

pale yellow oil (45 mg). Analysis by GLC (column A, 185 °C) now revealed a 2:1 mixture of 34 and of the compound which had originally accounted for 5% of the mixture. ¹H NMR (CCl₄) revealed a doublet of triplets at 3.5 ppm.⁴³ The less abundant of the two compounds was therefore 35.

Acknowledgment. We thank Dr. K. U. Ingold for helpful discussions, the Australian Research Grants Committee for financial support, and the Commonwealth Government for a postgraduate scholarship (to R.D.W.).

Registry No. 8, 65756-04-9; 9, 78086-89-2; 12, 10277-53-9; 14, 10277-52-8; 19a, 78019-30-4; 19b, 78019-31-5; 24a, 78019-32-6; 24b, 78019-33-7; 25a, 61376-30-5; 25b, 78019-34-8; 26a, 78086-90-5; 26b, 78086-91-6; 27a, 61376-28-1; 27b, 78086-92-7; 28a, 61376-36-1; 29a, 61376-34-9; 30a (isomer 1), 78019-35-9; 30a (isomer 2), 78086-93-8; 31a (isomer 1), 61348-92-3; 31a (isomer 2), 61348-91-2; 34, 78019-36-0; 35, 78019-37-1; 37, 78019-38-2; 40, 78019-39-3; 41, 78086-94-9; 42, 78019-40-6; 43, 78086-95-0; 44, 78019-41-7; thiophenol, 108-98-5; *o*-thiocresol, 137-06-4; *p*-thiocresol, 106-45-6; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; cyclopentene, 142-29-0; norbornene, 498-66-8; norbornadiene, 121-46-0.

Stereochemistry and Mechanism of Hydride Abstraction from Organostannanes¹

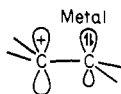
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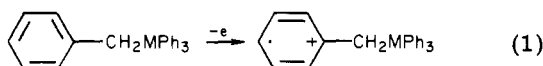
The reaction of trityl cation with *threo*-3-deuterio-2-(trimethylstannyl)butane to produce 2-butenes was shown to proceed with about 99% anti stereochemistry. The primary and secondary isotope effects are 3.7 and 1.1, respectively. These data are interpreted in terms of a hydride-abstraction mechanism leading to a σ - π -conjugated carbocation which subsequently loses the trimethyltin group.

The stabilizing interaction of carbon metal σ bonds with electron-deficient π systems has been demonstrated by



σ - π (vertical stabilization)

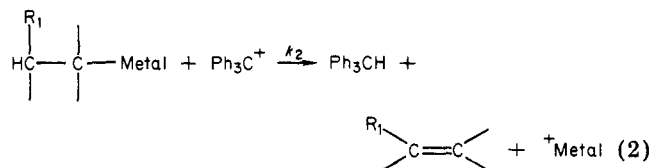
observing the low ionization potentials of allyl and benzyl metal compounds.²⁻⁴ These studies afforded estimates



of the resonance electron-donating abilities of the groups CH_2MR_3 and CH_2HgX where $\text{M} = \text{Si}, \text{Ge}, \text{Sn},$ or Pb . Expressed as $\sigma^+_{\text{CH}_2\text{M}}$ in the linear free-energy relationship $\Delta\text{IP} = \rho\sigma^+$, the values range from -0.4 for CH_2SiPh_3 to -1.2 for $\text{CH}_2\text{HgC}_6\text{H}_{11}$ compared to $\sigma^+_{\text{p-NH}_2} = -1.3$, indicating a powerful electron donation by C-metal σ - π conjugation.^{2a} Such resonance stabilization, observable in vertical ionization has been called "vertical stabilization"^{2a} to contrast the resonance nature of this stabilization to the neighboring-group participation in which a nucleophilic center moves closer to the cationic center. These spectroscopic results and their interpretation offer an attractive explanation of the " β effect"⁵ in organometallic chemistry.

Among the many chemical processes which tend to generate a positive charge β to a carbon-metal bond (the

β effect) and thus partake of this σ - π conjugation, the dehydrometalation of alkyl metal compounds with trityl cation⁶ stands out as both structure sensitive and well behaved^{7,8} (eq 2).



Kinetic studies of this reaction in our laboratories⁷ and those of Reutov, Uglova, and co-workers^{8c} have revealed several characteristics which are indicative of the heterolytic process. The reaction is characterized by the following: (1) almost quantitative yields of Ph_3CH and olefin;^{8d} (2) accurately second-order kinetics, first order in each reagent;^{7,8d} (3) increasing k_2 as the metal becomes more electropositive⁷ ($\log k_2 = \rho\sigma^+_{\text{CH}_2\text{MMe}_3} + \text{constant}$; $\text{M} = \text{Pb} > \text{Sn} > \text{Ge} > \text{Si}$); (4) an increase in k_2 when R_1 is a resonance electron-donating substituent;^{2a,c,8c} (5) an increase in k_2 with electron withdrawal by Y in YPhC^+Ph_2 ^{8c} ($\log k_2 = \rho\sigma^+_{\text{Y}} + \text{constant}$); (6) a primary isotope effect of $k_{\text{H}}/k_{\text{D}} = 2.5$ - 4 ;^{8b} (7) relative insensitivity to solvent polarity;^{8d} (8) a requirement of a periplanar transition state.^{2a} These observations indicate that hydride removal occurs at the transition state which is stereochemically rigid and has carbenium ion character.

