-2,3-butylene oxide, was subjected to identical elimination conditions and yielded *trans*-2-butene as the only gaseous product.

## Discussion

The deoxystannylation and deoxyplumbylation reactions are similar to deoxymercuration, with a few notable exceptions. Deoxymercuration<sup>3a</sup> in aqueous perchloric acid, deoxysilylation<sup>5</sup> in 50% methanol containing H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, HNO<sub>3</sub>, or HCl, and deoxystannylation in 73% aqueous methanol with perchloric acid all follow the Hammett acidity function with unit or nearly unit slopes, indicating a rapid prior protonation equilibrium. However, in acetic acid medium containing 0.6–3.2 *M* H<sub>2</sub>O, the effect of added water cannot be accounted for by consideration of changes in the basicity of the medium only. Increasing the water content causes a decrease in the acidity of the medium, with a concomitant deceleration in rate. The rate of elimination, however, does not fall so fast as expected by the decrease in  $H_0$ . This necessitates the inclusion of water as a reactant whose increased concentration causes an increase in the rate. This is supported by the change in the Hammett slope from 0.34 to 0.77 when  $\log k_1/[\text{H}_2\text{O}]$  is used rather than  $\log$

TABLE V  
 RELATIVE RATES OF THE ACID-CATALYZED ELIMINATION REACTION

Compd	Registry no.	HOAc (3.2 M H <sub>2</sub> O)		73% aqueous methanol	
		$k_{\psi}^a$	$k_{rel}$	$k_{\psi}^b$	$k_{rel}$
Ph <sub>3</sub> SiCH <sub>2</sub> CH <sub>2</sub> OH		No react	...	No react	...
Ph <sub>3</sub> SiCH <sub>2</sub> CH(CH <sub>3</sub> )OH		No react	...	No react	...
Ph <sub>3</sub> GeCH <sub>2</sub> CH(CH <sub>3</sub> )OH	23604-55-9	No react	...	No react	...
Ph <sub>3</sub> SnCH <sub>2</sub> CH <sub>2</sub> OH	23604-56-0	0.604 ± 0.035	(1.0)	0.35	(1.0)
Ph <sub>3</sub> SnCH <sub>2</sub> CH(CH <sub>3</sub> )OH	23604-57-1	7.52 ± 0.57	12	0.51	1.4
Ph <sub>3</sub> SnCH(CH <sub>3</sub> )CH(CH <sub>3</sub> )OH <sup>c</sup>	23601-91-4	10.8	18	2.3	6.6
Ph <sub>3</sub> SnCH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> OH	23604-58-2	>20	>33	4.4	12.4
Ph <sub>3</sub> PbCH <sub>2</sub> CH <sub>2</sub> OH	1802-70-6	5.13 ± 0.77	8.5 (1.0)	0.77	2.2 (1.0)
Ph <sub>3</sub> PbCH <sub>2</sub> CH(CH <sub>3</sub> )OH	23604-60-6	7.77 ± 0.47	13 (1.5)	1.9	5.4 (2.5)

<sup>a</sup>  $k_{\psi} = k_1/[H^+]$ ;  $[H^+] = 6 \times 10^{-3} M$ . <sup>b</sup>  $k_{\psi} = k_1/[H^+]$ ; the acid concentration is within the range  $6 \times 10^{-3}$ – $9 \times 10^{-2} M$  and is essentially linearly related to  $H_0$ . <sup>c</sup> Ca. 75:25 mixture of *erythro* and *threo* isomers.

$k_1$ . A similar dual role for water was noted by Eaborn<sup>9</sup> during a study of the acidity function–rate relationships for desilylation of *p*-methoxyphenyltrimethylsilane in aqueous methanol.

On the basis of acidity-function data alone this conclusion is at best tenuous. However, the entropy of activation for deoxystannylation is 19 eu more negative than that for deoxymercuration. Reactions proceeding with unimolecular decomposition of the protonated substrate usually exhibit entropies of activation near zero, while those proceeding with attack of water on the protonated substrate usually exhibit values which are large and negative.<sup>11</sup> Frost and Pearson estimate an entropy change of ca. –20 eu for the incorporation of a water molecule in the transition state.<sup>12</sup> See Table VI.

