anol-free chloroform[17] by mixing equal volumes of reactant solutions.

Product Analysis. In a typical run, 2 mL of Dabco, 0.3 M in $CDCl_3$, and 2 mL of chloropropanoyl chloride, 0.15 M in $CDCl_3$, were mixed at room temperature for 30 s; the chloroform solution was immediately washed with water to extract Dabco and dried over molecular sieves. The product, when analyzed by NMR (Table I) and mass spectra as described in the text, agrees with the structure $CH_3CHClCOC(CH_3)(Cl)COCl$.

(17) A. I. Vogel, "Practical Organic Chemistry", Longmans, Green and Co., New York, 1956, p 176.

Acknowledgment. We have enjoyed helpful discussions with Drs. R. McCrindle and A. McAlees. This work has been supported in part by the National Research Council of Canada.

Registry No. CPC, 7623-09-8; DMKC, 20320-72-3; 2-chloropropanoic anhydride, 39060-20-3; *cis*-DDC, 72206-86-1; *trans*-DDC, 72206-87-2; DMKTA, 72206-88-3; 1-(2,4-dichloro-2-methyl-3-oxopentanoyl)-1,4-diazabicyclo[2.2.2]octane·HCl, 72206-89-4; 2-chloropentanoic acid, 598-78-7; *endo*-7-chloro-7-methylbicyclo[3.2.0]hept-2-en-6-one, 13363-88-7; *exo*-7-chloro-7-methylbicyclo[3.2.0]hept-2-en-6-one, 13363-87-6; Dabco, 280-57-9; TEA, 121-44-8.

Stereochemistry and Mechanism of a Radical-Induced (E_H) Elimination Reaction. Reaction of Trichloromethyl Radicals with 2-(Trimethylstannyl)butane and 3-Deuterio-2-(trimethylstannyl)butane

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Received February 8, 1979

threo- and *erythro*-3-deuterio-2-(trimethylstannyl)butanes (**1**-*d*) were prepared with high purity by the reaction of trimethyltinsodium with *erythro*- or *threo*-3-deuterio-2-[(4-methylphenyl)sulfonoxy]butane. Reaction of these and (trimethylstannyl)butane (**1**) with trichloromethyl radical generated by thermal decomposition of benzoyl peroxide in bromotrichloromethane resulted in the formation of 1-butene plus *cis*- and *trans*-2-butene along with bromobenzene, chloroform, 2-bromo-2-(trimethylstannyl)butane (**2**), trimethyltin bromide, and other products. Analysis of the olefin distributions shows a primary/secondary preference of 15:1 for the hydrogen abstraction and a 75–77% preference for antiperiplanar elimination is calculated by using the experimentally determined primary deuterium isotope effect $k_H/k_D = 5.1 \pm 0.3$. The results are discussed in terms of two proposed elimination mechanisms: (1) a concerted E_H2 reaction with anti and syn elimination pathways, (2) a two-step E2ir reaction in which initial anti proton abstraction to a 3-(trimethylstannyl)-2-butyl radical occurs with subsequent competition between collapse to an olefin and rotation about the C-2,C-3 bond followed by olefin formation.

Solution-phase radical-induced β eliminations have been proposed to rationalize the results of a number of investigations,[1] and anchimeric assistance of hydrogen abstraction, with or without bridging, has been recognized in various systems.[2] Kampmeier and co-workers demonstrated the formation of olefins in the nonchain decomposition of *tert*-butyl sulfide, phenyl *tert*-butyl sulfide, and phenyl amyl sulfides.[3,4] The conclusions were that the reaction occurs by unassisted hydrogen abstraction, giving an intermediate radical, followed by collapse to an olefin and a thiyl radical as the most likely reaction path. It was suggested that a less reactive, more selective radical along with a weaker carbon leaving group bond might result in a concerted E_H2 reaction.

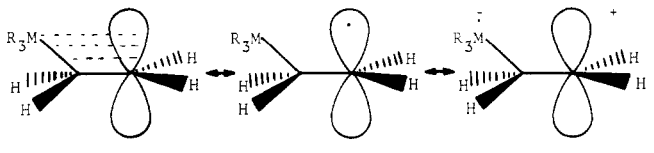
Another way in which a concerted E_H2 reaction might result is if the compound contained a leaving group with demonstrated ability to stabilize a radical center β to it. Kuivila et al.[5] found that tri-*n*-butyltin hydride dehalogenates vicinal dihalides according to the stoichiometry in eq 1. When *dl*- and *meso*-2,3-dibromobutanes were

$$\text{X—C—C—X} + 2(\text{Bu})_3\text{Sn—H} \rightarrow \text{C=C} + 2(\text{Bu})_3\text{SnX} + \text{H}_2 \quad (1)$$

treated independently with 2 mol of tri-*n*-butyltin hydride, mainly *cis*- and *trans*-2-butene, respectively, were produced, indicating preferential anti elimination. Various controls indicated a free-radical chain reaction, and stereospecificity increased with increasing tin hydride concentration. A stepwise pathway was proposed in which an initially formed bridged β-bromoalkyl radical undergoes rotation with concomitant loss of stereospecificity.

It is entirely possible that the stereospecificity originated not from a completely bridged structure but simply from a conformational preference in which the C–Br bond aligns itself with the p orbital of the lone electron to achieve maximum overlap. Evidence for this type of phenomenon will be discussed below.

Kochi and co-workers[6] have shown that compounds of the type $R_3MCH_2CH_2\cdot$ (M = Si, Ge, Sn) are considerably stabilized relative to $CH_3CH_2\cdot$ or $RCH_2CH_2\cdot$ (R = alkyl), and the most stable conformation of the molecule is with the metal–carbon bond lying in the plane described by the carbon–carbon bond axis and the p orbital occupied by the unpaired electron. The β-hydrogen hyperfine splitting and the anisotropic *g* factor were interpreted as indicative of both p–σ hyperconjugation and p–d homoconjugation in the radical–metal interaction.[7] In the case of M = Sn the stabilization was estimated to be approximately 2 kcal/mol.[6b]



p–σ hyperconjugation p–d homoconjugation

(1) G. A. Russell and A. Ito, *J. Am. Chem. Soc.*, **85**, 2983 (1963).
(2) P. S. Skell and K. J. Shea, *Free Radicals*, **2**, 809–52 (1973).
(3) J. A. Kampmeier, et al., *J. Am. Chem. Soc.*, **88**, 1257 (1966).
(4) J. T. Hepinstall, Jr., and J. A. Kampmeier, *J. Am. Chem. Soc.*, **95**, 1904 (1973).
(5) H. G. Kuivila, et al., *J. Am. Chem. Soc.*, **92**, 2849 (1970).
(6) (a) P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, **91**, 6161 (1969); (b) *ibid.*, **93**, 846 (1971).
(7) T. Kawamura and J. K. Kochi, *J. Am. Chem. Soc.*, **94**, 648 (1972).

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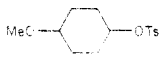
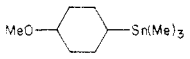
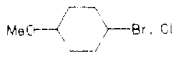
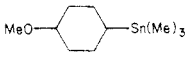
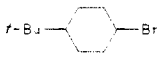
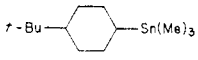
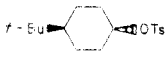
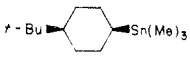
Table I. Stereochemical Results of the Reaction of $(Me)_3SnM$ with RX

M	RX[m]	product[m]	solvent	$[\alpha]^{25}_D$ (neat),[a] deg	% net inversion[b,m]	ref
Na	 c(t)	 t(c)	THF[c]		>99[d]	e
Li, Na, K	 c or t		THF[c]		equal c:t ratio from both RX, c:t ≈ 35.65	e
Li, K	 c or t		THF[c]		Li → c:t ≈ 49:51[f] K → c:t ≈ 40:60	e
Li			THF[c]		100	e, g
Li	*sec*-BuBr	Me_3Sn-*sec*-Bu	liquid NH_3	3.0	12	h
Na	*sec*-BuOTs	Me_3Sn-*sec*-Bu	NH_3/Et_2O[i]	−25.7	100[j]	this work
K	*sec*-BuOMs	Me_3Sn-*sec*-Bu	HMPA/THF[k]	−24.3	95	this work
K	*sec*-BuOMs	Me_3Sn-*sec*-Bu	HMPA	−25.4	99	this work
K	*sec*-BuOMs	Me_3Sn-*sec*-Bu	NH_3/Et_2O[l]	−24.4	95	this work