However, the stereochemistry of the reaction is not established nor is there a clear indication which of the three likely mechanisms (eq 3-5) occurs with organometallic compounds.

(1) (a) Taken from the Ph.D. Thesis of S.J.H., University of California at San Diego, 1975. The National Science Foundation supported this research (Grant MPS73-08414), and the NMR facilities which were used were supported by the National Institutes of Health (Grant RR00708).

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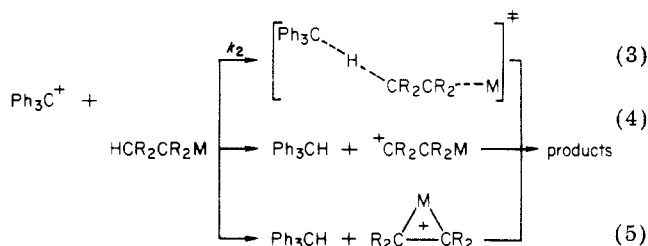
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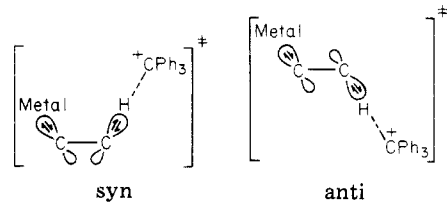
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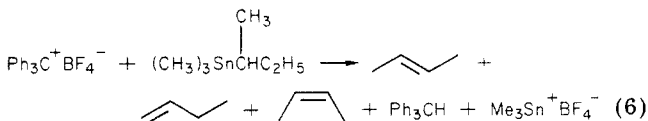
In order to further understand the mechanism of this reaction, we have determined stereochemistry and the primary and secondary isotope effects of the dehydrometalation of *sec*-butyltrimethylstannane. The bimolecular abstraction reaction could assume either the syn or anti transition states along the reaction paths of the mecha-



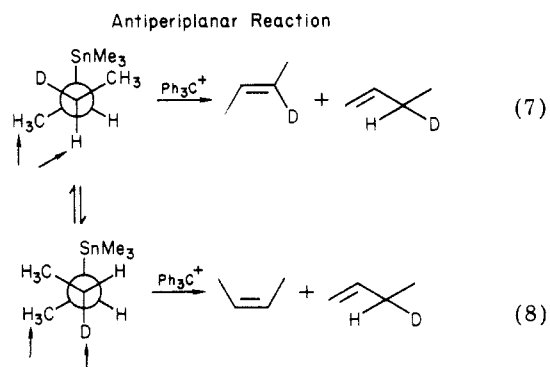
nisms of eq 3-5. Precedence of other elimination reactions⁹⁻¹¹ favor the anti geometry, but these indications require confirmation.

Results

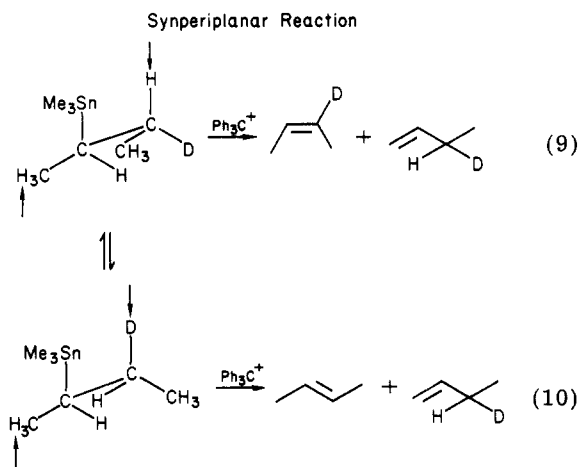
Stereochemistry. The stereochemistry of the dehydrometalation of (2-butyl)trimethylstannane (eq 6) was



determined by examining the products of the reaction of trityl fluoborate with *threo*-3-deuterio-2-(trimethylstannyl)butane as shown in the following schemes (eq 7-10). The production of three butene isomers provides

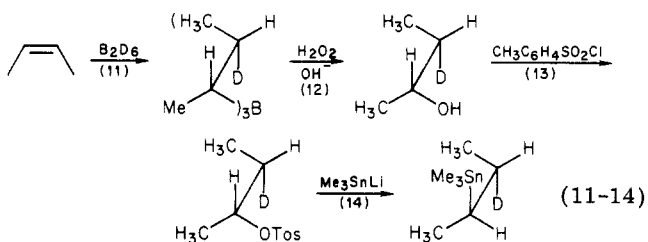


a method of determining both stereochemistry and isotope effects. The anti mechanism leads to *trans*-2-deuterio-2-butene and *cis*-2-butene whereas the syn mechanism produces *cis*-2-deuterio-2-butene and *trans*-2-butene. The accompanying 1-butene, having the deuterium remote from the reaction center, suffers no isotope effect and thus



serves as an internal standard for the measurement of k_H/k_D in the other positions.

