Free-Radical Reduction and Dehalogenation of Vicinal Dihalides by Tri-*n*-butyltin Hydride

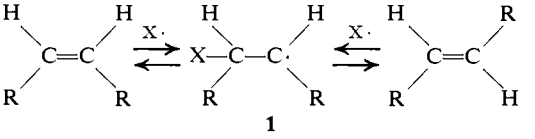
Richard J. Strunk, Peter M. DiGiacomo, Kasuhiro Aso, and Henry G. Kuivila

Contribution from the Department of Chemistry, State University of New York at Albany, Albany, New York 12203.
Received August 16, 1969

Abstract: The reaction of *dl*- and *meso*-2,3-dibromobutanes with tri-*n*-butyltin hydride gives 2-butenes as major products by a free-radical chain-debromination reaction in which *anti* elimination predominates. The stereospecificity increases with increased organotin hydride concentration and with decreasing temperature. The isomeric 2,3-dichlorobutanes give simple reduction as the major reaction with tri-*n*-butyltin hydride, and the same proportions of *cis*- and *trans*-butenes are formed from each isomeric chloride. 1,2-Dibromo-1-deuteriohexane gives preferred *anti* elimination, but the 2,3-dibromosuccinates and 1,2-dibromo-1,2-dichloroethanes give nonspecific debrominations. 1-Bromo-1-phenyl-2-chloroethane reacts more slowly with tri-*n*-butyltin radicals than does 1,2-dibromo-1-diphenylethane; *erythro*-2-bromo-3-chlorobutane reacts more slowly than does *meso*-2,3-dibromobutane. These results are consistent with a reaction scheme involving open and halogen-bridged free-radical intermediates. The bridged radicals are destabilized by chlorine and by carbethoxy groups in the α positions.

An investigation of the scope of the reaction of alkyl halides with organotin hydrides has revealed that geminal polyhalides undergo stepwise reduction to alkanes.[1] On the other hand, propylene and *meso*-stilbene dibromides do not undergo normal reduction to hydrocarbon upon reaction with tri-*n*-butyltin hydride.[1b] The major products of the reaction of 1 mol of the vicinal dibromide with 2 mol of the hydride were hydrogen, olefin, and tri-*n*-butyltin bromide. Since it had been demonstrated that the reduction of simple alkyl halides with organotin hydrides proceeds by a free radical chain mechanism,[2] it was of interest to determine some characteristics of this elimination, which might also be a free-radical process.

Ionic eliminations have been extensively studied and results have been reviewed.[3-5] Free-radical eliminations have received far less systematic investigation as shown in a recent summary by Kampmeier and coworkers.[6] Such processes are generally regarded as involving formation of free radicals from which β substituents can be lost, in turn, as free radicals. This is tantamount to reversibility in the first step of a free-radical addition to an olefin, a process which can be conveniently used as a means for isomerization of olefins, eq 1. Halogen atoms,[7,8] thiyl radicals,[9,10] and organotin radicals[11] can function as X· in eq 1. The intermediate radical **1** may be formed from a saturated molecule by hydrogen abstraction as in the photochlorination of bromocyclopentane,[12] by the reaction



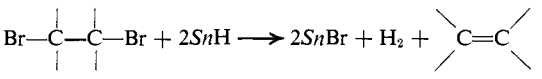
(1)

1

of dithioketals with *t*-butoxy radicals[13] and by the reaction of *t*-butyl sulfide with phenyl radicals.[14] It may also be formed by halogen abstraction as in the reaction of sodium in liquid ammonia with 2,3-dibromobutanes[15] and in the reaction of a variety of β-substituted halides with chromous chloride.[14,16] It may further be formed by free-radical attack at a double bond as in the reaction of carbon tetrachloride with β-pinene[17,18] and of bromotrichloromethane with vinylcyclopropanes.[19] In these cases ring-opened adducts are formed.

Results and Discussion

Course of Reaction. In the course of exploratory studies on the reductions of various alkyl halides with organotin hydrides we isolated 0.85 mol of *trans*-stilbene from the reaction of 1 mol of *meso*-stilbene dibromide with 2 mol of tri-*n*-butyltin hydride at about 100°. Hydrogen was evolved and 0.965 mol was collected in a similar experiment. Similar results were observed with 1,2-dibromopropane and 2,3-dibromobutanes. If only 1 mol of hydride was used about half of the dibromide remained unreacted. These results suggested a reaction with the stoichiometry represented by eq 2,



(2)

(1) (a) H. G. Kuivila and L. W. Menapace, *J. Org. Chem.*, **28**, 2165 (1963); (b) H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 47 (1964).
(2) L. W. Menapace and H. G. Kuivila, *J. Amer. Chem. Soc.*, **86**, 3047 (1964).
(3) D. V. Banthorpe, "Elimination Reactions," Elsevier Publishing Co., New York, N. Y., 1963.
(4) J. F. Bunnett, *Angew. Chem.*, **74**, 731 (1962).
(5) C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).
(6) J. A. Kampmeier, R. P. Geer, A. J. Meskin, and R. M. D'Silva, *J. Amer. Chem. Soc.*, **88**, 1257 (1966).
(7) R. M. Noyes, R. G. Dickenson, and V. Schomaker, *ibid.*, **67**, 1319 (1945).
(8) H. Steinmetz and R. M. Noyes, *ibid.*, **74**, 4141 (1952).
(9) C. Walling and W. Helmreich, *ibid.*, **81**, 1144 (1959).
(10) C. Sivertz, *J. Phys. Chem.*, **63**, 34 (1959).
(11) H. G. Kuivila and R. Sommer, *J. Amer. Chem. Soc.*, **89**, 5616 (1967).
(12) G. A. Russell and A. Ito, *ibid.*, **85**, 2983 (1963).
(13) A. B. Terent'ev and R. G. Petrova, *Bull. Acad. Sci., USSR Div. Chem. Sci. (Engl. Trans.)*, 1984 (1963).
(14) (a) J. K. Kochi and D. M. Singleton, *J. Amer. Chem. Soc.*, **90**, 1582 (1968); (b) J. K. Kochi, D. M. Singleton, and L. J. Andrews, *Tetrahedron*, **24**, 3503 (1968).
(15) W. M. Schubert, B. A. Rabinovitch, N. R. Larson, and V. A. Sims, *J. Amer. Chem. Soc.*, **74**, 4590 (1952).
(16) W. C. Kray, Jr., and C. E. Castro, *ibid.*, **86**, 4603 (1964).
(17) D. M. Oldroyd, G. S. Fisher, and L. A. Goldblatt, *ibid.*, **72**, 2407 (1950).
(18) G. Dupont, R. Dulous, and G. Clement, *Compt. Rend.*, **236**, 2512 (1953).
(19) E. S. Huyser and L. R. Munson, *J. Org. Chem.*, **30**, 1437 (1965).

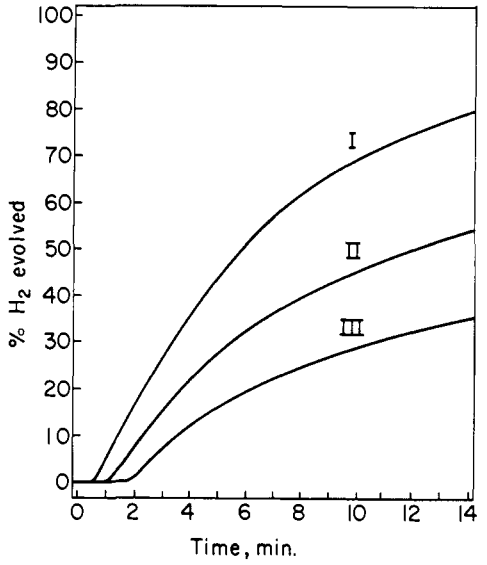
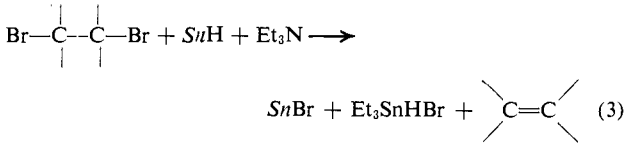


Figure 1. Inhibition of the reaction between *meso*-2,3-dibromobutane and tri-*n*-butyltin hydride: I, no inhibitor; II, 0.35 mol % galvinoxyl; III, 0.73 mol % galvinoxyl.