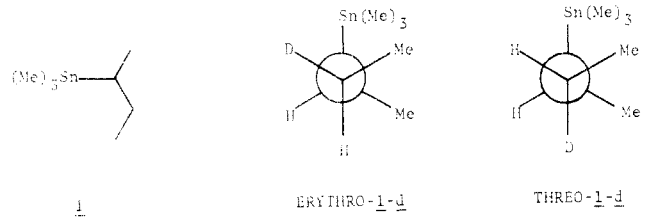
[a] Rotations corrected to 100% activity of RX.[10] [b] Total inversion, i.e., 99% inversion and 1% retention. [c] Me_3SnM was prepared in NH_3/tetrahydrofuran (THF) at −78 °C and allowed to warm to room temperature 6-8 h before adding RX. [d] Product analyzed by GLC. [e] C. Hsu, Ph.D. Thesis, University of California, Berkeley, 1975. [f] Koermer, Hall, and Traylor (footnote *g*) obtained >95% retention for cis bromide. [g] G. S. Koermer, M. L. Hall, and T. G. Traylor, *J. Am. Chem. Soc.*, 94, 7205 (1972). [h] H. E. Guard, Ph.D. Thesis, University of California, Berkeley, 1968. [i] Inversion addition; Me_3SnM formed in liquid NH_3 at −78 °C and then was slowly added to RX in ether at room temperature. [j] Assumed.[11] [k] 60:40 hexamethylphosphoramide/THF (v/v). [l] Me_3SnM formed in NH_3 at −78 °C, Et_2O was added, an aspirator vacuum was applied, and the solution was stirred until it warmed to −10 °C after which the *sec*-BuOMs was added. [m] *c* = cis and *t* = trans.

Jensen and Guard have shown metals to be good leaving groups in radical-induced β eliminations.[8] Di-*n*-butylmercury reacts with trichloromethyl radical in carbon tetrachloride to yield 1-butene (50% yield), butane, *n*-butyl chloride, and mercury in a free-radical chain process. Tetrabutyltin reacts with trichloromethyl radicals in $BrCCl_3$ to give 1-butene in 59% yield (based on 1 mol of butene/mol of tetrabutyltin), and 2-(trimethylstannyl)-butane under similar conditions gives 1- and 2-butenes.

The present work examines the stereochemical results of radical-induced eliminations of 3-deuterio-2-(trimethylstannyl)butane to probe the mechanistic possibilities of this interesting class of reactions. This system offers the possibility of examining geometric requirements of intermediates or transition states, primary deuterium isotope effects, and conditions which could be favorable for a concerted E_H2 reaction.

Results and Discussion

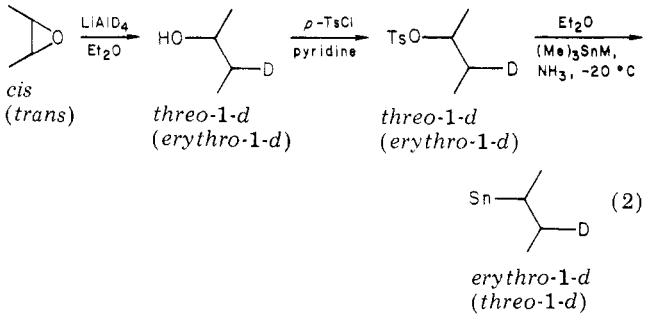
2-(Trimethylstannyl)butane (1) and the previously unreported *threo*- and *erythro*-3-deuterio-2-(trimethylstannyl)butanes (1-*d*) were synthesized and allowed to



1 ERYTHRO-1-d THREO-1-d

react with trichloromethyl radicals generated by the thermal decomposition of benzoyl peroxide in bromotrichloromethane solvent. Abstraction of the hydrogens β to the trimethylstannyl group gives 1- and 2-butenes which were analyzed for deuterium content and cis/trans ratio; however, in order to obtain meaningful data from this analysis, each deuterium-substituted diastereomer must be obtained uncontaminated by the other, or the precise ratio of diastereomers in each mixture must be known.

Scheme I



(2)

erythro-1-*d* (*threo*-1-*d*)

Synthesis of carbon–tin bonds with varying degrees of stereospecificity occurs via the reaction of trialkyl- or triaryltin alkalis (formed from R_3SnSnR_3 or R_3SnX reacting with Li, Na, or K) with the appropriate alkyl halide or tosylate and mesylate. Trimethyltinlithium, -sodium, or -potassium reacts with isomeric mesylates and tosylates under selected conditions to yield the inverted products with complete (or essentially complete) inversion of configuration (Table I). The optical rotation for 1 prepared via the inverse-addition technique (see Experimental Section) is in agreement with the indirectly obtained value reported by Rahm and Pereyre[9] of $[\alpha]^{22}_D$ 26.5° (neat) for 1.

Preparation of 3-Deuterio-2-(trimethylstannyl)butane (1-*d*). The sequence outlined in Scheme I was used

(8) F. R. Jensen and H. E. Guard, *J. Am. Chem. Soc.*, 90, 3250 (1968).

(9) A. Rahm and M. Pereyre, *J. Organomet. Chem.*, 88, 79 (1975).

(10) For 2-bromobutane the rotation was assumed to be $[\alpha]^{25}_D \pm 34.3°$ (neat) after consideration of all reasonable reported values. For *sec*-butyl tosylate and mesylate, roation of the 2-butanol precursor was assumed to be $[\alpha]^{25}_D \pm 13.63$ (neat) after Pickard and Kenyon.

(11) The reaction of Me_3SnM with 4-methoxycyclohexyl tosylate was shown to be 100% inversion within the limits of GLC detection; since inversion at cyclohexyl is known to be more difficult than at alicyclic secondary positions and with the good agreement of our optical rotations to the value of Rahm and Pereyre,[9] the reaction of Me_3SnM with *sec*-butyl tosylate must occur with 100% inversion.

Table II. Total Product Analysis from Decomposition of 2-(Trimethylstannyl)butane Induced by Benzoyl Peroxide in Bromotrichloromethane[a]

compd	mmol[b]	percent[c]
butenes	1.41	26
methyl bromide	0.17	3
chloroform	4.47	82
benzene	<0.03	<1
1	0.21	4
trimethyltin bromide	2.69	49
bromobenzene	2.17	66[d]
hexachloroethane	1.26	20[e]
2	2.49	45

[a] Initial reaction mixture: 5.48 mmol of 2-(trimethylstannyl)butane, 1.65 mmol of benzoyl peroxide, 30.34 g (15.1 mL) of bromotrichloromethane. [b] Low-boiling fraction referenced to pentane added as internal standard; pot fraction referenced to *tert*-butylbenzene added as internal standard. [c] Mole % vs. initial 2-(trimethylstannyl)-butane. [d] Mole % vs. initial benzoyl peroxide. [e] Each hexachloroethane counted as two trichloromethyl radicals in calculating percent yield.

to prepare *threo*- and *erythro*-1-*d* uncontaminated by each other. The first step of Scheme I occurs with 100% inversion as shown by a 60-MHz ^{1}H NMR spectrum of the 3-deuterio-2-butanol in the presence of a lanthanide shift reagent, since the protons of C-2 and C-3 have different chemical shifts for the threo and erythro alcohols.[12] Attempts to verify the purity of the diastereomeric 1-*d*'s by other physical or spectral methods were not successful. The protons of C-2 and C-3 give complex overlapping signals in the 100-MHz ^{1}H NMR spectrum even when heteronuclear deuterium decoupling is employed. The IR spectra show mutually exclusive bands at 1038 cm^{-1} (threo) vs. 1059 and 1015 cm^{-1} (erythro), but although the spectra indicate high diastereomeric purity, the ratio at which the band from one isomer disappears into the base line of the other is not known. Direct displacement reactions (S_N2) on cyclohexyl systems are usually difficult, but complete (within experimental uncertainty) inversion was achieved in the reaction of 4-substituted cyclohexyl tosylates with trimethyltin anions. The consistent results with optically active sulfonate esters alone are sufficient cause to assume that the diastereomers of 1-*d* were obtained with high isomeric purity by using the inverse-addition technique.