TABLE VI

Deoxymetalation of	ACTIVATION PARAMETERS FOR DEOXYMETALATION REACTIONS	
	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , eu
2-Triphenylstannylethanol	13.2	–19.8
2-Ethoxyethylmercuric chloride	20	1.0
$\alpha$ -2-Methoxycyclohexylmercuric chloride	17.8	4.6
$\beta$ -2-Methoxycyclohexylmercuric chloride	26.2	4.5

A reasonable proposition as to the function of the water in the reaction sequence is for nucleophilic assistance at the developing metal cation. The addition of salts to the medium, particularly those with nucleophilic anions, has little effect. Indeed, the salt effect appears to parallel the acidity of the conjugate acid of the anion:  $HClO_4 > HI > HBr > HCl > HF$ . It is not unreasonable that water should act as a more efficient nucleophile, since the triphenylmetal halides undergo extensive dissociation and complexation with water in aqueous systems.<sup>13</sup>

**Stereochemistry.**—The product obtained from the reaction of *cis*-2,3-butylene oxide with triphenylstannylsodium was a single compound to which we have assigned the *threo* configuration based upon the following facts.

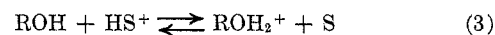
A. Unsymmetrical epoxides such as propylene and isobutylene oxides are opened to give the metal-substituted alcohol in which the metal is located on the least substituted carbon. This mode of opening is that which is most commonly found for nucleophilic opening

of unsymmetrical epoxides, proceeding with *trans* opening.<sup>14</sup>

B. We have noted similar nucleophilic activity in the reaction of triphenylstannylsodium with *sec*-butyl bromide, which proceeds with inversion of configuration.<sup>15</sup> Thus we assume that a nucleophilic, *trans* opening of *cis*-2,3-butylene oxide gives the *threo* product, and conversely.

When *threo*-3-(triphenylstannyl)butan-2-ol was treated with perchloric acid in acetic acid–water or methanol–water mixtures, 100% *cis*-2-butene was obtained, which indicates that the elimination also proceeds in a *trans* manner. Experiments involving the *erythro* isomer and a mixture of the *threo* and *erythro* isomers also showed complete stereospecificity in the opening and elimination reactions. This high degree of stereospecificity in the elimination reaction rules out the possible intervention of a carbonium ion whose lifetime is greater than the time required for rotation about the C–C single bond. On the basis of this stereochemical data, however, no conclusion can be made as to whether a bridged ion is involved, since the stereochemical outcome for both types of transition states is identical.

**Substituent Effects.**—The overall rate profile of the deoxystannylation reaction is similar to the order of the stability of the product alkenes and is compressed in comparison with the deoxymercuration reaction. However, the observed rate is also a function of the prior protonation equilibrium. As the functional group is changed from a primary to a tertiary alcohol, the base strength should be expected to change and a shift in the equilibrium occur. The observed order of basicity of the lower alcohols measured by Kolthoff<sup>16</sup> in acetic acid is 2-propanol > ethanol > methanol, which follows an inductive order. The equilibrium constants<sup>16</sup>



for the reaction of eq 3 are water, 68; 2-propanol, 17; ethanol, 15; and methanol, 8.8. Assuming the inductive order to hold in the triphenyltin-substituted alcohol series, the prior equilibrium constant increases in the same direction as the observed rate. However this increase is small, a factor of 2–5 at the most. As can be seen from Table VII, the relative rate spread for tin is much less than for mercury. Assuming that

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(16) I. M. Kolthoff and S. Bruckenstein, *J. Amer. Chem. Soc.*, **78**, 1 (1956).

TABLE VII  
 RELATIVE REACTIVITIES IN DEOXYMETALATIONS

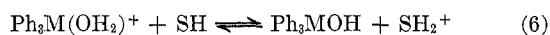
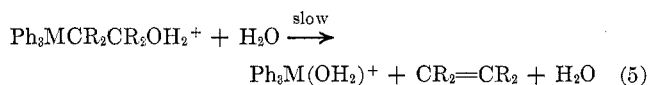
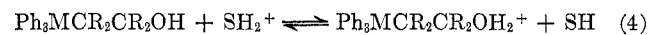
	M = Ph <sub>3</sub> Sn, X = OH 73% aq MeOH, 25°	M = Ph <sub>3</sub> Sn, X = OH 95% aq HOAc, 25°	M = Ph <sub>3</sub> Pb, X = OH 95% aq HOAc, 25°	M = HgCl, X = OEt 75% aq EtOH, 0°
MCH <sub>2</sub> CH <sub>2</sub> X	1	1	1	1
MCH <sub>2</sub> CH(CH <sub>3</sub> )X	1.4	12.4	1.5	14
MCH(CH <sub>3</sub> )CH(CH <sub>3</sub> )X	6.6	18	...	86
MCH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> X	12.4	>33	...	1560