The *threo*-3-deuterio-2-(trimethylstannyl)butane was synthesized by the well-known stereospecific deuterio-boration-oxidation¹² of *cis*-2-butene, followed by tosylation of the resulting *erythro*-3-deuterio-2-butanol and displacement of the tosylate with (trimethylstannyl)lithium (eq 11-14). Reaction 11 is at least 98% stereospecific,¹³



and reactions 12 and 13 show complete retention of configuration.^{13,14} Displacement of the tosylate group by all nucleophiles, including metal anions, proceeds with inversion of configuration.¹⁵⁻¹⁷ Therefore we expected 98% configurationally pure tin product which is 98% deuterated from the B_2D_6 (containing 2% H impurity). The results presented below confirm our expectations with regard to isotopic and stereochemical purity.¹⁸ But we rely on previous reports¹²⁻¹⁷ for the stereochemistry of reactions 11-14.

Reactions were carried out at 24 °C in methylene chloride at about a 1 M concentration in each reagent. Reaction times greatly exceeded those required for 99% consumption of one of the reagents. Separation and identification of the olefinic products by gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS) provided the experimental tools for the determination of the stereochemistry and the isotope effects.

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Table I. Stereospecificity of Each Olefin Produced, As Measured by Mass Spectral Peak Height Ratios of Deuterated and Nondeuterated Butenes Produced from *threo*-3-Deuterio-2-(trimethylstannyl)butane

products	peak height ratios ^a	normalized ^b	stereo-specificity
<i>cis</i> -2-butene	0.024 ^c	0 ^c	anti
<i>trans</i> -2-butene	0.051 ^d	0.027 ^d	>97% anti
1-butene	0.029 ^d	0 ^d	

^a Corrected for ¹³C and M - 1 fragmentation. ^b Normalized to 1-butene to correct for isotopic impurity.

^c 57/(56 + 57). ^d 56/(56 + 57).

Base-line separation of the three butene isomers was achieved in the GC by using a Duopak *n*-octane on Porasil C column packing at room temperature. This separation permitted the mass spectroscopic measurement of the deuterium content of each isomer, which was identified by comparing its *R_f* with that of an authentic sample of the olefin.

Mass spectral data were obtained at 10 or 15 eV to minimize fragmentation and to reduce background noise; the peak heights for the isotopically labeled reaction products were corrected for M - 1 fragmentation peaks and M + 1 peaks due to natural-abundance ¹³C, measured experimentally from the M - 1 and M + 1 peaks of the nonlabeled reaction products. Both *cis*- and *trans*-2-butene showed the same amount of M - 1 fragmentation in the nonlabeled olefins so that the same correction was applied to both in the labeled experiment. The 1-butene differed in M - 1 fragmentation, and the labeled 1-butene was corrected accordingly. The M + 1 peaks were the same throughout and agreed fairly well with the amounts predicted due to natural-abundance ¹³C.

Table I gives the corrected mass spectral peak height ratios for the butenes obtained from the elimination of a β hydride from *threo*-3-deuterio-2-(trimethylstannyl)butane by trityl fluoborate.

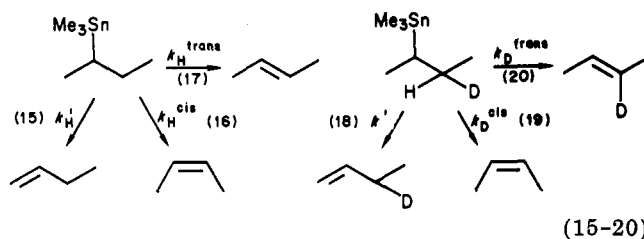
Minimum values for the correction factor for the loss of stereospecificity in the synthesis of the labeled compound (0.02),¹³ as well as for the amount of nondeuterated impurity in the sodium borodeuteride reagent (less than 0.02) compare favorably with the measured mass spectra of the 3-deuterio-1-butene and *cis*-2-butene produced from the deuterated stannane reactant (0.029 and 0.024, respectively). The *cis*-2-butene mass spectrum measures the cumulative effects of the loss of stereospecificity in the synthesis, the isotopic impurity in the reagents, and the amount of syn elimination under investigation. As the 3-deuterio-1-butene mass spectrum reflects only the amount of isotopic impurity in the reagents, it effectively accounts for the entire amount of monodeuterated product in the *cis*-2-butene sample. Thus the stereospecificity of the synthesis and the elimination reaction is absolute within the accuracy of this technique.