Radical Reaction Conditions and Product Analysis. The reactions of 1 and 1-*d* were carried out in bromotrichloromethane solvent with 10–15 mol % of benzoyl peroxide relative to the tin compound. A number of procedures were tested to effect quantitative separation of olefins and other low-boiling products in unchanged form. If the olefins are not swept rapidly from the reaction vessel, radical chain addition of $BrCCl_3$ to the olefins occurs, along with isomerization caused by reversible addition of trimethylstannyl radical. The following procedure was found to be effective and highly reproducible in eliminating these possible complications. The solution was heated under reflux with a pot temperature of 94–96 °C (540 torr) in a round-bottom flask equipped with a fractionating column and condenser attached in series to a cold trap (liquid N_2) so that the solvent slowly distilled from the reaction vessel, efficiently sweeping low-boiling products out of the reaction mixture.

In Table II are given the product yields and the amount of unreacted starting material for a typical experiment. The high yield of chloroform indicates that the trichloromethyl radical is the primary hydrogen-atom abstractor,

(12) N. T. Nelson, unpublished results.

Table III. Bond Energies Used To Estimate Reaction Enthalpies

bond	D(X-Y), kcal/mol	ref
Br-phenyl	80	16
Br-CCl_3	50-56	13
H-CCl_3	96	16
Br-$SnMe_3$	76	14
H-C(CH_3)(C_2H_5)($SnMe_3$)	92.5[a]	7, 16
Me_3Sn-CH(CH_3)(C_2H_5)	50[b]	14
CH_3CH=$CHCH_3$	60[c]	15

[a] 94.5 kcal/mol (secondary C-H) − ~2 kcal/mol[6] (conjugative weakening) = 92.5 kcal/mol. [b] D(Sn-C) for Me_3Sn-Et used, and large uncertainties are present. [c] Total energy of the π bond, including hybridization changes in σ bonds as estimated for ethylene.

Scheme II

$$Bz_2O_2 \rightarrow PhCO_2\cdot \rightarrow Ph\cdot + CO_2 + \text{other products} \quad (3)$$

$$Ph\cdot + BrCCl_3 \rightarrow PhBr + \cdot CCl_3 \quad (4)$$
$$\Delta H = -30 \text{ to } -24 \text{ kcal/mol}$$

$$\cdot CCl_3 + Me_3SnCH(CH_3)CH_2CH_3 \rightarrow HCCl_3 + \text{olefin} + \cdot SnMe_3 \quad (5)$$
$$\Delta H \approx -20 \text{ kcal/mol}$$

$$Me_3Sn\cdot + BrCCl_3 \rightarrow Me_3SnBr + \cdot CCl_3 \quad (6)$$
$$\Delta H = -26 \text{ to } -20 \text{ kcal/mol}$$

$$\cdot CCl_3 + Me_3Sn\text{-}\langle\rangle\text{-}H \rightarrow Me_3Sn\text{-}\langle\rangle\text{-}\cdot + HCCl_3 \quad (7)$$
$$\Delta H \approx -5 \text{ kcal/mol}$$

$$Me_3Sn\text{-}\langle\rangle\text{-}\cdot + BrCCl_3 \rightarrow Me_3Sn\text{-}\underset{2}{\langle\rangle}\text{-}Br + \cdot CCl_3 \quad (8)$$
$$\Delta H = -13 \text{ to } -8 \text{ kcal/mol}$$

and the yield of bromobenzene is close to previously reported[17] yields for the decomposition of benzoyl peroxide in bromotrichloromethane. Although the trimethylstannyl radical could act as a hydrogen abstractor, the unfavorable energetics [D(Sn-H) ≈ 35 kcal/mol[14]] coupled with an expected high efficiency of trapping by the solvent make this possibility unlikely. These results along with simple comparisons of bond energies (Table III) suggest a reasonable chain reaction for the decomposition of the 2-butyltin compounds, as shown in Scheme II. Energetically, the reaction of phenyl radicals with the tin compounds as hydrogen abstractors would be favorable, but the reaction with solvent is also favorable, and the large excess of solvent suggests that the scavenging of phenyl radicals by bromotrichloromethane is the principle initial reaction (eq 4).

The substantial yield of 2 which results from reactions 7 and 8 is not unexpected when the reactivity of a tertiary C–H bond toward radical abstraction is considered. Krusic and Kochi have concluded that C–H bonds α to tin are weakened considerably,[6a] since treatment of neopentane with *tert*-butoxy radicals gives a very weak ESR signal due to the neopentyl radical, whereas treatment of tetramethyltin gives an easily detected signal for $Me_3SnCH_2\cdot$. However, this weakening may be of relatively little im-

(13) T. L. Cottrell, "The Strengths of Chemical Bonds", Butterworths, London, 1958, p 207.
(14) W. P. Neumann, "The Organic Chemistry of Tin", Wiley-Interscience, New York, 1970, p 9.
(15) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).
(16) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, 1968.
(17) D. H. Hey and R. Tewfik, *J. Chem. Soc.*, 2402 (1965).

Table IV. Composition and Deuterium Content of Isomeric Butenes Formed from the Decomposition of Trimethyltin Compounds

compd	% 1-butene (% d_1)	% *trans*-2-butene (% d_1)	% *cis*-2-butene (% d_1)	cis/trans
2-(trimethylstannyl)butane[a]	9.5 ± 0.2	57.8 ± 0.8	32.7 ± 0.4	0.566 ± 0.015
erythro-(3-deuterio-2-butyl)trimethyltin[b]	17.6 ± 0.4 (96.6 ± 0.8)	37.4 ± 0.2 (51.9 ± 1.6)	45.0 ± 0.3 (88.7 ± 1.3)	1.20 ± 0.02
threo-(3-deuterio-2-butyl)trimethyltin[c]	13.8 ± 0.2 (99.2 ± 0.8)	67.5 ± 0.3 (93.9 ± 0.8)	18.7 ± 0.3 (63.2 ± 1.5)	0.277 ± 0.006

[a] Averaged from four experiments. [b] Averaged from three experiments. [c] Averaged from two experiments.

Table V. Relative Rates of Formation (k_{rel}) of Olefins in the Radical-Induced Elimination of Trimethyltin Compounds[a]

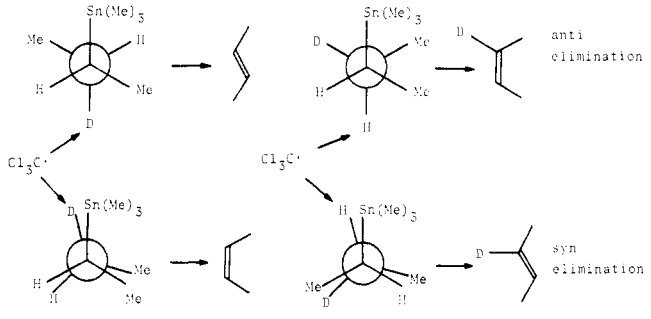
compd					
2-(trimethylstannyl)butane	1.00 ± 0.02	6.08 ± 0.15	3.44 ± 0.08		
erythro-3-deuterio-2-(trimethylstannyl)butane	1.00 ± 0.03	0.85 ± 0.13	0.18 ± 0.08	1.14 ± 0.04	2.35 ± 0.05
threo-3-deuterio-2-(trimethylstannyl)butane	1.00 ± 0.02	0.26 ± 0.04	0.48 ± 0.04	4.63 ± 0.03	0.86 ± 0.04

[a] Corrected for percentage deuterium enrichment in *erythro*- and *threo*-1-*d*.