(*Sn* = R_3Sn). The origin of the hydrogen was established when it was observed that conducting the reaction in the presence of triethylamine prevented its formation; triethylamine hydrobromide was formed[20] and the stoichiometry became that of eq 3.



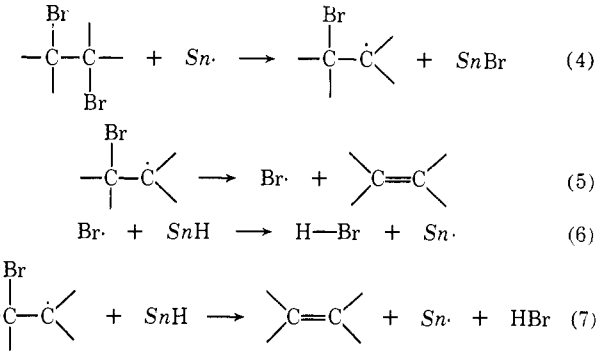
(3)

Thus, it follows that hydrogen bromide is a primary reaction product which then reacts with organotin hydride to form hydrogen and organotin bromide. As shown below, careful examination of the products from 2,3-dibromobutane showed that small amounts of butane were also formed.

When 2,3-dichlorobutane was allowed to react with 2 mol of tri-*n*-butyltin hydride the product contained over 95% of butane and less than 5% of 2-butenes. If 1 mol of hydride was used 2-chlorobutane was formed in high yield. Furthermore, 2-bromo-3-chlorobutane and 1-bromo-1-phenyl-2-chlorobutane reacted virtually quantitatively with 1 mol of hydride to form 2-chlorobutane and 1-chloro-2-phenylethane, respectively. Thus, reduction and elimination may occur, their proportions depending on the nature of the dihalide used.

An extension of the free radical chain mechanism formulated earlier for the reduction of halides,[2] as shown in eq 4–7, was used as a working hypothesis. In this scheme the radical formed in eq 4 may abstract hydrogen from organotin hydride to form simple reduction product. It may lose a bromine atom to form olefin by fragmentation as in eq 5 or by bimolecular reaction with hydride as in eq 7. Hydrogen bromide is formed directly in reaction 7 or by reaction of bromine atoms with hydride in reaction 6. Confirmation of the free radical chain character of the reaction was obtained through the observations that the 2,3-dibromo-

(20) A control experiment showed that the dibromide did not react with triethylamine under these conditions.



(4)

(5)

$Br\cdot + SnH \longrightarrow H{-}Br + Sn\cdot$ (6)

(7)

butanes did not react thermally with tri-*n*-butyltin hydride at −78°, but did react at this temperature upon irradiation with a mercury vapor lamp. Further confirmation came from experiments on the reaction between tri-*n*-butyltin hydride and *meso*-2,3-dibromobutane in the presence of galvinoxyl. It can be seen from Figure 1 that addition of this free radical in small amounts extended the induction period of the reaction. When the reactions began the galvinoxyl color persisted for some time. This is undoubtedly a major cause of the retardation observed after the elimination reaction began.

Stereochemistry of Elimination. Preliminary experiments indicated partial stereospecificity in the elimination reactions of *meso*- and *dl*-2,3-dibromobutanes. Therefore, the effects of some reaction parameters on the degree of stereospecificity were examined, with the results displayed in Tables I and II. Since *meso*-

Table I. Stereochemistry of Debromination of *dl*- and *meso*-2,3-Dibromobutanes

Entry	Dibromide concn[a]	T, °C	% butene-2 from[b,c] *meso* cis	*meso* trans	*dl* cis	*dl* trans
1	Neat	25	10.1	89.9	66.1	33.9
2	Neat	102	28.2	71.8	51.3	48.7
3	1.89 *M* in Et_2O	25	16.0	84.0	59.0	41.0
4	1.89 *M* in Et_2O	−78	8.5	91.5	80.5	19.5

[a] Two moles of tri-*n*-butyltin hydride per mole of dibromide. [b] Results of two or more experiments deviating by 2% or less from mean. [c] Product mixture also contained *n*-butane: (entry, %); 1, <0.8; 2, 6–14; 3, <1.0; 4, <2.7. At higher temperatures traces of a product with the same retention time as 1-butene were also found.

Table II. Effect of Organotin Hydride Concentration on Debromination of 2,3-Dibromobutanes at 25°

Entry	Hydride	(*Sn*H)/(CBr)	% butene-2 from[a,b] *meso* cis	*meso* trans	*dl* cis	*dl* trans
1	Bu_3SnH	1[c]	16.0	84.0	59.0	41.0
2	Bu_3SnH	1	10.1	89.9	66.1	33.9
3	Bu_3SnH	5	10.5	89.5	80.0	20.0
4	Bu_2SnH_2	1	12.0	88.0	74.8	25.2
5	Bu_2SnH_2	5	6.2	93.8	84.7	15.3

[a] Results of two or more experiments deviating by 1% or less from mean. [b] Only traces of butane detected in reaction product mixtures. [c] 1.89 *M* dibromide in Et_2O.

dibromide yields a predominance of *trans*-2-butene and *dl*-dibromide yields a predominance of *cis*-2-butene

a preferred *anti* elimination is revealed. The data in Table I show a pronounced increase in stereospecificity with a decrease in temperature with each dibromide. A decrease in stereospecificity occurs upon dilution of the reaction mixture. The results in Table II show that increased hydride concentration increases the degree of stereospecificity, as does a change from tri-*n*-butyltin hydride to di-*n*-butyltin dihydride. In general, these effects are more pronounced with the *dl*-dibromide than with the *meso* isomer.

Examination of the reactions of the 2,3-dichlorobutanes with 2 mol of tri-*n*-butyltin hydride revealed *n*-butane to be the major product, as shown in Table III, and the isomeric composition of the 2-butene mixture was independent of the configuration of the dichloride and of the degree of dilution of the reaction mixture. The proportion of 2-butene increased with temperature. If 1 mol of hydride was used per mole of dichloride, a high yield of 2-chlorobutane was formed.

Table III. Product Distribution and Stereochemistry in the Reaction of *dl*- and *meso*-2,3-Dichlorobutanes with Tri-*n*-butyltin Hydride[a,b]

Entry	Dichloride	*T*, °C	% 2-butene	*cis*	*trans*
1	*dl*-	22	0.7	23	77
2	*meso*-	22	0.8	17	82
3	*meso*-	65	4.8	25	74
4	*meso*- 1.26 *M* in *m*-xylene	65	3.4	27	72
5	*meso*- 0.38 *M* in *m*-xylene	70	4.5	+29	+71

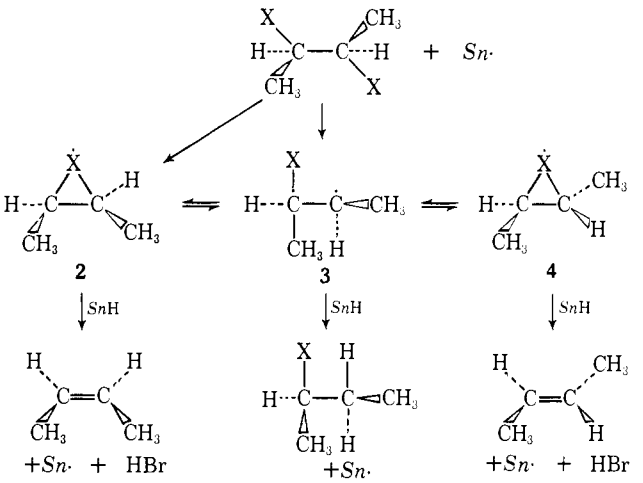
[a] *Sn*H/CCl ratio = 1. [b] Results from two or more experiments deviating 4% or less from mean.