The elimination is greater than 99% antiperiplanar in producing *cis* olefin and is greater than 97% stereospecific in producing *trans*-2-butene.

Isotope Effects. The primary isotope effect was obtained from an analysis of integrated GC peak areas of the reaction products from both the deuterated and nondeuterated substrates. The secondary isotope effect was also measured in the same manner and verified through a competition experiment analyzed by mass spectroscopy. The GC analysis was performed with a flame-ionization detector, and a disk integrator was used to measure peak areas; column conditions were identical with those used for the GC/MS work. The peak areas were not corrected for instrumental response factors or differential solubilities

or vapor pressures because the difference between deuterated and nondeuterated olefins should be negligible. All data were used as a ratio of areas so that these factors cancel out. Because the reaction forming 1-butene has the same rate constant in the deuterated and nondeuterated compounds, this rate constant can be used to determine the isotope effects, provided that the reaction is completely stereospecific. Since it is not (Table I), small corrections are made for loss of stereospecificity.

Comparing separate experiments for the deuterated and undeuterated tin compound, we can safely assume that $k'_H = k'_D$. Therefore, if the reactions are stereospecific, as shown, we can use eq 15-22 and obtain $(k_H/k_D)_{\text{primary}}$ and $(k_H/k_D)_{\text{secondary}}$. Corrections for the isotopic and stereo-



$$(k_H/k_D)_{\text{primary}} = (k_H^{\text{cis}}/k'_H)/(k_D^{\text{cis}}/k'_D) \quad (21)$$

$$(k_H/k_D)_{\text{secondary}} = (k_H^{\text{trans}}/k'_H)/(k_D^{\text{trans}}/k'_D) \quad (22)$$

chemical impurity (2% and 1%) are trivially small in the primary isotope effect and barely significant for the secondary isotope effect (see eq 23). In the latter case, 2.7%

$$(k_H/k_D)_{\text{secondary}} = \frac{k_H^{\text{trans}}/k'_H}{k_D^{\text{trans}}/k'_D} = \frac{(k_H^{\text{trans}})_{\text{obsd}}/1.027}{(k_D^{\text{trans}})_{\text{obsd}}/1.016} \quad (23)$$

loss of stereospecificity means that $(k_H^{\text{trans}})_{\text{obsd}} = 1.027k_H^{\text{trans}}$ and $(k_D^{\text{trans}})_{\text{obsd}} = [1 + 0.027/(k_H/k_D)_{\text{prim}}]k_D^{\text{trans}}$.

As a further verification that the normalization to 1-butene is valid and that the other corrections are insignificant, the GC peak areas may be compared by taking the *cis/trans* ratios from the elimination of the nondeuterated substrate and dividing by *cis/trans* ratio from the deuterated substrate (eq 24-26). With an intermediate

$$\frac{[\text{cis}]_{\text{nonD}}/[\text{trans}]_{\text{nonD}}}{[\text{cis}]_{\text{D}}/[\text{trans}]_{\text{D}}} = \frac{k_H^{\text{cis}}/k_H^{\text{trans}}}{k_{D,\text{prim}}^{\text{cis}}/k_{D,\text{sec}}^{\text{trans}}} = \frac{(k_H/k_D)_{\text{prim}}^{\text{cis}}}{(k_H/k_D)_{\text{sec}}^{\text{trans}}} \quad (24)$$

$$\frac{0.203}{0.062} = \frac{(k_H/k_D)_{\text{prim}}^{\text{cis}}}{(k_H/k_D)_{\text{sec}}^{\text{trans}}} \quad (25)$$

$$(k_H/k_D)_{\text{prim}}^{\text{cis}} = 3.24 (k_H/k_D)_{\text{sec}}^{\text{trans}} \quad (26)$$

value of 1.10 for the secondary isotope effect, a primary isotope effect of 3.56 obtains, in reasonable agreement with the value of 3.70 from the previous treatment. An additional determination of the secondary isotope effect was made by carrying out a competitive elimination experiment between a known molar ratio of nondeuterated and deuterated reactants with a limiting amount of trityl fluoborate. Mass spectral peak heights were measured for each isomer and the numbers corrected as before for M - 1 fragmentation and M + 1 peaks. Table II summarizes these data.