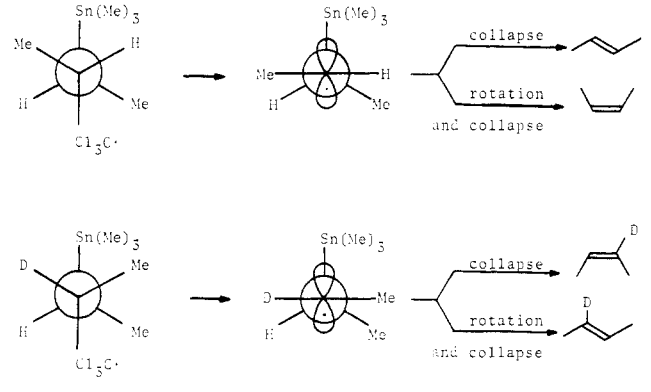
portance for the already weaker tertiary C–H bond of 1, and indeed the ratio of α to β abstraction observed, 46:26 (2:total butene), is considerably smaller than might be expected from normal tertiary vs. secondary + primary reactivities. Thus, stabilization of the transition state for abstraction of the β hydrogens must occur to a greater extent than for the α hydrogen. Stabilization of the α radical can occur by p–d conjugation and by hyperconjugation with the Sn–Me bond which puts unpaired electron density on the methyl carbon, but stabilization for the β radical can occur by p–d homoconjugation and hyperconjugation with the Sn–C bond, placing unpaired electron density on the tin. Kochi interpreted the stabilization of a radical β to tin as a combination of hyperconjugation and p–d homoconjugation of comparable magnitudes and effects[7] but Ingold presented evidence that R_3C and R_3Sn have similar hyperconjugative interactions with β radical centers and argued that any special stabilization from tin must result from p–d homoconjugation.[18] Traylor has shown that hyperconjugation has a pronounced effect on the charge-transfer band of $ArCH_2$–SnR_3 with tetracyanoethylene and on the reactivity of these compounds toward electrophilic aromatic substitution.[19] Since the effect of hyperconjugation is to stabilize a cationic center, Traylor's results suggested that hyperconjugation might be of particular importance in β abstraction by an electrophilic radical such as trichloromethyl.

Distribution of Butenes from Elimination. The butenes were collected by GLC and were identified by mass spectrometry and by comparison of retention times and coinjection with known samples of *cis*- and *trans*-2-butene and 1-butene; quantitative determination of the relative proportions of the butenes was also accomplished by GLC. The isomeric butenes were collected separately by using preparative-scale GLC, allowing the deuterium enrichment of each to be determined by high-resolution mass spectrometry utilizing low ionizing voltage. The deuterium content of the 1-butene gives a convenient internal standard for determining the deuterium incorporation in the starting tin compound. Given in Table IV are the results of the butene analyses. Control experiments were conducted to determine if the 2-butenes were isomerized under the reaction conditions (added *cis*-2-butene-2-*d*, was recovered with 2.4% isomerization) and to

Scheme III



Scheme IV



determine the efficiency of the trapping of the olefin products collected in the cold trap (no olefins were detected in a second cold trap placed in series with the initial trap).

The relative rates of formation of the various butenes can be determined from the product distribution, neglecting the very small concurrent equilibration of olefins. Since the substitution of deuterium at C-3 should have no effect on the reactivity of the C-1 hydrogens, the formation of 1-butene is assumed to be equal for deuterated and nondeuterated 1, and the relative rates of the production of 2-butene can then be calculated and compared between 1, *threo*-1-*d*, and *erythro*-1-*d*.

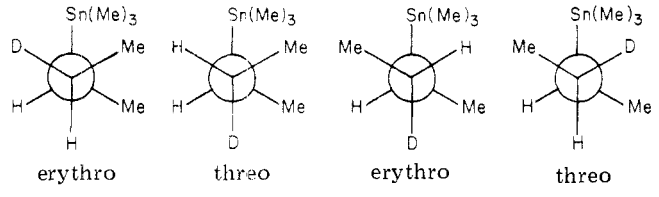
Radical Elimination Reactions. Examination of the data in Tables IV and V shows a strong preference for anti elimination; assuming a primary deuterium isotope effect >1 anti elimination would give cis-rich olefin from *erythro*-1-*d* and trans-rich olefin from *threo*-1-*d*, as the results indicate. However, there is little stereospecificity of the reaction since all possible 2-butenes from both *threo*-

(18) D. Griller and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 6715 (1974).
(19) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Am. Chem. Soc.*, **92**, 7476 (1970).

and *erythro*-1-*d* are found. These facts can be accounted for by two possible mechanisms of elimination: (1) concerted elimination, E_H2, with anti and syn components in competition (Scheme III, illustrated with *erythro*-1-*d*) and (2) anti hydrogen abstraction, giving an intermediate radical, E2ir, with a subsequent partitioning between collapse and rotation about the C-2, C-3 bond followed by collapse (Scheme IV, illustrated with *erythro*-1-*d*).

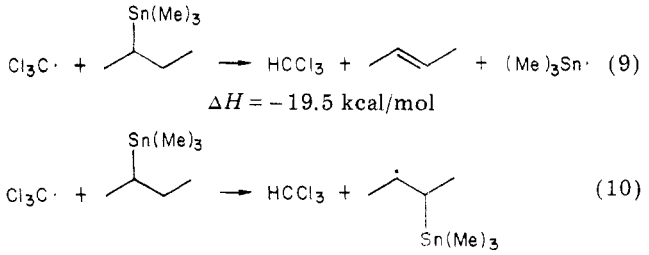
Both mechanisms allow for anchimeric assistance, shown by the strong preference for anti elimination. Also, the reduced primary/secondary hydrogen selectivity shown in the reaction of 1 (k_{sec}/k_{prim} = 15, whereas in alkanes primary/secondary completion by trichloromethyl radical yields[20] k_{sec}/k_{prim} = 33) is in accord with that expected for anchimeric weakening of the bonds. It is reasonable that anchimeric weakening should show a maximum effect for the reaction with the highest activation energy, thus attenuating the selectivity. The E_H2 mechanism has anchimeric assistance as a built-in feature since any amount of double bond character in the transition state would decrease the bond strength to the hydrogen being abstracted. In the $E_H2$ir mechanism the lack of a stabilizing interaction with tin would result in a cis/trans ratio for *threo*- or *erythro*-1-*d* the same as that observed for 1 due to the lack of a preferred conformation for elimination and rapid rotation about the C-2,C-3 bond at room temperature; thus, participation of the tin–carbon σ bond with the developing radical is necessary to rationalize the observed preference for anti elimination.

Deuterium Isotope Effects. Previously, Guard[21] determined a primary deuterium isotope effect of k_H/k_D = 4.5 ± 0.3, assuming no secondary deuterium isotope effect, by comparison of deuterated and nondeuterated olefin from the reaction of a nearly 50:50 mixture of *threo*- and *erythro*-1-*d* where k_H/k_D = total nondeuterated olefin/total deuterated olefin. From our system a similar analysis comparing the rates of production of total deuterated vs. total nondeuterated olefin for *threo*- and *erythro*-1-*d* gives k_H/k_D = 5.1. Another analysis of the data, fitting the rates of product formation to a parametric equation (see eq 12), gives k_H/k_D = 4.75, assuming anti and syn concerted elimination. If elimination with an intermediate radical is assumed, then abstraction from the conformation with trans-staggered methyl groups gives k_H/k_D = 4.7, while abstraction from the methyl gauche form gives k_H/k_D = 5.4. Values of primary deuterium isotope effects in this



methyl gauche forms methyl trans forms

range are normally associated with abstractions close to thermoneutrality which have relatively symmetric transition states. The calculation of a ΔH value for the reaction is complicated by the lack of accurate data for D(Sn–C) for 1, but by using the values in Table III the ΔH's for eq 9 and 10 can be estimated. Ordinarily the ΔH associated with eq 10 would be considered more in line with the isotope effect determined for this reaction, and if eq 9 were operative, a smaller k_H/k_D would be expected on the basis of the large negative ΔH. However, the activation energy



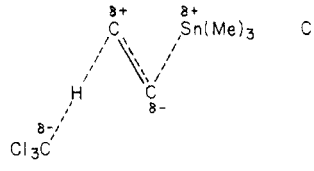
for eq 9 could be larger than expected due to the loss of rotational entropy about the C-2,C-3 bond in the transition state, and thus a larger k_H/k_D would result. Considering the uncertainties involved, the primary deuterium isotope effect does not seem to be clearly diagnostic of eq 9 or eq 10 as the step involving the rate-limiting transition state, although the two-step mechanism is more reasonable.