It has been shown[11] that trimethyltin hydride can catalyze the isomerization of 2-butenes, presumably due to reversibility of attack on the olefin by the organotin radical. It was, therefore, of interest to ascertain to what degree the lack of complete stereospecificity in the elimination might be due to isomerization of olefinic products. When *cis*-2-butene was allowed to stand for 20 hr under ambient conditions with tri-*n*-butyltin hydride, 3.2% isomerization to *trans* isomer occurred. It seemed likely that the level of radical concentrations under these conditions would not achieve those attained in the course of the dehalogenation reactions. Therefore, a more meaningful control experiment was performed. This entailed carrying out the reaction of *meso*-2,3-dibromobutane with tri-*n*-butyltin hydride in the presence of *cis*-2-pentene and examining this olefin after the reaction of the hydride was complete. There resulted 11–15% isomerization of the *cis*-2-pentene to the *trans* isomer. Thus it is clear that the actual extent of *anti* elimination is generally greater than that reported for the dibromide in Tables I and II, but less than 100%.

An alternative approach was used with 1,2-dibromo-1-deuteriohexane. An elimination reaction was carried out with the *threo* isomer. Determination of the amounts of the isomeric 1-deuteriohexenes provided a minimum figure for the extent of *anti* elimination. The experiment was repeated with added *cis*-1-deuteriohexene, and the composition of the hexene mixture determined. From the increase in the amount of *trans*-1-deuteriohexene in the product one could compute a maximum figure for the extent of *anti* elimination (see Experimental Section for details).

Mechanism. The results given are consistent with the free radical chain mechanism shown in eq 4–7 except for the need to account for aspects of the stereospecificity of the elimination. This is met by the assumption of three radical intermediates: a simple open radical and two halogen-bridged species for which ample evidence is available in the literature.[14,16,21–28] The elaborated scheme in Chart I is similar to those considered in dehalogenation induced by chromium(II) species.[14,16] Abstraction of a halogen atom from the dihalide may result in formation of a halogen-bridged radical **2** stereospecifically, or an open carbon radical **3**, which can also function as an intermediate in the equilibration of **2** and **4**. When X is bromine, the bridged species is formed preferentially and it can lose a bromine atom by fragmentation, or by reaction with an organotin hydride molecule as shown in Chart I. That the latter process occurs at least to some extent is indicated by the fact that the *anti* stereospecificity increases with hydride concentration. The bridged radical may open up to form **3** which may react with hydride to form monohalide, or close up again to form either **2** or **4** with resultant loss in memory concerning the stereochemistry of the precursor of the first-formed radical. It is assumed here, but not required, that hydrogen of the organotin hydride is transferred preferentially to the atom which bears the highest unpaired electron density.[29] Bridging is much less effective when X is chlorine[21] and the primary reaction path is *via* **3** leading to reduction. The data of Table III indicate no stereospecificity of elimination with the chlorides, suggesting complete equilibration of **2** and **4** before olefin formation occurs.[30,31]

Chart I



(21) P. S. Skell, Special Publication No. 19, The Chemical Society, London, 1964, p 131.
(22) P. S. Skell, R. G. Allen, and N. D. Gilmour, *J. Amer. Chem. Soc.*, **83**, 504 (1961).
(23) P. I. Abell and L. H. Piette, *ibid.*, **84**, 916 (1962).
(24) W. Thaler, *ibid.*, **85**, 2607 (1963).
(25) P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, **85**, 2849 (1963).
(26) P. S. Skell and P. D. Readio, *ibid.*, **86**, 3334 (1964).
(27) P. D. Readio and P. S. Skell, *J. Org. Chem.*, **31**, 753 (1966).
(28) P. S. Skell and R. R. Pavlis, *J. Amer. Chem. Soc.*, **86**, 2956 (1964).
(29) Since the reactions are highly exothermic one would expect that the transition states would resemble reactants.
(30) A reservation concerning this statement stems from the fact that

α Substituents and Stereochemistry. The relative extents of *anti* elimination from *dl*- and *meso*-2,3-dibromobutanes are as expected on the basis of steric effects anticipated in the transition states for bridged radical (**2** or **3**) or product (*cis*- or *trans*-2-butene) formation, respectively. It was of interest to determine the effect of diminishing the nonbonded steric interactions by examining a 1,2-dibromide, specifically *threo*-1,2-dibromo-1-deuteriohexane. The results obtained, shown in Table IV, indicate a degree of *anti* elimination

Table IV. Effect of α Substituents on the Degree of *anti* Debromination by Tri-*n*-butyltin Hydride

Dibromide	% *anti* elimination
$CH_3(CH_2)_3CHBrCHDBr$	>60; <77[a,b]
$CH_3CHBrCHBrCH_3$	>90(*meso*); >66(*dl*)[a,c]
ClCHBrCHClBr	Nonspecific[d]
EtOOCHBrCHBrCOOEt	Nonspecific[d]

[a] Neat reactants, *Sn*H/CBr = 1. [b] 0°. See Experimental Section. [c] 25°. [d] Control experiments showed insignificant isomerization of the olefinic products under the reaction conditions.

similar to that observed with *dl*-2,3-dibromobutane. This suggests that nonbonded interactions between the two methyl groups which are becoming eclipsed in the transition state when the latter compound reacts are not very significant in determining the stereochemistry of elimination.

When the methyl groups of the 2,3-dibromobutanes are replaced by chlorines, nonbonded steric interactions would remain about the same. On the other hand, dipole–dipole interactions are introduced, and the ability of an α-chlorine atom to stabilize a free radical becomes a factor to be reckoned with. To test the resultant of these effects, mixtures of *dl*- and *meso*-1,2-dibromo-1,2-dichloroethanes were debrominated with tri-*n*-butyltin hydride. Both mixtures gave the same proportions of *cis*- and *trans*-1,2-dichloroethylene within the experimental error. No isomerization of *cis*-1,2-dichloroethylene occurred under the conditions of the debromination.

Similar experiments were carried out with the diethyl 2,3-dibromosuccinates. The course of the reaction appeared to be complex in that the product mixture included diethyl succinate as well as diethyl fumarate and maleate. It was shown that diethyl succinate was not the result of stepwise reduction of the dibromo compound: no monobromosuccinate was present in the reaction product mixture; it was shown that the monobromo succinate was reduced to succinate by tri-*n*-butyltin hydride at 0.9 times the rate at which the latter reacted with *dl*-2,3-dibromosuccinate. Thus, if the monobromo compound were an intermediate it should have accumulated to some extent in the course of reaction of the dibromide with organotin hydride. When excess organotin hydride was used, the amount of succinate increased with time after all of the dibromide was consumed. Furthermore, diethyl fumarate was shown to react with the hydride under the dehalogenation conditions to produce succinate. Thus, the latter is an artifact undoubtedly formed by the sequence in eq 8 for which precedents have been reported.[32]

$$\mathrm{EtOOCCH{=}CHCOOEt} + \mathrm{Bu_3SnH} \longrightarrow$$
$$\mathrm{EtOOCCH_2{-}CH{=}C(OSnBu_3)(OEt)} \xrightarrow{\mathrm{Bu_3SnH}} \mathrm{Bu_3SnSnBu_3} +$$
$$\mathrm{EtOOCCH_2{-}CH{=}C(OH)(OEt)} \longrightarrow \mathrm{EtOOCCH_2CH_2COOEt} \quad (8)$$

Examination of the debromination products from the *dl*- and *meso*-2,3-dibromosuccinates showed fumarate to predominate to a large extent in each case. That this was due to lack of stereospecificity in the elimination process was shown by the fact that dimethyl maleate was not isomerized under the conditions of the reactions.