the relative substituent effects on the prior equilibrium are the same as those observed by Kolthoff, mercury appears to be much more sensitive to alkyl substitution than is tin or lead in the elimination reaction.

The effect of the leaving group appears to be Hg > Pb > Sn >> Ge, Si >> H, with relative rates of 5, 3, 1, 10<sup>-6</sup>, and 10<sup>-11</sup>, respectively. Quantitative data are not available because of the disparity of the reaction conditions; however, it is clear from Table V that the silicon and germanium compounds react much more slowly than comparable tin or lead analogs. Based upon Sommers data<sup>5</sup> for the deoxysilylation of 2-(trimethylsilyl)ethanol, we estimate that 2-(triphenylsilyl)ethanol deoxymetalates 10<sup>-6</sup>-10<sup>-8</sup> times slower than the triphenylstannyl ethanol. Kreevoy and Kowitt<sup>8a</sup> estimate that deoxymercuration is 10<sup>11</sup> times faster than dehydration of alcohols. The great ease of deoxymetalation can be rationalized by consideration of the bond strengths of the leaving groups (kcal/mol): C-Hg, 27; C-Pb, 31; C-Sn, 54; C-Ge, 57; C-Si, 60; C-H, 96. This must account for a majority of the rate difference; however, both the ionization energy of the leaving group and the stability of cation in solution must also be considered. A precise quantitative explanation of the rate sequence for deoxymetalation reactions involving the group IV metals is lacking and is one of our current areas of investigation.

On the basis of the kinetics, stereochemistry, and the rate profile for the substituted compounds, we propose that the deoxymetalation reaction of organotin compounds, and probably the rest of the group IV organometallics, proceeds by Scheme I.

## SCHEME I



A reasonable structure for the transition state involved in the rate-determining step would be similar to that commonly postulated for a bimolecular elimination reaction. Although the evidence presented does not rule out the intervention of a bridged-ion species, there is no compelling reason to propose such a structure.

Experimental Section<sup>17</sup>

**2-(Triphenylsilyl)ethanol.**—A solution of 0.0386 mol of triphenylsilyllithium<sup>18</sup> in tetrahydrofuran (THF) was cooled in an

(17) Reactions involving organometallic compounds were carried out in an atmosphere of dry, oxygen-free argon using three-neck flasks equipped with reflux condenser, self-equalizing addition funnel, mechanical stirrer, and an inlet for argon. No attempts were made to determine optimal conditions for preparation of the organometallic compounds.

ice bath. Then 2.2 g (0.050 mol) of cold ethylene oxide was added slowly with stirring. The solution turned tan in color immediately. After the solution had been stirred for 0.5 hr, the work-up by hydrolysis, extraction with ether, drying of the organic layer with sodium sulfate, and removal of the solvents gave an oil. With addition of 50 ml of heptane the oil solidified upon stirring. The solid was filtered, dried, and recrystallized three times from heptane to give 4.2 g (36%) of 2-(triphenylsilyl)ethanol: mp 99-100° (lit.<sup>18</sup> mp 99-100°); nmr (CCl<sub>4</sub>) δ 7.3 (complex m, Ph<sub>3</sub>Si-), 3.7 (t, SiCH<sub>2</sub>-), and 1.7 (complex m, -CH<sub>2</sub>OH).

**1-(Triphenylsilyl)propan-2-ol.**—A solution of 0.0386 mol of triphenylsilyllithium in THF was cooled in an ice bath. Then 3.0 g (0.0517 mol) of propylene oxide was added with stirring. After the solution had been stirred for 0.5 hr at room temperature, the work-up as described before gave 4.3 g (35%) of 1-(triphenylsilyl)propan-2-ol: mp 86-86.5° after recrystallization three times from heptane (lit.<sup>18</sup> mp 86-88°); nmr (CCl<sub>4</sub>) δ 7.3 (complex m, Ph<sub>3</sub>Si-), 3.9 [complex m, -CH<sub>2</sub>CH(OH)-], 1.62 (complex m, SiCH<sub>2</sub>-), and 1.12 (d, -CH<sub>3</sub>).