In this experiment, the hydride-abstracting reagent, in limiting amount, kinetically competes for the deuterated

Table II. Ratios of Gas-Liquid Chromatographic Peak Areas of Olefin Products and Derived Isotope Effects

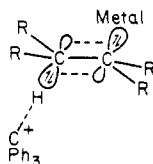
reactant	<i>cis</i> -2-butene/ 1-butene	<i>trans</i> -2-butene/ 1-butene	trans/ <i>cis</i>	1-butene/2-butenes
(CH ₃) ₃ SnCH(CH ₃)C ₂ H ₅	28.5 ± 3.0	1.79 ± 0.18	0.0626 ± 0.003	0.0326 ± 0.0027
(CH ₃) ₃ SnCH(CH ₃)CHDCH ₃	7.74 ± 0.7	1.57 ± 0.14	0.202 ± 0.012	0.108 ± 0.0078
	k_H/k_D		k_H/k_D	
	primary 3.7 ^a (3.56) ^b		secondary 1.10 ^c (1.12, ^d 1.04 ^e)	

^a Calculated from GLC integrated peak areas normalized to 1-butene (eq 21). ^b Calculated from GLC integrated peak areas and the secondary isotope effect (eq 26). ^c Calculated from eq 23 and the competition experiment (vide infra). ^d Calculated from eq 22. ^e Calculated from the competition experiment.

and the nondeuterated substrates in proportion to their molar ratios and the primary and secondary isotope effects. The molar ratio of the substrates may be taken from the weighed amounts of each reagent or from the measured isotopic ratio of the 1-butene products, which should be formed with identical rates, as any isotope effect should be vanishingly small. This experiment yields a secondary isotope effect of 1.04 ± 0.10 when the isotopic ratio of *trans*-2-butene was divided by the corresponding number for 1-butene; when the weighed molar ratio was used to correct the *trans*-2-butene mass spectral ratio, a value of 1.10 was obtained. The primary isotope effect is not calculable from this experiment.

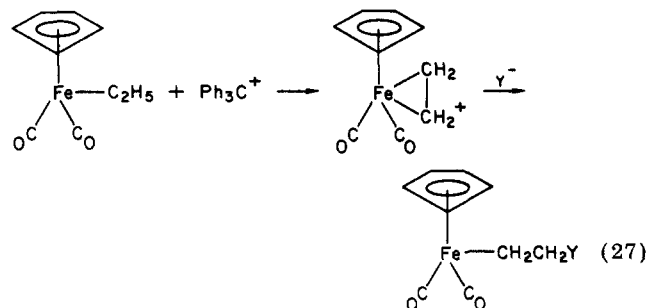
Discussion

The stereochemical results are in agreement with previous conclusions based upon the faster dehydrometalation of *cis*- than of *trans*-(4-*tert*-butylcyclohexyl)trimethyltin.^{2a} Anti hydride abstraction has also been observed with transition-metal organometallic compounds⁹⁻¹¹ and many other heterolytic elimination reactions. This result and the enormous acceleration of the hydride abstraction rate afforded by β -metal substituents^{2a} suggest the transition state shown below. The simplest mechanism for this



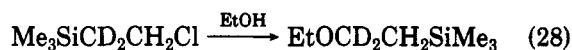
reaction, consistent with this stereochemistry, is concerted elimination, called E_B2 by Uglova et al.^{8a} (eq 3). After attempting to trap an intermediate cation by exchange, they concluded that the tin compounds eliminate by this mechanism. However, the trapping method does not conclusively rule out a short-lived β -trimethyltin alkyl cation (eq 4).

There are very convincing arguments for a β -metallo-alkyl cation in which the metal is SiMe₃, HgR, or various transition metals. For example, abstraction of hydride from ethyl cyclopentadienyldicarbonyliron yields a stable cation⁵ (eq 27). The stability of this cation has been



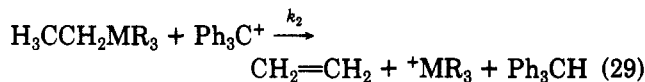
attributed to the Fe d-orbital interaction^{5a,10} although the

rate of its formation must derive most of its driving force from σ - π conjugation.⁷ Similar results and interpretations have been offered for the now well-established mercurinium ion.¹⁹ Again π back-bonding could contribute to the stability of the cation. Recently the solvolysis of β -(trimethylsilyl)ethyl bromide was shown by Cook, Eaborn, and Walton²⁰ to involve a discrete cationic intermediate by observing rearrangement (eq 28). The bridged



ion suggested by this result was supported by theoretical calculations²¹ although there are no available filled d orbitals on silicon. The contribution of this bridging to the rate of hydride abstraction will be discussed in the following paper. The fact that MCR₂CR₂⁺ is an established intermediate for M = SiMe₃²⁰ and HgR¹⁸ in solution and for SnR₃ in the gas phase²² make it very likely that such an intermediate also forms in solution when M is GeMe₃ or SnMe₃. The ⁺HgR group is less electronegative and is known to be a better leaving group than either ⁺SnMe₃ or ⁺GeMe₃.²³