β Substituents and Rates. If formation of a bromine-bridged radical such as **2** is occurring in the transition state for the abstraction of the halogen from the adjacent carbon atom rate acceleration due to anchimeric assistance might be observed. The relative rates of reaction of two pairs of vicinal dihalides with the tri-*n*-butyltin radical were compared by means of competition experiments. When 2-bromo-2-phenyl-1-chloroethane and 2-bromo-2-phenyl-1-bromoethane react with the organotin radical, the benzylic bromine will be abstracted preferentially and the relative rates will measure the effects of bromine *vs.* chlorine in the β position on the rate. Inductive effects should be similar, for the Taft σ* values for CH_2Cl and CH_2Br are 1.05 and 1.00, respectively.[33] Steric effects, when the halogens are in a transoid conformation, should be nearly the same. Thus any difference in rate should provide information concerning differences in anchimeric assistance between bromine and chlorine. The relative rates given in Table V show the dibromide to react

Table V. Effect of β-Substituents on Rates of Reaction of Bromides with Tri-*n*-butyltin Radicals at 25°

Halide	Rel rate
$C_6H_5CHBrCH_2Br$	3.1[a]
$C_6H_5CHBrCH_2Cl$	2.4
meso-$CH_3CHBrCHBrCH_3$	1.6[b]
erythro-$CH_3CHBrCHClCH_3$	1.00
$CH_3CHBrCH_2CH_3$	0.21

[a] Not corrected for statistical factor of two. Only benzylic bromine assumed to be abstracted. [b] Corrected for statistical factor of two.

about 30% faster than the chlorobromide. In the case of the configurationally related 2,3-dihalobutanes the dibromide reacts about 64% faster than the chlorobromide. These figures are in the direction expected for anchimeric assistance, but do not begin to approach the magnitude found in SN1 reactions. (Indeed the

significant isomerization of the olefins can occur during the reaction. However, the most significant difference between the dibromides and dichlorides lies in the nature of the reaction products.

(31) An experiment was carried out between tri-*n*-butyltin deuteride and 2,3-dichlorobutane to ascertain whether any isotope effect which might attend the reaction between intermediate radicals and organotin hydride would alter the course of the overall reaction. The amount of 2-butene formed at 65° was 5%, whether hydride or deuteride was used.

(32) M. Pereyre and J. Valade, *Bull. Soc. Chim. France*, 1928 (1967).

(33) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 619.

polar affect of the β-halogen is greater in the present case as revealed by the fact that 2-bromo-3-chlorobutane reacts 4.8 times faster than 2-bromobutane with the organotin radical.) The small anchimeric effect observed may be related to the relatively low selectivity of organotin radicals in reactions with organic halides. For example, *t*-butyl bromide reacts only seven times faster than *n*-butyl bromide with tri-*n*-butyltin radicals.[2]

It should not be inferred from the mechanistic scheme shown in Chart I that a transoid conformation for the dihalide is a prerequisite for dehalogenation. This is shown by the fact that *endo-cis*-2,3-dibromonorbornane reacted with tri-*n*-butyltin hydride cleanly to form norbornene as the major product; it was accompanied by only a trace of norbornane.

Experimental Section

All experiments employing organotin hydrides were carried out under an atmosphere of either nitrogen or argon. The infrared spectra were obtained with a Perkin-Elmer Model 337 grating infrared spectrometer. Proton magnetic spectra were determined on a Varian Model A-60A nuclear magnetic resonance spectrophotometer. Chemical shifts are given in parts per million downfield from internal tetramethylsilane. Analytical experiments involving gas–liquid partition chromatography were carried out on an F & M Model 5750 or Model 720 gas chromatograph. All melting points are uncorrected.

Materials. Organotin hydrides were prepared by previously described methods.[34,35] Tri-*n*-butyltin deuteride was prepared by the reduction of bis(tri-*n*-butyltin) oxide with lithium aluminum deuteride, SnD: $\nu = 1305\ cm^{-1}$. *meso*- and *dl*-2,3-dibromobutanes were prepared according to the procedure of Young, Dillon, and Lucas.[36] Separation of the 2,3-dihalobutane isomers was carried out on a 15 ft × 0.25 in. column packed with Tide detergent. The *dl* and *meso* isomers of 2,3-dichlorobutane were prepared by the method of Lucas and Gould.[37]

erythro-**2-Bromo-3-chlorobutane** was prepared by a method similar to one developed by Buckles and his coworkers[38] for other vicinal bromochlorides. Into a 250-ml three-necked flask equipped with a dewar condenser, addition funnel, and a gas-inlet tube which extended close to the bottom of the flask and containing 75 ml of chloroform cooled to −40°, was distilled 5.3 g (0.15 mol) of chlorine gas. An equivalent amount of bromine (12 g, 0.15 mol) was added to the magnetically stirred solution. The reaction flask was then irradiated with a 100-W mercury vapor lamp for 5 min. *trans*-2-Butene was added at a temperature below 0° until the reaction mixture became clear. The solvent was removed by distillation. Distillation of the residue afforded the crude product (~70%) and 2,3-dichloro- and 2,3-dibromobutanes. Redistillation of the bromochloro compound afforded relatively pure (96%) material; bp 133–135°. Its infrared spectrum possessed the following characteristic bands: 1176 (s), 1151 (m), 1116 (w), 1071 (m), 1055 (m–s), 1006 (s), 975 (m), 961 (s), 843 (s), 686 (s), 665 (s), and 595 cm^{-1} (s). The product was purified further by glpc on the column described above; $n^{19}D$ 1.4757.

Anal. Calcd for C_4H_8BrCl: C, 28.01; H, 4.70; Br, 46.64; Cl, 20.69. Found: C, 28.14; H, 4.80; Br, 46.48; Cl, 20.69.

The *erythro* configuration was assigned to the compound by comparison of its infrared spectrum with those of *meso*-2,3-dichlorobutane, *meso*-2,3-dibromobutane, *dl*-2,3-dichlorobutane, and *dl*-2,3-dibromobutane in the 1030–950 cm^{-1} region. The bromochloride and the two *meso* isomers have similar absorption bands in this region as shown in Table VI.

1-Bromo-2-chloroethylbenzene. A 250-ml three-necked flask equipped with a mechanical stirrer and a reflux condenser and containing 130 ml of carbon tetrachloride dried over calcium chloride, 13 g (92.6 mmol) of 2-chloroethylbenzene and 23 g (129 mmol) of N-bromosuccinimide was heated to reflux temperature. Benzoyl peroxide (0.5 g) was added and the mixture was irradiated for 3 hr with a 150-W clear incandescent lamp. On cooling, the solid material was filtered and the solvent was removed by evaporation at reduced pressure. Distillation of the residue at reduced pressure afforded 15.1 g, 74%, of crude 1-bromo-2-chloroethylbenzene, bp 72° (2 mm). Redistillation yielded a clear liquid bp 55–56° (0.05 mm), mp 28–29°. The infrared spectrum of the product exhibited strong bands at 1795, 1450, 1141, 935, 765, and 689 cm^{-1}.