As stated earlier, the data in Tables II and V indicate a preference for anti elimination, and the fraction of anti elimination which results can be calculated by using eq 11,

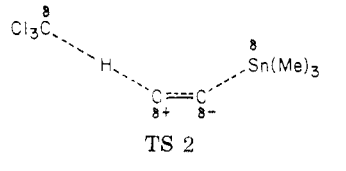
$$N_A = N_S \frac{R_H - R_D k_H/k_D}{R_D - R_H k_H/k_D} \quad (11)$$

where k_H/k_D = the primary deuterium isotope effect, $R_{D(H)}$ = the cis/trans ratio from the deuterium (hydrogen) organotin compound (Table II), N_A = the fraction of anti elimination, and N_S = the fraction of syn elimination (or rotated product from the intermediate radical) = 1 − N_A. Assuming k_H/k_D = 5.1 gives 76% anti elimination from *threo*-1-*d* and 77% from *erythro*-1-*d*. Since the remainder of the products must come from the syn pathway if the concerted E_H2 mechanism is operating, the probability of competing syn and anti pathways will be considered.

The interplay of anti and syn pathways in base-induced β eliminations has been subject to debate recently, but the complex interplay of steric factors, electrostatic interactions, counterion association with the attacking base and leaving group, geometric constraints, and nucleophilic assistance by the attacking base make conclusions from these ionic reactions inapplicable to the results of this study. The electrophilic character and relative sensitivity to polar effects of the trichloromethyl radical lead to consideration of transition states TS 1 and TS 2; consideration of simple electrostatics shows a somewhat more favorable dipolar interaction in TS 2, although the extent of polarization is not known. Steric repulsions would favor



TS 1



TS 2

TS 1 over TS 2, since trichloromethyl radical has a planar configuration, and although there is evidence that the effective steric requirement[22] of trimethylstannyl is somewhat smaller than that of methyl, examination of space-filling molecular models indicates an unfavorable interaction for TS 2. Orbital overlap is possible in both TS 1 and TS 2 if C-2 and C-3 have rehybridized to give sufficient p character in the transition state.

A simple pictorial molecular-orbital argument (Figure 1) shows a preference for antiperiplanar abstraction.

(20) G. A. Russell, *Free Radicals*, 1, 279 (1973).
(21) H. E. Guard, Ph.D. Thesis, University of California, Berkeley, 1969.
(22) (a) D. D. Davis, A. J. Surmajis, and G. L. Robertson, *J. Organomet. Chem.*, **46**, C9 (1972); (b) T. I. Moder, Ph.D. Thesis, University of California Berkeley, 1976.

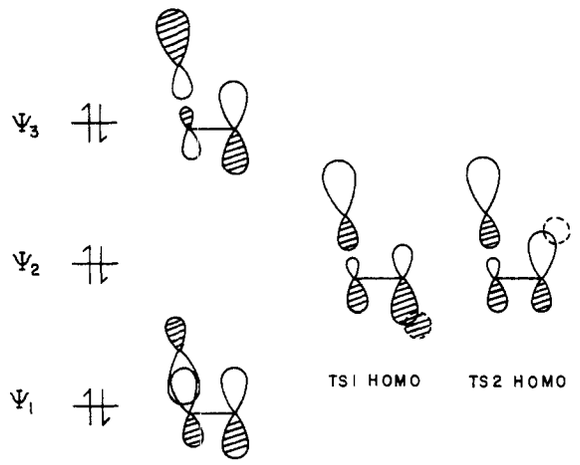


Figure 1. Molecular orbitals for the transition state leading to β elimination.

Table VI. Observed and Calculated Relative Rates of Product Formation from Equation 12[a]

	Anti Pathway			
k_{rel}	E → *t*-*d*	T → *t*-d_1	T → *c*-d_0	E → *c*-d_1
obsd[b]	0.85	4.63	0.48	2.35
calcd	0.90	4.42	0.48	2.34
	Syn Pathway			
k_{rel}	E → *t*-d_1	T → *t*-d_0	T → *c*-d_1	E → *c*-d_0
obsd	1.14	0.25	0.86	0.18
calcd	1.19	0.24	0.88	0.18

[a] E = *erythro*-1-*d*; T = *threo*-1-*d*; *c* = cis; *t* = trans. [b] Observed rates from Table V.

Assuming that the transition state has a highly developed radical character, this can be analyzed as a carbon radical center interacting with a carbon–tin σ bond, which gives rise to a set of molecular orbitals similar to those of an allyl system. The hydrogen being abstracted can be viewed as an additional radical center interacting with the highest occupied molecular orbital (HOMO). Figure 1 shows maximum overlap and minimum antibonding would occur for the anti attack; however, the extent of the antibonding interaction between the tin orbital and the β-carbon π orbital in the HOMO of TS 2 could be small, thus minimizing the preference.

Comparison of Observed and Calculated Rates. The rates of product formation were fitted to a parametric equation[23] of the form shown in eq 12, where $A = k_H/k_D$,

$$dp/dt = aABC \qquad (12)$$

B = the trans/cis preference, C = the anti/syn preference for the cis or trans product, and a = a normalizing constant. The calculated rates in Table VI show good agreement with the observed relative rates. Other solutions for k^{calcd} using eq 12 are possible, but their fits are much inferior to the one presented in Table VI. The parameters in Table VII indicate a preference for trans olefin regardless of pathway and agree with the previously calculated isotope effect and anti elimination preference. Also, the small favoring of the syn → cis pathway could be an expression of the relatively larger relief of steric repulsion in the transition state of this pathway. The foregoing discussion shows the plausibility of the concerted E_H2 mechanism but does not rule out any other possibilities. An additional point is that the same analysis would hold if anti- and synperiplanar elimination to an intermediate radical which then collapses too rapidly for internal rotation to compete was occurring.

Table VII. Parameters Used To Calculate Relative Rates[a]

	trans/cis	anti/syn preference	
k_H/k_D	preference	trans product	cis product
4.91	1.35	3.73	2.66

[a] Normalizing constant a = 0.0179.

Observations of Stabilized Alkyl Radicals. None of the previously investigated free-radical eliminations have required invoking a concerted mechanism to explain the results. Instead, radicals with stabilizing β substituents have been proposed[1,2] or observed via ESR spectroscopy.[6,7] Skell and co-workers[2] have shown that free-radical bromination at C-3 of 2-butyl bromide proceeds by almost exclusive antiperiplanar abstraction of the 3-hydrogen, and a strong anchimeric acceleration of the abstraction rate at C-3 is observed. A bromine-bridged radical is proposed as the intermediate to explain the nearly complete stereospecificity of the reaction (>94%) and the complete scrambling of radioactivity between the 2- and 3-positions in the photobromination of 3-bromopentane-^{82}Br. Similar results were obtained for the bromination of optically active 2-bromo-3-methylpentane.[2]

Kochi was able to observe the ESR spectrum of the β-(trimethylstannyl)ethyl radical at −101 °C. The observation[24] of isomerization of 2-butenes by trimethyltin radical indicates that the incipient 3-(trimethylstannyl)-2-butyl radical has a sufficient lifetime at 10 °C for internal rotation about the C-2,C-3 bond to compete with collapse to olefin and tin radical. Kochi's observation, in β-(trimethylstannyl)ethyl radical, of the preference for the eclipsed conformation using a model with a twofold potential minimum is consistent with this observation if the activation energy for collapse of the radical is not much smaller than ~2 kcal/mol.

If an intermediate radical with restricted internal rotation is present, one would expect relatively more radicals formed with an initial gauche methyl–methyl interaction to rotate to the methyl trans configuration than initial trans would tend to rotate to gauche. Assuming pure initial antiperiplanar attack, the product ratios show this effect, the trans-like radical rotated to the cis-like radical 17 ± 7% for *erythro*-1-*d* and 16 ± 1% for the *threo*-1-*d*, while the cis-like form rotated to the trans-like form 33 ± 2% for *erythro*-1-*d* and 35 ± 6% for *threo*-1-*d*.

Conclusions

The data presented for this free-radical elimination reaction show strong evidence for neighboring-group assistance to β-hydrogen abstraction by the trimethylstannyl group. The preference for anti elimination, lack of complete stereospecificity, primary deuterium isotope effects, and reduced primary vs. secondary vs. tertiary selectivities are best explained by an assisted antiperiplanar abstraction to form an intermediate radical. The proven existence of radicals β to tin, both by hydrogen atom abstraction from stannylalkanes and by addition of trialkylstannyl radicals to olefins, further substantiates this possibility. Steric interaction of the attacking radical and the trimethylstannyl group considered along with the molecular-orbital argument presented indicates the syn pathway is unlikely

(23) A, B, and C were determined by comparison of pairs of rates in which only the desired parameter varies; i.e., the trans/cis preference for syn is determined by T → *t* = d_0/E → *c* = d_0. Small adjustments were then made until the best fit of the observed rates was obtained. The criteria of fit were to minimize $\sum(k_{rel}^{calcd} - k_{rel}^{obsd})/k_{rel}^{obsd}$.