**1-(Triphenylgermyl)propan-2-ol.**—A solution of 13.76 g (0.0358 mol) of triphenylbromogermene in 50 ml of ethylene glycol dimethyl ether (GDME) was added to 75 ml of sodium naphthalene in GDME [prepared by addition of 3.45 g (0.15 g-atom) of sodium metal and 3.84 g (0.030 mol) of naphthalene to GDME]. Triphenylbromogermene was added slowly to maintain a green color at all times. After complete addition the green solution was stirred for 2 hr and then cooled in an ice bath. Then 8.3 g (0.143 mol) of propylene oxide in 25 ml of GDME was added slowly, the solution turning tan in color. After usual work-up and recrystallization three times from heptane, 6.85 g (52.7%) of 1-(triphenylgermyl)propan-2-ol was obtained: mp 72-73°; nmr (CCl<sub>4</sub>) δ 7.3 (complex m, Ph<sub>3</sub>Ge-), 4.0 [complex m, -CH<sub>2</sub>CH(OH)-], 1.7 (complex m, GeCH<sub>2</sub>-), and 1.2 (d, -CH<sub>3</sub>).

*Anal.* Calcd for C<sub>21</sub>H<sub>22</sub>GeO: C, 69.48; H, 6.11. Found: C, 69.45; H, 6.05.

**2-(Triphenylstannyl)ethanol.**—A solution of 40.0 g (0.104 mol) of triphenyltin chloride in 100 ml of GDME was added to 100 ml of sodium naphthalene in GDME [prepared by addition of 6.0 g (0.26 g-atom) of sodium metal and 7.0 g (0.055 mol) of naphthalene to GDME]. Triphenyltin chloride was added slowly to maintain a green color at all times. After complete addition the solution was stirred for 2 hr and then cooled in an ice bath, and 10.0 g (0.227 mol) of ethylene oxide was added slowly. The resulting tan solution was stirred for 1.5 hr. After usual work-up and recrystallization three times from heptane, 27.45 g (67%) of 2-(triphenylstannyl)ethanol was obtained: mp 67-68° (lit.<sup>19</sup> mp 67-68°); nmr (CCl<sub>4</sub>) δ 7.3 (complex m, Ph<sub>3</sub>Sn-), 3.8 (t, SnCH<sub>2</sub>-), and 1.7 (complex m, -CH<sub>2</sub>OH).

**1-(Triphenylstannyl)propan-2-ol.**—This compound was pre-

Infrared spectra were recorded using the Beckman IR-8 and Perkin-Elmer 621 spectrophotometers. Nmr spectra were obtained with Varian Associates A-60A spectrometer using tetramethylsilane (TMS) as an internal standard in 10-20% solutions of carbon tetrachloride. Chemical shifts are reported in parts per million downfield from TMS.

The gas chromatographic analyses of the alkenes were performed by Gene Taylor, Department of Chemistry, New Mexico State University. The gas chromatograph (Aerograph A-90-P3) was equipped with a thermistor detector. The polyethylene chromatographic column measured 40 ft × 0.25 in. and was packed with saturated silver nitrate in 1,4-butanediol on 40-60 mesh Chromosorb. The following conditions were employed: helium flow rate, 200 ml/min; block temperature, 70°; injection port temperature, 25°; column temperature, 12-15°. The materials were identified by comparing their retention times with those of authentic samples.

Melting points were taken with a Mel-Temp capillary melting point apparatus and are corrected.

Elemental analyses were performed by Crobaugh Laboratories, Cleveland, Ohio. Only compounds not previously reported were analyzed.

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pared in a similar manner as described above from 38.5 g (0.10 mol) of triphenyltin chloride, 4.6 g (0.20 g-atom) of sodium metal, 5.25 g (0.041 mol) of naphthalene, and 8.3 g (0.143 mol) of propylene oxide. After work-up and recrystallization from heptane, 25.40 g (62%) of 1-(triphenylstannyl)propan-2-ol was obtained: mp 83–84.5°; nmr (CCl<sub>4</sub>)  $\delta$  7.3 (complex m, Ph<sub>3</sub>Sn-), 4.1 [complex m, -CH<sub>2</sub>CH(OH)-], 1.7 (complex m, SnCH<sub>2</sub>-), and 1.1 (d, -CH<sub>3</sub>).