Isotope effects are also consistent with a carbenium ion reaction. Table III compares the isotope effects and stereospecificities observed in this study with other elimination processes. The primary isotope effect shows that hydrogen is removed in the rate-limiting process, and the secondary isotope effect is typical of those for carbenium ion forming reactions.²⁶ It accords well with that observed by Kreevoy et al. for the deoxymercuration reaction.²⁴ On the basis of the correlation between log k_2 for the reaction (eq 29) with the vertical stabilization parameter $\sigma^+_{\text{CH}_2\text{MR}_3}$



for group 4a metals, we have concluded that this reaction derives its acceleration from vertical stabilization without requiring bridging or concerted elimination.^{2a}

Product Ratios. The product ratio data verify and confirm the mechanistic implications provided by the

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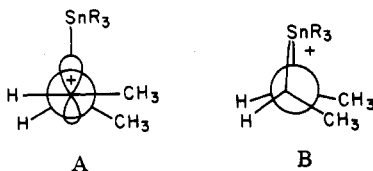
Table III. Summary of the Stereospecificities and Deuterium Isotope Effects for Eliminations of β -Hydrides from Organometallics Induced with Trityl Cations and for Other Related Reactions

	% stereospecificity of elimination		isotope effects			ref
	cis olefin	trans olefin	primary	α secondary	β secondary	
<i>threo</i> -PhCHDCHDFeCp		85	2.5			9
<i>threo</i> -CH ₃ CHDCH(CH ₃)Sn(CH ₃) ₃	99 (anti)	97 (anti)	3.7		1.10	this work
[(CH ₃) ₂ CDCH ₂] ₄ Sn			3.8			8b
(CH ₃ CHDCHCH ₃) ₂ Hg			4.2			8b
(CH ₃) ₃ CCHDCHDZrCp ₂ Cl		anti	2.5			10
PhCH(OCH ₃)CH ₂ HgCl ^a	98 (anti)	90 (anti)		0.91	1.12	24
Me ₃ SiCH ₂ CH ₂ X ^b				1.02	1.10	25

^a Elimination of HgClOCH₃. ^b Elimination of Me₃SiX.

isotope effects and our prior results.^{2a} The rate-limiting step is the initial abstraction of a hydride which is bimolecular and leads to an intermediate organostannane cation. This is exothermic, as is evidenced by the lack of reversibility with added triarylmethane,^{8a} and it does not equilibrate by rotation about the C-C bond as is evidenced by the high degree of stereospecific anti elimination. Thus the product ratios reflect the "rate-determining", kinetic, transition state rather than a separate "product-determining", thermodynamic, transition state.

The high cis/trans ratio is consistent with a transition state where eclipsing interactions do not dominate since this would ordinarily favor trans olefins. Also implied is a ground-state rotamer population effect which is smaller than that in the transition state. These conditions usually apply to E1-type eliminations with "early" transition states favored by strong bases or powerful leaving groups. This agrees with the assessment of the β -hydride elimination reaction from an organostannane as being exothermic and passing through a stabilized intermediate cation. The formation of cis olefin must then proceed through an intermediate which possesses a relatively small eclipsing methyl interaction; this is more characteristic of σ - π -stabilized carbocation A than a bridged species (B) and is more favorable for an anti elimination than for a syn mechanism.



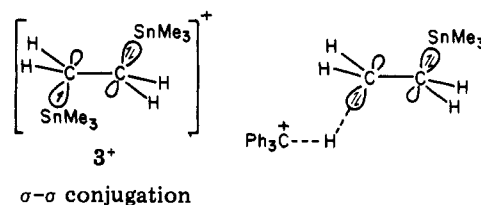
The driving force for the cis preference in the transition state, which is sufficient to overcome both a ground-state rotamer population handicap as well as the transition-state gauche methyl interaction, has been ascribed to asymmetric steric requirements of the abstracting reagent or the departing group.^{9c,27} This can be easily visualized for E2 eliminations from tosylates with strong or bulky bases because of the nonlinearity of the oxygen bond angle between the tosylate group and the carbon of the substrate. However, the importance of a similar effect with the trityl cation induced elimination from organostannanes is not clear.

Steric bulk of the abstracting trityl cation alone plays a role in the determination of the reaction products, as evidenced by the increase in 1-butene as the trialkylstannane leaving group is made more bulky,^{8c,d} but does not dominate the course of the reaction, as the amount of 1-butene produced remains small. The dominant forma-

tion of 2-butene except under forcing conditions accords with the interpretation that a stable cationic intermediate is produced. Although the σ - π conjugative interaction of the carbon-stannane bond with the cation center provides the bulk of the cation stabilization, a secondary cation would be expected to be preferred over a primary cation, thus leading to a preference for 2-ene products, as is found.