Anal. Calcd for C_8H_8BrCl: C, 43.75; H, 3.67; Cl, 16.16; Br, 36.42. Found: C, 43.58; H, 3.84; Cl, 15.96; Br, 36.47.

The infrared spectrum of its hydrolysis product exhibited a broad band from 3120 to 3610 cm^{-1} and no carbonyl absorption. Therefore, the halogen atoms were not geminal. Reduction of the product with tri-*n*-butyltin hydride afforded 2-chloroethylbenzene. The nmr spectrum[38] of the chlorobromide was similar to that of 1,2-dibromoethylbenzene.

endo-cis-**1,2-Dibromonorbornane** was prepared by the hydrogenation of *endo-cis*-5,6-dibromo-2-norbornene over Adam's platinum oxide catalyst according to the procedure of LeBel,[39] mp 58–60°; reported mp 60.5–61.5°. The infrared spectrum gave the bands reported in the literature.

Diethyl *meso*-**2,3-Dibromosuccinate.** Bromine in 5% excess was added to a carbon tetrachloride solution of diethyl fumarate and stirred at room temperature until the bromine color disappeared. The solvent was removed with an aspirator. The product remained as crude crystals. Recrystallization from ethanol–water yielded white crystals: mp 55°, 75% yield; nmr (CCl_4) δ 4.60 (singlet), 4.31 (quartet, J = 7.0 Hz), 1.32 (triplet, J = 7.0 Hz), area ratio, 2:4:6, respectively.

Diethyl *dl*-**2,3-Dibromosuccinate.** The procedure followed was as above except that diethyl maleate was used. The colorless liquid was distilled: bp 120–121° (4 mm); 80% yield; nmr (CCl_4) δ 4.65 (singlet), 4.25 (quartet, J = 7.0 Hz), 1.45 (triplet, J = 7.0 Hz); area ratio, 2:4:6, respectively.

Diethyl 2-Bromosuccinate. Dry hydrogen bromide was bubbled through diethyl maleate, 25 g (0.14 mol), until most of the maleate was converted (glpc, 10% apiezon, 6 ft × 1/8 in.). The mixture was washed with dilute sodium bicarbonate (10% w), taken up in ether, and dried over magnesium sulfate. Distillation gave 28 g (80%) of product: bp 129° (15 mm); nmr (CCl_4) δ 4.57 (doublet of doublets, X part of ABX pattern, J_{AX} = 7 Hz, J_{BX} = 8 Hz, 1 H), 4.21 (quartet, J = 7 Hz), and 4.13 (quartet, J = 7 Hz, 4 H), 3.07 (1/2 ($V_A \leftarrow V_B$), AB part of the ABX pattern, J_{AB} = 17 Hz, 1/2 ($J_{AX} + J_{BX}$) = 7.5, 2 H), 1.25 (triplet, J = 7 Hz), and 1.28 (triplet, J = 7 Hz, 6 H).

threo-**1,2-Dibromohexane-1-*d*.** To 25 ml of acetic acid was added 8.5 g (0.10 mol) of *cis*-1-deuterio-1-hexene[40] followed by 33.0 g (0.105 mol) of pyridinium hydrobromide perbromide.[41] When the red color was virtually gone, the reaction mixture was neutralized with 10% sodium bicarbonate and extracted with ether. The extract was washed with saturated sodium chloride solution, dried over magnesium sulfate, and distilled yielding 19 g (78%) of dibromide: bp 92–94° (12 mm) (lit. 88–90° (15 mm) for 1,2-dibromohexane[42]); nmr (CCl_4) δ 4.14 (multiplet, 1 H), 3.80 (doublet of triplets, $J_{doublet}$ = 4.5 Hz, $J_{triplet}$ = 1.0 Hz, 1 H), 2.0 (multiplet), 1.4 (multiplet), and 0.93 (unsymmetrical triplet, J = 6 Hz, 9 H).

erythro-**1,2-Dibromohexane-1-*d*.** The procedure was the same as above for the *threo* compound except *trans*-1-deuterio-1-hexene[40]

Table VI. Characteristic Infrared Absorption Bands for Vicinal Dihalides between 1030 and 950 cm^{-1}

Dihalide	Absorption bands (cm^{-1})
meso-$CH_3CHClCHClCH_3$	965 (s), 978 (m), 1007 (s)
meso-$CH_3CHBrCHBrCH_3$	958 (s), 973 (m), 1005 (s)
erythro-$CH_3CHBrCHClCH_3$	961 (s), 975 (m), 1006 (s)
dl-$CH_3CHClCHClCH_3$	955 (s), 978 (m), 996 (s), 1020 (m)
dl-$CH_3CHBrCHBrCH_3$	947 (s), 982 (w), 997 (w), 1012 (w)

(34) H. G. Kuivila and O. F. Beumel, Jr., *J. Amer. Chem. Soc.*, **83**, 1246 (1964).
(35) W. J. Considine and J. J. Ventura, *Chem. Ind.* (London), 1683 (1964).
(36) W. G. Young, R. T. Dillon, and H. J. Lucas, *J. Amer. Chem. Soc.*, **51**, 2528 (1929).
(37) H. J. Lucas and C. W. Gould, *ibid.*, **63**, 2541 (1941).
(38) R. E. Buckles, J. L. Forrester, R. L. Burham, and T. W. McGee, *J. Org. Chem.*, **25**, 24 (1960).
(39) N. A. LeBel, *J. Amer. Chem. Soc.*, **82**, 623 (1960).
(40) H. G. Kuivila and R. Sommer, *ibid.*, **89**, 5616 (1967).
(41) L. Fieser and M. Fieser, "Reagents for Organic Synthesis," Reinhold Publishers, New York, N. Y., 1967, p 967.
(42) W. H. Puterbaugh and M. S. Newman, *J. Amer. Chem. Soc.*, **79**, 3469 (1959).

Table VII. A Reduction of 2,3-Dihalobutanes with Organotin Hydrides[a]