*Anal.* Calcd for C<sub>21</sub>H<sub>22</sub>O<sub>2</sub>Sn: C, 61.65; H, 5.42. Found: C, 61.94; H, 5.34.

**threo-3-(Triphenylstannyl)butan-2-ol.**—A solution of triphenyltin sodium was prepared in the usual manner from 38.5 g (0.10 mol) of triphenyltin chloride, 4.6 g (0.20 g-atom) of sodium metal, and 5.25 g (0.041 mol) of naphthalene in 125 ml of GDME. A solution of 7.2 g (0.10 mol) of *cis*-2,3-butylene oxide<sup>20</sup> in 25 ml of GDME was added slowly to the green solution of triphenyltin sodium. After addition the mixture was stirred for 6 hr, at which time a tan solution had developed. After work-up, 15.2 g (43.5%) of hexaphenylditin was recovered. The ether layer was evaporated and after two recrystallizations of the remaining solid from heptane, 9.76 g (23.2%) of *threo*-3-(triphenylstannyl)butan-2-ol was obtained: mp 88–89°; nmr (CCl<sub>4</sub>)  $\delta$  7.3 (complex m, Ph<sub>3</sub>Sn-), 3.91 [q, *J* = 6 cps, -CH(OH)CH<sub>3</sub>], 1.9 [q, *J* = 7.5 cps, SnCH(CH<sub>3</sub>)-], and 1.1 [d, *J* = 6 cps, -CH(OH)CH<sub>3</sub>]; *J* = 3 cps for H<sub>2</sub>-H<sub>3</sub>.

*Anal.* Calcd for C<sub>22</sub>H<sub>24</sub>O<sub>2</sub>Sn: C, 62.45; H, 5.72. Found: C, 62.50; H, 5.53.

**1-(Triphenylstannyl)-2-methylpropan-2-ol.**—A solution of triphenyltin sodium was prepared in the usual manner from 38.5 g (0.10 mol) of triphenyltin chloride, 4.6 g (0.20 g-atom) of sodium metal, and 5.25 g (0.041 mol) of naphthalene in 125 ml of GDME. A solution of 7.2 g (0.10 mol) of isobutylene oxide in 25 ml of GDME was added slowly to the green solution of triphenyltin sodium. After addition the mixture was stirred for 18 hr, at which time a tan colored solution had developed. After work-up and recrystallization from heptane, 18.70 g (44.3%) of 1-(triphenylstannyl)-2-methylpropan-2-ol was obtained: mp 84–85°; nmr (CCl<sub>4</sub>)  $\delta$  7.3 (complex m, Ph<sub>3</sub>Sn-), 1.9 [s, SnCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>-PH], and 1.3 [s, -C(CH<sub>3</sub>)<sub>2</sub>OH].

*Anal.* Calcd for C<sub>22</sub>H<sub>24</sub>O<sub>2</sub>Sn: C, 62.45; H, 5.72. Found: C, 62.62; H, 5.77.

**2-(Triphenylplumbyl)ethanol.**—A solution of 0.133 mol of triphenylplumbyllithium<sup>21</sup> was placed in an adding funnel and added to 8.8 g (0.20 mol) of ethylene oxide in 50 ml of GDME at -45°. After addition the solution was allowed to warm to room temperature. After the solution had been stirred for 1 hr, the contents of the flask were cooled to -45° and acetic acid was added dropwise until the solution was neutral to litmus paper. Cold water and diethyl ether were added, and the ether layer was separated, dried over sodium sulfate, and removed with the use of a rotary evaporator. The solid was recrystallized from heptane to yield 22.7 g (35.5%) of 2-(triphenylplumbyl)ethanol: mp 69–70° (lit.<sup>21</sup> mp 72°); nmr (CCl<sub>4</sub>)  $\delta$  7.3 (complex m, Ph<sub>3</sub>Pb-), 3.6 (t, PbCH<sub>2</sub>-), and 1.7 (complex m, -CH<sub>2</sub>OH).