(24) H. G. Kuivila and R. Sommer, *J. Am. Chem. Soc.*, 89, 5616 (1967).

to contribute significantly. Competing rotation about the C-2,C-3 bond prior to collapse of the intermediate radical would explain the lack of stereoselectivity observed. On balance the E_H2ir pathway is the more reasonable choice over the concerted E_H2 pathway for the compounds investigated, but with proper choice of substrate E_H2 may be the preferred course.

An investigation of the radical-induced elimination using a stannane with larger, more hindered alkyl substituent could further elucidate this interesting reaction. (Trineopentylstannyl)butanes would eliminate any possibility of a syn pathway so that the C-2,C-3 rotation or lack thereof in the intermediate could be shown. Alternately, the reaction of 1-(trimethylstannyl)-1,2-dideuterio-3,3-dimethylbutane could provide additional stereochemical information.

The existence of the intermediate β-stannylalkyl radical might be investigated in several ways. Electron spin resonance experiments could be conducted under conditions similar to those of the radical decompositions in this work. Introduction of DBr during the course of the reaction, followed by analysis of deuterium enrichment of recovered starting material, is another possibility.

If the concerted E_H2 reaction is to be demonstrated conclusively, perhaps an even weaker carbon leaving group bond is necessary. The corresponding organolead compounds might be of interest in this regard, but the well-known carbon–lead thermal homolysis would be a complicating factor.

Experimental Section

General Methods. NMR spectra were taken on a Varian Associates T-60 or HA-100 high-resolution spectrometer with analytical determinations by electronic integration. High-resolution IR spectra were obtained on a Perkin-Elmer 421 spectrometer while others were obtained on a Perkin-Elmer 337 grating instrument. Analytical and preparative GLC work was done on a Varian Associates A-90-P3 gas chromatograph equipped with a disk integrator for peak-area determination. Mass spectral analyses were done on a Consolidated Electrodynamics Corp. Model 103 mass spectrometer. Melting points are uncorrected as recorded with a Buchi melting point apparatus. Optical rotations were measured against racemic material or solvent on a Carl Zeiss photoelectric precision polarimeter. Measurements were corrected to the sodium D line by

$$\alpha_{589} = \frac{\alpha_{578}/(\alpha_{546} - a_{578})}{[\alpha_{578}/(\alpha_{546} - \alpha_{578})] + 1.3727}\alpha_{546}$$

Trimethyltin chloride and bromide were obtained from Alfa Chemicals and used without purification. Hexamethylditin was obtained from PCR, Inc., or Alfa Chemicals and distilled before use; bp 75 °C (15 mmHg). Lithium aluminum deuteride was obtained from Stohler Isotope Chemicals; isotopic purity 99%. *p*-Toluenesulfonyl chloride was recrystallized from diethyl ether; mp 67.5–69 °C. *cis*- and *trans*-2,3-epoxybutane were obtained from Farchan Research Labs; GLC showed that each isomer was contaminated with less than 1% of the other. *threo*- and *erythro*-3-deuterio-2-butanols were obtained from the reduction, respectively, of *cis*- and *trans*-2,3-epoxybutanes by the method of Helmkamp, Joel, and Sharman;[25] bp 98–100 °C. Partially resolved (−)-2-butanol was prepared by the stereospecific hydroboration of *cis*-2-butene developed by Brown;[26] $[\alpha]_D$ −8.02° (neat). (*S*)-(+)- and (*R*)-(−)-2-butanol were partially resolved by the method of Kantor and Hauser;[27] $[\alpha]_D$ +11.22° (neat) and $[\alpha]_D$ −4.77° (neat), respectively. *sec*-Butyl tosylates were prepared by the method of Fieser and Fieser[28] using equivalent numbers of moles of alcohol and *p*-toluenesulfonyl chloride and a one molar excess of pyridine with a reaction time of 4 h and temperature of 0 °C. *sec*-Butyl mesylates were prepared by the method of Crossland and Servis.[29] Diethyl ether and THF used for tin anion or Grignard reactions were Mallinckrodt AR grade freshly distilled from lithium aluminum hydride under dry N_2. HMPA was purified by multiple distillation from sodium; bp 60° (0.050 torr). Bromotrichloromethane was obtained from Aldrich or MCB and used without further purification for runs in which only butene product analyses were performed. Bromotrichloromethane used for runs in which total product analysis was done was fractionated from P_2O_5 through a 36-in. tantalum wire spiral column, bp 104 °C, stored under N_2, and passed through activity grade 1 alumina immediately prior to use. All other reagents obtained commercially were used without purification unless otherwise noted. Reactions were protected from air by a positive-pressure dry N_2 atmosphere, and glassware was flamed under flowing N_2 where appropriate.

Preparation of 1 and 1-*d* by the Inverse-Addition Technique. A 250-mL three-necked round-bottomed flask which had a 6-mm stopcock attached to a 24/40 ground-glass inner joint blown to the bottom of the flask was fitted with a Teflon-bladed Trubore stirrer and a dry ice–acetone condenser. The flask was charged with approximately 200 mL of anhydrous liquid ammonia and trimethyltin chloride (28.3 g, 0.142 mol). To this solution was added sodium (6.53 g, 0.284 mol plus a small excess) until the deep red color of possibly tin dianion persisted for about 1 min, after which the solution remained the characteristic green color of tin anions. This solution was added by means of the 6-mm stopcock over about 0.5 h to a magnetically stirred solution of optically active *sec*-butyl tosylate (32.4 g, 0.142 mol), prepared from (−)-2-butanol, $[\alpha]_D$ −7.95° (neat), and 150 mL of diethyl ether in a 500-mL three-necked flask. The solution was stirred for 3 h as the ammonia was allowed to evaporate. Enough water was added to form two homogeneous layers, the layers were separated, and the water layer was washed twice with ether. The ether layers were combined, dried over $MgSO_4$, and then fractionated through a 12-in. gold spinning band column to yield 12 g of crude 2-(trimethylstannyl)butane, bp 47–51 °C (19 torr). To remove any ditin present, we dissolved this crude material in ether and treated it with Br_2 at 0 °C until a yellow color persisted for about 2 min. After removal of the ether, the residue was distilled to give 8.4 g (27% yield) of the desired product, bp 52–55 °C (24 mmHg). For subsequent preparations the product was isolated by preparative GLC on a $^1/_2$-in. × 10-ft column (30% SF-96 on acid-washed Chromosorb P, column temperature 180 °C), giving a product with an NMR spectrum and elemental analyses similar to those of the distillation: ^{1}H NMR (CH_2Cl_2) δ −0.23, −0.22, 0.02, 0.28 (9 H, s and tin-coupled side bands, Me_3Sn), 0.83–1.01 (3 H, t, C-4 Me), 1.13–1.21 (3 H, d, C-1 Me), 1.39–1.75 (3 H, m, CH_2 and methine H); $[\alpha]^{25}_D$ 14.99° (neat). Anal. Calcd for $C_7H_{18}Sn$: C, 38.06; H, 8.21. Found: C, 38.36; H, 8.03.

Preparation of 1 in HMPA/THF or HMPA. To a magnetically stirred solution of hexamethylditin (2.2 g, 0.0067 mol) in 40 mL of HMPA and 25 mL of THF maintained under an argon atmosphere was added potassium (0.55 g, 0.0141 mol) in several small pieces. The solution was stirred vigorously while being maintained at −10 to −20 °C with an external ice/ethanol bath until all the potassium had dissolved and the blue color due to solvated electrons had disappeared, after which the pale green color due to the tin anion remained. (*S*)-(+)-*sec*-Butyl mesylate (2.0 g, 0.0131 mol), which had been prepared from (+)-2-butanol, $[\alpha]_D$ +11.22° (neat), was added by means of a syringe, and the ice/ethanol bath was removed; after 15 min the solution became viscous, and 20 mL of water was added. The mixture was transferred to a separatory funnel with an additional 40 mL of water and extracted with 3 × 27 mL of pentane. The combined pentane extracts were washed with 4 × 50 mL of water and then dried over $MgSO_4$. The solution was fractionated through a 36-in. tantalum spiral column until 10–15 mL of liquid remained in the pot. Compound **1** [0.9 g, 0.004 mol, 31%, $[\alpha]^{25}_D$ −20.04° (neat)] was collected by preparative GLC of the pot residue on a $^1/_2$-in.