Dihalide, mmol	Organotin hydride, mmol	Temp,[b] °C	2-Butene[c] *trans*, %	2-Butene[c] *cis*, %	*n*-Butane, %[d]	Product, %
dl-A (3.78)	Bu_3SnH (7.57)	25	34.3	65.7	0.8	21 (2-butene)[g]
dl-A (3.78)	Bu_3SnH (7.57)	25	33.4	66.6	0.5	16 (2-butene)[g]
dl-A (3.78)	Bu_3SnH (7.57)	102	51.4	48.6	9.0	76 (2-butene)[g,i]
dl-A (3.78)	Bu_3SnH (7.57)	102	51.0	49.0	8.5	83 (2-butene)[g,i]
dl-A (3.78)	Bu_3SnH (7.57)	102	45.5	54.5	14.0	68 (2-butene)[g,i]
dl-A (3.78)	Bu_3SnH (7.57)	102	47.0	53.0	9.5	*f,i*
dl-A (1.89)	Bu_3SnH (18.9)	25	20.0	80.0	Trace	40 (2-butene)[g]
dl-A (3.78) 1.89 *M* in Et_2O	Bu_3SnH (7.57)	25	39	61	Trace	*f*
dl-A (3.78) 1.89 *M* in Et_2O	Bu_3SnH (7.57)	−75[e]	18	82	1.0	90 (hydrogen)[h]
dl-A (3.78) 1.89 *M* in Et_2O	Bu_3SnH (7.57)	−75[e]	21	79	3.0	*f*
dl-A (5.0)	Bu_2SnH_2 (5.0)	25	25.5	74.5	Trace	58 (2-butene)[g]
dl-A (5.0)	Bu_2SnH_2 (5.0)	25	24.9	75.1	Trace	59 (2-butene)[g]
dl-A (5.0)	Bu_2SnH_2 (25.0)	25	15.8	84.2	Trace	30 (2-butene)[g]
dl-A (3.0)	Bu_2SnH_2 (15.0)	25	14.8	85.2	Trace	*f*
meso-A (3.78)	Bu_3SnH (3.78)	Room temp	*f*		*f*	50.6[m]
meso-A (3.78)	Bu_3SnH (7.57)	25	89.8	10.2	Trace	16 (2-butene)[g]
meso-A (3.78)	Bu_3SnH (7.57)	25	90.0	10.0	Trace	53 (2-butene)[g]
meso-A (3.78)	Bu_3SnH (7.57)	102	71.6	28.4	7.6	83 (2-butene)[g,i]
meso-A (3.78)	Bu_3SnH (7.57)	102	72.2	27.8	5.7	77 (2-butene)[g,i]
meso-A (3.78)	Bu_3SnH (7.57)	102	72	28	8.9	89 (2-butene)[g,i]
meso-A (3.78)	Bu_3SnH (7.57)	102	71.4	28.6	14.5	*f,i*
meso-A (1.89)	Bu_3SnH (18.9)	25	90.0	10.0	Trace	30 (2-butene)[g]
meso-A (3.78) 1.89 *M* in Et_2O	Bu_3SnH (7.57)	25	83.7	16.3	*f*	*f*
meso-A (3.78) 1.89 *M* in Et_2O	Bu_3SnH (7.57)	25	84.3	15.7	Trace	*f*
meso-A (3.78) 1.89 *M* in Et_2O	Bu_3SnH (7.57)	−78[e]	92.0	8.0	*f*	*f*
meso-A (3.78) 1.89 *M* in Et_2O	Bu_3SnH (7.57)	−78[e]	91.0	9.0	1.0	*f*
meso-A (3.78) 1.89 *M* in Et_2O	Bu_3SnH (7.57)	−78[e]	96.0	4.0	2.7	31 (2-butene)[g]
meso-A (15.1) 1.5 *M* in *n*-heptane Et_3N (15.1)	Bu_3SnH (30.2)	Room temp	*f*		*f*	81 ($Et_3N \cdot HBr$)[j]
meso-A (5.0)	Bu_2SnH_2 (5.0)	25	87.2	12.8	Trace	50 (2-butene)[g]
meso-A (5.0)	Bu_2SnH_2 (5.0)	25	88.9	11.1	Trace	*f*
meso-A (5.0)	Bu_2SnH_2 (25.0)	25	93.7	6.3	Trace	25.5 (2-butene)[g]
meso-A (3.0)	Bu_2SnH_2 (15.0)	25	94.0	6.0	Trace	*f*
dl-B (3.78)	Bu_3SnH (7.57)	22[e]	79.0	21.0	99.2	*f,i*
dl-B (3.78)	Bu_3SnH (7.57)	22[e]	75.0	25.0	99.4	*f,i*
meso-B (3.78)	Bu_3SnH (7.57)	20[e]	*f*		99	83 (Bu_3SnCl)
meso-B (3.78)	Bu_3SnH (7.57)	22[e]	83	17	99.0	*f,i*
meso-B (3.78)	Bu_3SnH (7.57)	22[e]	82	18	99.3	*f,i*
meso-B (3.78)	Bu_3SnH (7.57)	65[e]	78	22	94.9	41 (hydrocarbon)[i,k]
meso-B (3.78)	Bu_3SnH (7.57)	65[e]	71.3	28.7	95.5	46 (hydrocarbon)[i,k]
meso-B (3.78) 1.26 *M* in *m*-xylene	Bu_3SnH (7.57)	65[e]	75.8	24.2	96.8	26.5 (hydrocarbon)[i,k]
meso-B (3.78) 1.26 *M* in *m*-xylene	Bu_3SnH (7.57)	65[e]	68.4	31.6	96.4	27.7 (hydrocarbon)[i,k]
meso-B (3.78) 0.38 *M* in *m*-xylene	Bu_3SnH (7.57)	70[e]	70	30	95.4	*f,i*
meso-B (3.78) 0.38 *M* in *m*-xylene	Bu_3SnH (7.57)	70[e]	72	28	95.5	*f,i*
meso-B (3.78)	Bu_3SnH (3.78)	22[e]	*f*		*f*	77 (2-chlorobutane)[l]
meso-B (3.78)	Bu_3SnH (3.78)	22[e]	73	27	84	86 (2-chlorobutane)[l]
meso-B (3.78)	Bu_3SnD (7.57)	65[e]	74	26	95.8	44 (hydrocarbon)[i,k]
meso-B (3.78)	Bu_3SnD (7.57)	65[e]	73	27	93.7	*f,i*
meso-B (3.78)	Bu_3SnD (7.57)	65[e]	70	30	95.2	61 (hydrocarbon)[i,k]
erythro-C (7.57)	Bu_3SnH (7.57)	Room temp	*f*		*f*	90 (2-chlorobutane)[l]

[a] Neat, unless otherwise indicated; A = 2,3-dibromobutane, B = 2,3-dichlorobutane, C = 2-bromo-3-chlorobutane. [b] 65 ± 2°, −75 ± 2°, 25 ± 1°, 22 ± 2°. [c] Percentage based on 100% 2-butene. [d] Percentage based on total hydrocarbons. [e] Photocatalyzed reaction run in Pyrex glass tubes. [f] Quantity not determined. [g] Yield of olefin determined by titration with Br_2–HOAc solution. [h] Determined by measuring the volume of hydrogen evolved in a gas buret. [i] A third gaseous product was present which had the same retention time as that of an authentic sample of 1-butene. [j] $Et_3N \cdot HBr$, identified by comparison of its infrared spectrum with that of an authentic sample. [k] Based on the volume of condensed gas. [l] Same retention time as an authentic sample of 2-chlorobutane. [m] Yield = 100 − amount of dibromide left unreacted (49.4), amount of dibromide determined by glpc.

is used. Boiling point is the same as *threo:* nmr (CCl_4) δ 4.16 multiplet (1 H), 3.56 (broad doublet, J = 10 Hz, 1 H), 2.0 (multiplet), 1.4 (multiplet), and 0.93 (unsymmetrical triplet, J = 6 Hz, 9 H).

1,2-Dibromo-1,2-dichloroethane. I. Equimolar amounts of *cis*-1,2-dichloroethylene and bromine were dissolved in carbon tetrachloride. After the disappearance of the red color, the dibromodichloro compound was separated by distillation, bp 70–71° (10 mm). II. A 100% excess of *cis*-1,2-dichloroethylene was added to bromine at 10° and kept cold in the dark for 2 months, after which the red color of the bromine was reduced in intensity. The mixture was distilled, bp 70–71° (10 mm). The nmr showed the mixture from I to consist of two isomers: A, δ 6.12, 55%, and B, δ 6.06, 45%. The mixture from II was composed of 70% A and 30% B. On this basis, the lower field absorption was assigned to the *dl* compound since the cold, dark reaction would be expected to proceed to a larger extent by a polar path.