Conclusion

It now becomes clear that σ - π conjugation, like elimination processes, has a preferred anti orientation. This results from the better overlap between sp^3 orbitals aligned antiperiplanar. The very strong geometry-sensitive interaction between the C-metal σ bonds in 1,2-bis(trimethyltin)alkanes, observed by photoelectron spectroscopy,²⁸ is in keeping with this conclusion. The removal of an electron from 3 to give 3⁺ indicates a σ - σ interaction



of 2.2 eV, and this radical cation is a good model for the dehydrometalation transition state. This view of the transition state is similar to that proposed by Uglova et al. except for the requirement that the C-M bond be broken at the transition in their mechanism.^{8a}

The ion which is formed could have either an open or bridged structure. However, the difference in the energies of the open and bridged ions is very small.²⁹ This means that even if bridging occurs it is unimportant in the stabilization of the transition state because vertical stabilization is sufficient to provide the full driving force.

The following paper offers additional evidence against bridging or concerted elimination.

Experimental Section

All manipulations of organometallic compounds were carried out in an argon atmosphere. Diglyme (MCB), boron trifluoride etherate (MCB), pyridine (Baker, analytical), tetrahydrofuran (Matheson), and *p*-toluenesulfonyl chloride were purified by methods described by Fieser.³¹ The solvents were freshly distilled

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(30) Tamborski, C.; Ford, F. E.; Soloski, E. J. *J. Org. Chem.* 1963, 28, 237-239.

(31) Fieser, L. F.; Fieser, M., "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, pp 70, 255, 958, 1140, 1180, respectively, for boron trifluoride etherate, diglyme, pyridine, tetrahydrofuran, and tosyl chloride.

(27) Saunders, W. H.; Cockerill, A. F., "Mechanisms of Elimination Reactions"; Wiley-Interscience: New York, 1973; p 105 ff.

before use. Other reagents were used as received.

Gas chromatographic-mass spectral analysis was performed on an LKB Model 9000 equipped with a 10 ft \times 1/4 in. column packed with Duopak *n*-octane on Porasil C. The column temperature was at 35 °C and the He flow rate was 25 cm³/min. Mass spectra were taken at 10 or 15 eV to minimize the background and M - 1 fragmentation. Gas chromatographic analysis was done on a Hewlett-Packard Model 700 chromatograph with a flame-ionization detector, a disk integrator, and a 10 ft \times 1/8 in. copper column with the same packing material. NMR spectra were recorded on either a Varian Model T-60 or HR-220. Data were treated to calculate the standard deviations and are included in the tables.

erythro-3-Deuterio-2-butanol (1) was synthesized by the method of Brown and Subba Rao¹² in 19.5% yield from *cis*-2-butene (Matheson, CP), and NaBD₄ (99% D, Stohler Isotopes): bp 97 °C; NMR δ 0.87 (d, 3 H), 1.10 (d, 3 H), 1.4 (m, 1 H), 3.56 (q, 1 H), 4.47 (s, 1 H).

erythro-3-Deuterio-2-butyltosylate (2) was synthesized by the method of Tipson¹⁴ in 74.5% yield from the alcohol: NMR δ 0.77 (d, 3 H), 1.18 (d, 3 H), 1.50 (m, 1 H), 2.34 (s, 3 H), 4.55 (q, 1 H), 7.58 (q, 4 H).

(Trimethylstannyl)lithium in tetrahydrofuran (THF) was prepared by the method of Tamborski, Ford, and Soloski.³⁰ Lithium wire (1% Na) and Me₃SnCl from Alfa were used without further purification.

threo-3-Deuterio-2-(trimethylstannyl)butane (3) was synthesized in 22% yield from the tosylate 2. A twofold excess of Me₃SnLi was added slowly with stirring to the tosylate 2, and the reaction was allowed to stir for 0.5 h. The reaction was quenched with water and extracted into ether, and the ether layer was washed with saturated NaHCO₃, 2 N HCl, and saturated NaCl solution, dried with MgSO₄, and then vacuum distilled: bp 25 °C (5 mm); NMR δ 0.11 (s, 9 H), 0.72 (m, 1 H), 0.99 (d, 3 H), 1.24 (m, 3 H), 1.64 (m, 1 H). The mass spectrum has its most abundant isotope peak at 223 mass units, and its isotope pattern agrees to within about 5% of the predicted pattern.

Quantitative Measurement of Butenes Produced from Reaction of 2-(Trimethylstannyl)butane with Trityl Fluoborate. Methylene chloride (2 mL) containing 2.7×10^{-4} mol of trityl fluoborate was mixed with 3.39×10^{-4} mol of *sec*-butyltrimethylstannane in 0.3 mL of CH₂Cl₂ in a 10-mL flask closed with a stopcock. Gaseous products were sampled with a gas-tight syringe (Precision Sampling Co.) through a septum connected to the flask through the stopcock. Withdrawn samples were diluted with air in the syringe and mixed by closing the needle valve and pumping the plunger. Then the needle valve was opened, and the sample size was reduced. Samples withdrawn were typically 0.025–0.05 mL in the 1-mL syringe, with the dilution being 1:4 to 1:8, such that the injected volume was typically 0.025 to 0.05 mL. Repeated injections of the products were made, and the amounts of each product were determined by a disk integrator.

threo-3-Deuterio-2-(trimethylstannyl)butane was treated similarly, 2.44×10^{-4} mol being reacted with 3.24×10^{-4} mol of trityl fluoborate.