**1-(Triphenylplumbyl)propan-2-ol.**—This compound was prepared in a similar manner as described above from 0.133 mol of triphenylplumbyllithium and 11.62 g (0.20 mol) of propylene oxide. After work-up and recrystallization from hexane, 29.05 g (44%) of 1-(triphenylplumbyl)propan-2-ol was obtained: mp 84–85° (lit.<sup>21</sup> mp 83–84°); nmr (CCl<sub>4</sub>)  $\delta$  7.3 (complex m, Ph<sub>3</sub>Pb-), 4.1 [complex m, -CH<sub>2</sub>CH(OH)-], 1.7 (complex m, PbCH<sub>2</sub>-), and 1.1 (d, -CH<sub>3</sub>).

**Kinetic Measurements.**—The solvents used in the kinetic studies were carefully purified according to Weissberger's monograph on solvents.<sup>22</sup> Glacial acetic acid (Du Pont, reagent grade) was refluxed with potassium permanganate for 6 hr in order to oxidize any aldehydes present. The acid was then dried over and distilled from magnesium perchlorate at atmospheric pressure. Methanol (Baker analyzed reagent grade) was used as received. The amount of water in these solvents were determined by Karl Fisher titrations.<sup>23</sup> Perchloric acid (72%, Baker analyzed reagent grade) was used as supplied. The acid solutions used in the studies were prepared by adding the calculated amount of perchloric acid to the solvents used. Total acid concentration was determined by titrations according to Fritz's monograph on nonaqueous titrations.<sup>24</sup>

The alcohols were weighed into small 25-ml reaction flasks equipped with a side arm for connection to the gas-measuring buret and a rubber septum for injection of perchloric acid by use of a syringe. Then 10 ml of acetic acid-water or methanol-water was added by means of a calibrated pipet. The mixture was then placed in a 25.0° constant-temperature water bath, saturated with the appropriate alkene, and stirred for 10 min to establish thermal and gas-liquid equilibrium. The levels in the gas-measuring buret were adjusted to zero and the reaction was initiated by injecting 1 ml of perchloric acid of known concentration through the septum. The timer was started and volume readings were begun at once. The values were measured by moving the leveling bulb until the levels in the buret and the leveling bulb coincided. (For extremely fast reactions a tape recorder was used to record data. With this method reactions with half-lives between 5 sec and 2 hr could easily be followed.) Infinity volumes were determined by observing where the gas volume became constant, usually after 10 half-lives.

**Product Analysis. A. Acetolysis of 2-(Triphenylstannyl)ethanol.**—A sample of 0.2009 g (0.508 mmol) of 2-(triphenylstannyl)ethanol was dissolved in 10 ml of glacial acetic acid at 25°, 1 ml of 0.066 *M* perchloric acid was added, and the solution was stirred for 2 hr. Ice-water and ether were added and the acid was neutralized by addition of sodium bicarbonate. The ether layer was separated and dried over sodium sulfate, then removed with a rotary evaporator to yield 0.188 g (90.5%) of triphenyltin acetate, mp 120–121° (lit.<sup>25</sup> mp 121–122°).

**B. Methanolysis of 2-(Triphenylstannyl)ethanol.**—A sample of 0.2009 g (0.508 mmol) of 2-(triphenylstannyl)ethanol was dissolved in 10 ml of 9 vol. % water in methanol, 1 ml of 0.992 *M* perchloric acid was added, and the solution was stirred for 2 hr. Ice-water and ether were added and the acid was neutralized by addition of sodium bicarbonate. The ether layer was separated and dried over sodium sulfate, then removed with a rotary evaporator to yield 0.172 g (92.5%) of triphenyltin hydroxide, mp 118–119° (lit.<sup>25</sup> mp 119°).

**C. Acetolysis of threo-3-(Triphenylstannyl)butan-2-ol. Gas Product Analysis.**—A sample of 0.200 g (0.473 mmol) of *threo*-3-(triphenylstannyl)butan-2-ol was dissolved in 10 ml of 18 vol. % water in methanol at 25°, 1 ml of 0.992 *M* perchloric acid was added, and the solution was stirred for 0.5 hr. The gas that evolved was analyzed by gas chromatography and found to be 100% *cis*-2-butene.

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