Reduction of 2,3-Dihalobutanes. Reduction of 2,3-dihalobutanes with organotin hydrides was carried out in a small, three-necked reaction flask or in a Pyrex tube possessing a ground-glass joint. The reactions were run in a constant temperature bath under a blanket of argon. The reactions of the vicinal dichlorides with tri-*n*-butyltin hydride and tri-*n*-butyltin deuteride and those of the vicinal dibromides with tri-*n*-butyltin hydride at −75° were photoinitiated with a 100-W G.E. mercury vapor lamp. A quartz tube (i.d. = 3.4 cm) containing the lamp was immersed in a constant temperature bath (22°) or in a bath of methanol or petroleum ether cooled to −78°. The tube containing the reactants was placed 3 cm from the lamp in the bath and 0.5 cm or less away from the lamp in the −78° bath.

A measured amount of the organotin hydride was introduced dropwise from a syringe through a rubber septum into the reaction flask containing the 2,3-dibromobutane. The reaction with dibromides began almost immediately upon contact of the reactants with each other. In reactions involving dichlorides, and those involving dibromides at −75°, measured amounts of dihalide and tri-*n*-butyltin hydride or deuteride were introduced into a Pyrex tube under argon and then irradiated at the desired temperature until the reaction was complete.

The gaseous products were collected in a trap, cooled to −78°, and analyzed by glpc at room temperature on a 15-ft column containing 28% dimethylsulfolane on C-22 Firebrick (40–60 mesh). The identity of the 2-butenes were ascertained on the basis of comparison of their infrared spectra and glpc retention times with those of authentic samples. *n*-Butane was identified by comparison of its retention time with that of an authentic sample. Yields of 2-butenes were obtained by titration of the olefins with a standardized solution of bromine in acetic acid.[43] Other detailed information concerning the individual experiments is summarized in Table VII.

Inhibition Experiments. Into a 50-ml round-bottomed flask equipped with serum cap and connected to a gas buret was added a solution of 1.00 ml (3.78 mmol) of tri-*n*-butyltin hydride and a weighed amount of galvinoxyl in 3.0 ml of *p*-xylene. The system was flushed with nitrogen and placed in a bath at 25 ± 1°, and then 3.00 mmol of *meso*-2,3-dibromobutane in 2.0 ml of *p*-xylene was added by syringe through the serum cap. The reaction mixture was stirred and the volume of hydrogen evolved measured as a function of time. Results are plotted in Figure 1.

Isomerization of *cis*-2-Pentene in the Reaction of *meso*-2,3-Dibromobutane with Tri-*n*-butyltin Hydride. Following a procedure similar to the general one described above, 2 ml (7.57 mmol) of tri-*n*-butyltin hydride was treated with 0.82 g (3.78 mmol) of *meso*-2,3-dibromobutane and 1 ml (9.28 mmol) of *cis*-2-pentane at 25° for 24 hr, and with a 1.9 *M* solution of *meso*-2,3-dibromobutane (3.78 mmol) in ether and 1 ml (9.28 mmol) of *cis*-2-pentene at −75° for 7 hr. After the reactions were completed, the 2-butene and 2-pentene were removed from the reaction mixture under reduced pressure and collected in a trap cooled to −78°. Analysis of the olefins by glpc was carried out isothermally on a 15 ft × 1/4 in. copper column of 28% dimethylsulfolane on C-22 Firebrick (40–60 mesh) immersed in an ice–water mixture (gas flow of about 30 ml/min). At 25°, the 2-pentene consisted of a mixture of 15.5% *trans* and 84.5% *cis;* at −75°, it consisted of a mixture of 11% *trans* and 89% *cis*. These figures were not as accurate as those found for the 2-butenes in other experiments because complete separation of the isomers was not possible under these analytical conditions.

(43) B. R. Stanerson, *et al.*, *Ind. Eng. Chem., Anal. Ed.*, **14**, 782 (1942).

Hydrogen Bromide Trapping Experiments. A typical experiment is described. To 3.27 g (1.84 ml, 15.15 mmol) of *meso*-2,3-dibromobutane and 1.54 g (2.1 ml, 15.15 mmol) of triethylamine in 10 ml of *n*-heptane was slowly added, with stirring, 8 ml (30.3 mmol) of tri-*n*-butyltin hydride under nitrogen at room temperature. The reaction mixture was stirred at room temperature for 1 hr; an additional 15 ml of *n*-heptane was added, and the flask was heated at reflux for 3 hr. After cooling the flask, the triethylamine hydrobromide was filtered off, washed with pentane, and dried in an oven at 110° for 1 hr: yield 2.23 g (81%); mp 247–249°; reported[40] mp 248°. Its infrared spectrum was identical with that of an authentic sample. The results of this and several other experiments are summarized in Table VIII.

Table VIII. Hydrogen Bromide Trapping Experiments. The Reaction of 2,3-Dibromobutanes with Tri-*n*-butyltin Hydride at Room Temperature

Expt no.[d]	Dibromide, mmol	Et_3N, mmol	% 2-butene *trans*	% 2-butene *cis*	% yield of $Et_3N{\cdot}HBr$
1	*meso*-(3.78), 1.9 *M* in *n*-pentane	3.78	*a*		75
2	*meso*-(3.78), 1.9 *M* in *n*-heptane	3.78	85	15	67
3	*dl*-(3.78), 1.9 *M* in *n*-heptane	3.78 3.78	25 30[b]	75	65
4	*meso*-(15.1), 1.5 *M* in *n*-heptane	15.1			81
5[c]	*meso*-(3.78), 1.9 *M* in *n*-heptane	3.78			0

[a] Quantity not determined. [b] Yield of olefin determined by titration with a standardized Br_2–HOAc solution. [c] No tri-*n*-butyltin hydride present. Et_3NHBr was not formed in 24 hr at room temperature. Glpc showed only the presence of starting materials. [d] *Sn*H (7.57 mmol) in experiments 1–3 and 30.3 mmol of *Sn*H in experiment 4.

Reduction of 1,2-Dibromo-1,2-dichloroethanes. To 1 mmol of dibromide at 0° was added an appropriate amount of tri-*n*-butyltin hydride, also at 0°. After standing for 2 hr to allow for complete reaction, diethyl malonate was added as an internal standard and the proportions of *cis*- and *trans*-1,2-dichloroethanes were determined by integration of the nmr spectrum. The amounts of *dl*- and *meso*-1,2-dibromo-1,2-dichloroethane were determined by comparing the areas under the proton singlets at δ 6.12 (*dl*) and 6.06 (*meso*) with that under the two-proton singlet of diethyl malonate at 3.20. Amounts of *cis*- and *trans*-1,2-dichloroethylene were determined similarly by comparing areas under the two-proton singlets at δ 6.39 (*cis*) and 6.34 (*trans*) with the malonate singlet. Results are presented in Table IX.

Table IX. Reactions of 1,2-Dibromo-1,2-dichloroethanes with Tri-*n*-butyltin Hydride at 0°

Mixture[a]	*Sn*H/CBr	1,2-Dichloroethene % yield	1,2-Dichloroethene % *cis*	1,2-Dichloroethene % *trans*
I	0.22	98	74	26
I	0.47	98	74	26
I	1.0	93	72	28[b]
II	0.25	97	80	20
II	0.50	93	75	25
II	1.0	97	75	25[b]

[a] I contained 55% *dl* and 45% *meso* isomer; II contained 70% *dl* and 30% *meso* isomer. [b] Repetition of this experiment with 1 mol of *cis*-1,2-dichloroethane per mol of dibromodichloride did not change the amount of *trans*-1,2-dichloroethane in product; thus no isomerization of the added *cis*-dichloride occurred during the debromination reaction.