Analysis for Deuterium Content in Butenes Produced from Reaction of *threo*-3-Deuterio-2-(trimethylstannyl)butane with Trityl Fluoborate. The reactions described above were utilized for mass spectral studies. The analysis for deuterium content in each isomer was achieved by measuring the *m/e* 55, 56, 57, and 58 peak heights from the mass spectra and correcting these for background peaks if necessary. The M - 1 fragmentation was measured as a ratio of the *m/e* 55/56 peaks from the non-deuterated *cis*- and *trans*-2-butenes, and the M + 1 (¹³C) was measured similarly as a ratio of the *m/e* 57/56 peaks. These ratios

were 0.033 ± 0.002 and 0.047 ± 0.003 , respectively, for the M - 1 and M + 1 peaks for both *cis*- and *trans*-2-butene. The 1-butene produced a value of 0.056 ± 0.003 for the M - 1 fragmentation, but the M + 1 peak ratio was identical with the other isomers. The butene products produced from the elimination of the deuterated organostannane were analyzed, and the peak-height ratios were computed after correction for the background and the M - 1 and M + 1 peaks by using the numbers above as correction factors for the *m/e* 56 and 57 peak heights. The corrected peak heights were used to obtain the *m/e* 56/(56 + 57) and 57/(56 + 57) average peak height ratios which represented the isomeric composition as a fraction of the total and are listed in Table I. The ratio for 1-butene thus reflected the amount of nondeuterated 1-butene contributed by the isotopic impurity in the deuterium source (NaBD₄, Stohler Isotopes, <2%). The ratios for *cis*- and *trans*-2-butene represented, in addition to the loss of stereospecificity in the elimination, the amount of isotopic impurity in the deuterium source, the amount of *trans*-2-butene isomeric impurity in the *cis*-2-butene reagent, and the loss of stereospecificity in the deuterioboration reaction. Clearly, from the measured ratios for 1-butene and *cis*-2-butene, the isotopic impurity in the NaBD₄ alone accounted for correcting the *cis*-2-butene sample, and the other sources of error appeared to be unimportant. Correcting the *trans*-2-butene similarly (0.024) gave a value of 0.027 for the ratio of nondeuterated *trans*-2-butene to total *trans*-2-butene.

Analysis for Deuterium Content in Butenes Produced from the Reaction of a Mixture of 2-(Trimethylstannyl)butane and *threo*-3-Deuterio-2-(trimethylstannyl)butane with Trityl Fluoborate. The reaction was carried out as above with 6.58×10^{-5} mol of 2-(trimethylstannyl)butane and 6.68×10^{-5} mol of *threo*-3-deuterio-2-(trimethylstannyl)butane in 0.5 mL of methylene chloride combined with 7.60×10^{-5} mol of triphenylmethyl fluoborate in 2 mL of methylene chloride. Mass spectral peak heights were measured as before and corrected for background, the M - 1 fragmentation (0.18 correction factor, measured from the *m/e* 55/56 and 56/57 peak height ratios from this experiment), and the ¹³C contribution to the M + 1 peak height (again measured to be 0.047). The average ratio of the *m/e* of 56/57 peaks was computed for *trans*-2-butene and was found to be 1.08 ± 0.12 . The ratio for the 1-butene peak was calculated from a graphical presentation of the measured peak height ratios as a function of position along the time coordinate of the GC trace. This was necessary because the peak height ratio changed linearly with the sampling time during elution of the peak, indicating some separation of the deuterated and nondeuterated 1-butenes. This was not a problem for the 2-butenes. A linear regression analysis by the method of least squares was used to plot the data and the reported isotopic ratio was that value taken at the midpoint of the GC peaks. This value (1.16) was subsequently corrected for the M - 1 and M + 1 contributions as before to yield the *m/e* 56/57 isotopic ratio for 1-butene of 1.04 ± 0.10 , in reasonable agreement with the measured molar ratio of reagent organostannanes of 0.984. Using the 1-butene ratio to normalize the *trans*-2-butene ratio gives a value of 1.04, whereas normalizing with the molar ratio of reagents gives a value of 1.10, the latter in agreement with the value calculated from the GC integrated peak areas.

Acknowledgment. We are grateful to Dr. John Wright for assistance in obtaining the mass spectral results.

Registry No. 1, 10277-59-5; 2, 7429-09-6; 3, 71195-43-2; 2-(trimethylstannyl)butane, 15095-79-1; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 1-butene, 106-98-9.