(25) G. K. Helmkamp, C. D. Joel, and H. Sharman, *J. Org. Chem.*, **21**, 844 (1956).
(26) H. C. Brown and G. Zwiefel, *J. Am. Chem. Soc.*, **83**, 486 (1961).
(27) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **75**, 1744 (1953).
(28) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley, New York, 1967, Vol. 1.
(29) R. K. Crossland and K. L. Servis, *J. Org. Chem.*, **35**, 3195 (1970).

× 10-ft column (30% SF-96 on acid-washed Chromosorb P). When pure HMPA was used as the reaction solvent, the yield of 1 was 0.95 g [0.0043 mol, 32.8%, $[\alpha]^{25}_{D}$ −20.49°].

Reaction of 1 and 1-*d* with $BrCCl_3$ Initiated by Benzoyl Peroxide to Determine the Stereochemistry of Olefin Formation. A 50-mL three-necked round-bottomed flask was equipped with a thermometer, magnetic stirring bar, and pressure-equalizing addition funnel. To it was attached an 18-in. spiralling tantalum-wire fractionating column wrapped with aluminum foil. A small condenser was attached to the column. The condenser was connected in series first to a 14-in. gas trap, the inlet and outlet of which were equipped with 4-mm stopcocks and a 14/20 ground-glass joint, and then to a regular gas trap which was connected to the vacuum pump. The first gas trap contained a magnetic stirring bar so that liquids being transferred to a smaller container could be stirred. The traps were immersed in methylcyclopentane slurries for the early experiments, and thereafter liquid N_2 was used. After several experiments showed no gases in the second trap, it was omitted.

To the 50-mL flask was added 1 or 1-*d* (2.0 g, 0.009 mol), benzoyl peroxide (0.22 g, 0.000 91 mol), and 25 mL of $BrCCl_3$. The pressure was then lowered to 500–540 mmHg and maintained throughout the reaction. The reaction flask was immersed in an oil bath (~115 °C); after 5 min the pot temperature was 94–96 °C, where it was maintained during the course of the reaction. At this time refluxing commenced, and after 15–20 min all of the column had become wet and distillation and collection of the $BrCCl_3$ in the cooled gas trap began. Over the course of the reaction about 20–25 mL of $BrCCl_3$ was distilled into the trap; by means of the pressure-equalizing funnel 20 mL of $BrCCl_3$ was added to the reaction flask over the course of the reaction in order to maintain a nearly constant amount of $BrCCl_3$.

After 3 h the reaction was stopped by removing the oil bath. The contents of the traps were vacuum transferred to a round-bottomed flask by use of a T-tube (with appropriate ground-glass joints and a three-way stopcock) attached to a low-pressure vacuum line. The relative amounts of the butenes produced were determined by GLC using 80–100-mL injections of this solution on a $^1/_2$-in. × 20-ft column (20% SE-52 on 60/80 mesh acid-washed Chromosorb P at room temperature).

For several experiments the 2-(trimethylstannyl)butane compounds were dissolved in 17.5–20 mL of $BrCCl_3$ in the addition funnel and added to the reaction flask in 5-mL aliquots at 0, 45, 85, and 120 min of reaction time.

Determination of the Percent Deuterium Enrichment in the Butenes Produced from the Decomposition of the 3-Deuterio-2-(trimethylstannyl)butane (1-*d*) Diastereomers. The volatile components of the distillate from the experiments described above were transferred along with 1–2 mL of $BrCCl_3$ into a 10-mL cylindrical flask by freeze–thawing, utilizing the T-tube and vacuum line. This process selectively removed the butenes and a small amount of $BrCCl_3$. Gaseous volumes of 1-butene (7.5 mL), *trans*-2-butene (32.5 mL), and *cis*-2-butene (10 mL) were subjected to the freeze–thaw transfer above, and GLC analysis of the $BrCCl_3$ residue in the initial flask showed the complete absence of any butenes. The three isomeric butenes were collected by preparative GLC on the $^1/_4$-in. × 20-ft column (20% SE-52 on 60/80 mesh acid-washed Chromosorb P at room temperature); glass wool was inserted into the collection tube for more surface area. The collection tube was protected from atmospheric moisture with a $CaCl_2$ drying tube as it was immersed in a dry ice–isopropyl alcohol bath at −78 °C. The separated butenes were submitted for mass spectral analysis at low ionizing voltage. Examination and tabulation of the P − 1, P, and P + 1 relative peak heights for each butene allowed the height percentage of the P − 1 and P + 1 peaks to be calculated with respect to the parent peak. This analysis was conducted for the butene products of the decomposition of 1 since this allows a correction for natural abundance and deuterium enrichment in the product butenes of nonenriched starting material. These percentage results are tabulated in Table VIII and are the average of six scans.

Utilizing these percentages, we determined the percent deuterium enrichment of the three butene isomers obtained in the elimination reaction of the diastereomers. From the percentages in Table VII, two simultaneous equations for each isomer were written in which it was recognized that both natural-abundance and deuterium-enriched alkene contribute to the total peak units of P_{56} and P_{57} for a particular butene isomer. After summation of peak-height units for P_{56} and P_{57} for a particular butene isomer produced from the elimination of one of the diastereomers, these units were substituted into the formulas, and the percent deuterium enrichment for the alkene was calculated. For example, the simultaneous equations for 1-butene are $\text{units}_{56} = X + 0.016Y$ and $\text{units}_{57} = Y + 0.048X$ (X = units of naturally occurring 1-butene and Y = units of deuterium-enriched 1-butene).

Table VIII. Peak-Height Percentages of P − 1 and P + 1 with Respect to the Parent Peak (P_{56}) of the Isomeric Butenes from the Elimination Reaction of 2-(Trimethylstannyl)butane

	m/e 55	*m/e* 56	*m/e* 57
1-butene	1.6 ± 0.5	100	4.8 ± 0.4
trans-2-butene	0.9 ± 0.1	100	4.6 ± 0.2
cis-2-butene	1.1 ± 0.1	100	4.5 ± 0.25

Determination of the Amount of Isomerization of *cis*-2-Butene to *trans*-2-Butene under the Reaction Conditions for the Decomposition of 1. With the experimental apparatus described above, a mixture of 1 (2.0 g, 0.0091 mol) and benzoyl peroxide (0.22 g, 0.000 91 mol) in 25 mL of $BrCCl_3$ was heated to 95 °C at reduced pressure for 3 h. To this solution over the course of the reaction was added approximately 0.09 g of *cis*-2-butene which had 63.7% monodeuterium enrichment. The butane as a gas was added through a syringe needle below the surface of the liquid. The syringe needle was attached to the flask by means of a rubber septum. When the process was completed, the butenes in the distilled liquid were analyzed in the previously described manner by GLC and mass spectral methods. The butene yields were as follows: 1-butene, 6.8%; *trans*-2-butene, 35.3%; *cis*-2-butene, 57.9%. The relative units of P_{56} and P_{57} for *trans*-2-butene were P_{56} − 5657 and P_{57} − 368 and for *cis*-2-butene were P_{56} − 7675 and P_{57} − 5595. From these results were calculated the monodeuterium enrichment of *trans*-2-butene (1.9% d_1) and *cis*-2-butene (40.7% d_1). From these percentages the amount of isomerization was calculated to be 2.4%.