Reduction of 1,2-Dibromohexane-1-*d*. The dibromide and tri-*n*-butyltin hydride were individually equilibrated at the reaction temperature, mixed, and irradiated in a Pyrex vessel with a 100-W mercury vapor lamp for 30 min. The amounts of *cis*- and *trans*-

1,2-dibromohexene-1-*d* were determined from the areas under the low-field half of the terminal vinyl doublet centered at δ 5.05 (*trans*) and 4.93 (*cis*), which were compared with that of two-proton singlet at 3.20 of diethyl malonate used as a standard. Results are given in Table X.

Table X. Reaction of *threo*-1,2-Dibromohexane-1-*d* with Tri-*n*-butyltin Hydride[a]

Entry	SnH/CBr	Mmol of olefin, At end of reaction *cis*	Mmol of olefin, At end of reaction *trans*	Mmol of olefin, Added *cis*	"Corrected" % olefin formed *cis*	"Corrected" % olefin formed *trans*
1	0.48	0.25	0.21		72	28
2	0.48	0.67	0.33	0.55		
3	0.97	0.67	0.44		77	23
4	0.97	1.55	0.67	1.16		
5	0.50	0.33	0.28		72	28
6	0.50	0.70	0.42	0.51		
7	0.50	0.33	0.28		75	25
8	0.50	0.80	0.46	0.65		
9	0.50	0.38	0.23		78	22
10	0.50	0.84	0.35	0.58		
11	0.50	0.37	0.24		74	26
12	0.50	0.87	0.34	0.60		

[a] Experiments 1–8 at 0°; experiments 9–12 at −75°. Experiments 1–4 neat; experiments 5–12 1.22 *M* dibromide in heptane.

To gain information concerning extent of isomerization of the olefinic product during the course of the reaction *cis*-1-hexene-1-*d* was added initially in duplicates of the simple reduction experiments. It was then assumed that the amounts of *cis*- and *trans*-1-hexene-1-*d* formed in the experiments with and without added olefin were the same. The increase in the amount of *cis* isomer present at the end of the control experiment was taken to correspond to the amount of the added olefin which remained unisomerized. Thus, taking figures from the first two entries of the Table X, of the 0.55 mmol of *cis*-olefin introduced in the second experiment 0.67–0.25 = 0.42 mmol or 76% remains unisomerized. If it be assumed that the olefin formed in first experiment is isomerized to the same degree, the amount of *cis*-olefin actually formed would be 0.27/0.76 = 0.33 and the corrected percentage of *anti*-elimination product would be 72. This figure is too high because the olefin formed in the reduction would not be isomerized to the same extent as that added at the beginning of the experiment; the actual figure will lie between 55 and 72%.

Reduction of Diethyl 2,3-Dibromosuccinates. The procedure was identical with that used for the dibromohexanes. When excess hydride was used it was destroyed by allowing it to react with bromoform before analysis. Product compositions were determined by glpc using a column of diethylene glycol succinate on Diatoport S using diethyl malonate as an internal standard. Results are summarized in Table XI.

Table XI. Reactions of Diethyl 2,3-Dibromosuccinates with Tri-*n*-butyltin Hydride[a]

Entry	Dibromide	SnH/CBr	Products, % Fumarate	Products, % Maleate[b]	Products, % Succinate
1	*meso*	2.4	64	9	28
2	*dl*	2.4	67	11	22
3	*meso*	4.9	42	7	51
4	*dl*	4.6	36	9	55
5	*dl*[c]	3.0	72	5	23
6	*dl*[d]	3.0	61	3	36

[a] 0°, irradiation in Pyrex vessels. [b] ±4–5%. [c] Reaction quenched after 4 min. [d] Reaction quenched after 8 min.

The reaction of *dl*-diethyl 2,3-dibromosuccinate (1.10 mmol) and tri-*n*-butyltin hydride (1.89 mmol) was carried out in the presence of dimethyl maleate (0.935 mmol). Analysis of the product using the same chromatographic procedure as above showed the mixture of diethyl esters to contain 90% of fumarate, 10% of succinate, and negligible maleate and the dimethyl ester mixture to contain 3% fumarate, 50% succinate, and 47% maleate.

Reduction of Diethyl 1,2-Dihaloethylbenzenes. The reductions of 1,2-dibromoethylbenzene and 1-bromo-2-chloroethylbenzene with tri-*n*-butyltin hydride were carried out by comblning the dihalide (3.78 mmol) with the hydride at room temperature under nitrogen in a 50-ml stoppered flask. The stoichiometry of the reaction, isolated products, and yields are shown in Table XII.

Table XII. Reduction of 1,2-Dihaloethylbenzenes with Tri-*n*-butyltin hydride[a]

Expt no.	Dihalide (*Sn*H/CX)	Product(s)	Reduction product,[b] %	Organotin halide, %
1	$C_6H_5CHBrCH_2Cl$ (0.5)	$C_6H_5CH_2CH_2Cl$	90[c]	95
		$C_6H_5CH{=}CH_2$	Trace	
2	$C_6H_5CHBrCH_2Br$ (1.0)	$C_6H_5CH{=}CH_2$	99[d]	*e*
3	$C_6H_5CHBrCH_2Br$ (0.5)	$C_6H_5CH{=}CH_2$	48[d,f]	*e*

[a] Reactants mixed at room temperature; in expt 2, the dihalide was 0.75 *M* in toluene. [b] Based on dihalide. [c] Determined by isolation, infrared spectrum compared with that of an authentic sample. [d] Determined by glpc using the internal standard method. [e] Not determined. [f] 96% based on hydride.

Relative Reactivities of Vicinal Dihalides. The relative rate constants for the tri-*n*-butyltin hydride reduction of four vicinal dihalides were determined by allowing a suitable pair to compete for an insufficient amount of tri-*n*-butyltin hydride and analyzing the resulting reaction mixture for unreacted halides or reduction products. The glpc analysis of the unreacted *erythro*-2-bromo-3-chlorobutane and *meso*-2,3-dibromobutane was carried out using a 15 ft × 1/4 in. copper column containing a support of Tide detergent whereas the analysis for 2-chloroethylbenzene and styrene was conducted on a 6 ft × 1/4 in. steel column containing 10% Lac-728 (diethylene glycol succinate) on a support of Diatoport W, 60–80 mesh, or 10% Apiezon L on Diatoport W. The competitors with an internal standard were transferred into a two-necked round-bottomed flask fitted with a rubber septum. After the solvent was added, the flask was flushed with argon, stoppered, and immersed in a temperature controlled bath set at 25°. The organotin hydride was added, with stirring, by means of a hypodermic syringe. The flask remained in the bath until all the organotin hydride, as indicated by disappearance of the band at 1815 cm^{-1} in its infrared spectrum was consumed. The concentration of unreacted competitors was determined by gas chromatography using the procedure described by Keulemans.[44] The relative rate constants were computed by the equations of Ingold and Shaw.[45]

Reduction of *endo-cis*-2,3-Dibromonorbornane. To 169 mg (0.67 mmol) of *endo-cis*-2,3-dibromonorbornane in 2 ml of methylene chloride under nitrogen was added 0.35 ml (1.33 mmol) of tri-*n*-butyltin hydride at room temperature with magnetic stirring. After a short time, the reaction became warm and was then allowed to remain overnight. The reaction mixture was analyzed by glpc on a 20 ft × 1/4 in. copper column of 10% silicone gum rubber (SE 30) on 60–80 Chromosorb W. Coinjection of the reaction mixture with norbornene and norbornane separately showed the product to be norbornene accompanied by a trace of norbornane. The yield, determined by the internal standard method,[44] was 62%.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. G5285.

(44) A. I. M. Keulemans, "Gas Chromatography," Reinhold Publishing Corp., New York, N. Y., 1959, p 34.
(45) C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 2918 (1927).