Total Product Determination of Reaction of 1 with $BrCCl_3$ Initiated by Benzoyl Peroxide. To a 100-mL round-bottomed flask was added 1 (2.14 g, 0.00 969 mol), benzoyl peroxide (0.37 g, 0.00153 mol), and $BrCCl_3$ (20.85 g, 0.105 mol). The flask was then attached to a 12-in. platinum spinning band column which had been flushed with flowing dry N_2. The receiver was a 14-in. gas trap immersed in liquid N_2 and attached to a vacuum line. The pressure was lowered to 540 mmHg and the flask was immersed in a thermostated oil bath (110–115 °C). The column was heated to 75 °C by an external heating coil, and after 10 min the entire column was wet. The band drive was brought up to speed, and after 5 min reflux commenced. The oil bath temperature was lowered to 105 °C, and the reflux value was adjusted so that 1 drop/min was delivered. The head temperature was initially 70 °C and after 3.5 h had risen to 85 °C at which time the oil bath was allowed to cool slowly to 70 °C while the pressure was slowly reduced to 200 mmHg. After an additional 2 h of distillation with a delivery rate of 1 drop/30 s, the oil bath was removed; the reaction flask was cooled to −15 °C with an ice/ethanol bath, and the pressure was lowered to 1 mmHg for 15 min. The gas trap was then isolated, and dry N_2 was introduced into the column and reaction flask. *tert*-Butylbenzene (0.3231 g, 0.00241 mol) was introduced for internal standardization, and the pot residue was analyzed by electronic integration of the 100-MHz NMR spectrum of the reaction solution (trimethyltin bromide, 2, and unreacted 1) and by GLC on a 4-mm × 10-ft Pyrex column with 20% SF-96 on 110/120 mesh Anakrom SD, column temperature of 135 °C, flow rate of He of 120 mL/min, with a Pyrex insert in the injection port (bromobenzene and hexachloroethane). The volatile fraction was transferred by a T-tube on a low-pressure vacuum line into a 6-mL bulb to which was blown a 2-mm glass stopcock attached to a 14/35 outer ground-glass joint and a 2-mm glass stopcock attached to a 0.5-in. glass tube which was fitted with a serum stopper. Pentane (0.2789 g, 3.87 mmol) was added to the bulb along with sufficient heptane to fill most of the dead volume of the bulb. The bulb was maintained at 0 °C, and 20–40-mL aliquots were removed through the serum stopper and stopcock

with a 50-mL syringe for GLC analysis on the 20-ft SE-52 column at room temperature for the low-boiling fraction (butenes and methyl bromide) and at 108 °C for chloroform. A small amount (<1%) of the low-boiling fraction and chloroform were also detected in the reaction solution. All compounds except **2** were identified by retention-time comparison and coinjection with known samples. Response factors for all compounds except the butenes were determined by injection of standard solutions containing *tert*-butylbenzene. Following detection of **2** by GLC and NMR, it was isolated by preparative GLC on a $^3/_8$-in. × 10-ft Pyrex column with 15% SE-52 on acid-washed and DMCS-treated 60/80 Chromosorb P at 135 °C with a Pyrex insert in the injection port. ^{1}H NMR (CH_2Cl_2) δ 0.13, -0.12, 0.14, 0.40, 0.41 (9 H, s and tin-coupled side bands, Me_3Sn), 0.9-1.06 (3 H, t, C-4 Me), 1.59, 1.60, 1.84, 2.09, 2.10 (3 H, s and tin-coupled side bands, C-1 Me), 1.87-2.10 (2 H, q, CH_2). Anal. Calcd for $C_7H_{17}SnBr$: C, 28.04; H, 5.72; Br, 26.65. Found: C, 28.1; H, 6.1; Br, 26.5. The results of the GLC and NMR analyses of this reaction are in Table IV.

Attempted Thermal Decomposition of 2 in $BrCCl_3$. A sample of **2** (0.339 g, 0.001 13 mol) was dissolved in 4 mL of $BrCCl_3$, and *tert*-butylbenzene (0.0472 g, 0.000 351 mol) was added. This solution was placed in the apparatus used for the total product analysis for the decomposition of **1** and heated to 95 °C (540 mmHg) for 3 h during which time approximately 1 mL of $BrCCl_3$ distilled into the gas trap. Analysis of the volatile fraction by GLC indicated no butenes were present. Comparison of **2** to *tert*-butylbenzene by NMR integration before and after the heating period showed a 15% decrease in **2**, but no trimethyltin bromide was detected.

In an independent experiment 1.5 mL of the pot fraction from the total analysis reaction containing approximately 0.000 71 mol of **2** was placed with 1 mL of $BrCCl_3$ in the reaction apparatus. The solution was heated to 95 °C (520 mmHg) for 3 h during which time approximately 1 mL of $BrCCl_3$ distilled into the gas trap. Comparison of **2** to *tert*-butylbenzene by NMR integration before and after the heating period showed a 4% loss of **2** and a corresponding increase in trimethyltin bromide.

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Registry No. **1**, 15095-79-1; *erythro*-**1**-*d*, 71195-42-1; *threo*-**1**-*d*, 71195-43-2; **2**, 71195-44-3; $(Me)_3SnNa$, 16643-09-7; $(Me)_3SnK$, 38423-82-4; 1-butene, 106-98-9; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1; methyl bromide, 74-83-9; chloroform, 67-66-3; benzene, 71-43-2; trimethyltin bromide, 1066-44-0; bromobenzene, 108-86-1; hexachloroethane, 67-72-1; *p*-toluenesulfonyl chloride, 98-59-9; *threo*-3-deuterio-2-butanol, 10277-60-8; *erythro*-3-deuterio-2-butanol, 10277-59-5; trimethyltin chloride, 1066-45-1; (-)-*sec*-butyl tosylate, 61530-30-1; hexamethylditin, 661-69-8; (*S*)-(+)-*sec*-butyl mesylate, 50599-13-8; $BrCCl_3$, 75-62-7.

Thermal Rearrangement of Alkynyl Three-Membered Rings. Evidence for an Oxacycloheptatriene Intermediate[1]

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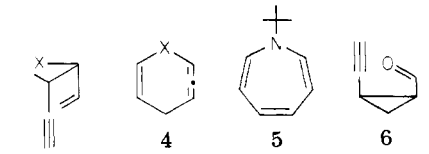
The substituted ethynylvinyloxiranes **9a-e** were obtained by condensation of vinylsulfonium ylides with acetylenic carbonyl compounds. Thermolysis of the cis isomers of **9** was investigated in both the gas phase and the liquid phase. The first procedure afforded only cyclopropanecarboxaldehydes **17a-e**, the stereochemistry of which depended on the nature and position of the substituents and on the experimental conditions. In the liquid phase **9a-e** rearranged to yield, besides **17a-e**, dihydrooxepins **20** and **21c-e** or phenol **19a**, these products also being obtained from **17a-e**. Moreover, thermolysis of **21c,d** led to the corresponding phenols **19c,d**. Compounds **19** are believed to arise from arene oxides in equilibrium with substituted oxepin intermediates. All these findings are consistent with the initial formation of an oxacycloheptatriene (**22**) by a Cope reaction from **9** or a retro-Claisen reaction from **17**. The observed stereoselectivity of the reaction is explicable in terms of conformational preferences.

During the last few years, several authors have reported the thermal isomerization of ethynyl vinyl three-membered rings. In every case the isolated products strongly suggested the intermediacy of the highly reactive heptacyclic compound **4** (Scheme I). Thus, Dolbier and co-workers[2] obtained a dimer arising from cycloheptatriene **4** (X = CH_2). Manisse and Chuche[3] prepared *N*-*tert*-butylazepine (**5**) by thermal isomerization of *N*-*tert*-butylaziridine (**2**) and also *cis*-2-ethynyl-1-formylcyclopropane (**6**) from *cis*-2-ethynyl-3-vinyloxirane (**3**).

This last molecular rearrangement (**3** → **6**) seemed of interest to us, from both mechanistic and synthetic viewpoints: (i) the formation of a heptacyclic intermediate (X = O) has not heretofore been experimentally proved; (ii) a [1,3] hydrogen shift similar to that affording **5** (X = *N*-*t*-Bu), not yet observed from **4** (X = O), should give oxepins which are valence isomers of arene oxides; (iii) compounds **6**, which can be used as starting material in natural product synthesis,[4] are not readily available by other methods.

Scheme I



4 5 6

1, X = CH_2
2, X = N+
3, X = O

A general study of the thermal isomerization of variously substituted epoxides **3** was undertaken to obtain further information about the proposed mechanism and to test the

(1) Preliminary accounts of this work may be found in *Tetrahedron Lett.*, 283 (1978), and *J. Chem. Soc., Chem. Commun.*, 584 (1979).
(2) W. R. Dolbier, O. T. Garza, and B. H. Al Sader, *J. Am. Chem. Soc.*, **97**, 5038 (1975).
(3) N. Manisse and J. Chuche, *Tetrahedron*, **33**, 2399 (1977); *J. Am. Chem. Soc.*, **99**, 1272 (1977).
(4) Experiments in progress.

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