in 20 ml. of tetrahydrofuran was treated with 0.0040 mole of borane and allowed to stand for 15 min. at room temperature. The reaction mixture was worked up as described in A above giving no benzaldehyde or benzyl alcohol.

C.—A solution of 0.5 g. of benzaldehyde in 10 ml. of tetrahydrofuran was stirred for 1 hr. at room temperature with 5 ml. of 30% sodium hydroxide and 5 ml. of 30% hydrogen peroxide.

Isolation and analysis of the material as described in A above showed that no benzyl alcohol had been formed.


Mechanism of Reduction of Alkyl Halides by Organotin Hydrides[1,2]

By Lawrence W. Menapace and Henry G. Kuivila[3]
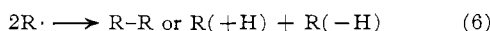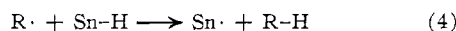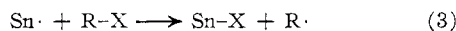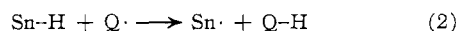
Evidence is presented which leads to the conclusion that the reduction of alkyl halides by organotin hydrides proceeds by a free-radical mechanism. Pertinent observations are: (a) Optically active α-phenylethyl chloride gives racemic α-deuterioethylbenzene. (b) Allylic and propargylic halides give both rearranged and unrearranged reduction products. (c) The reaction is subject to retardation by hydroquinone. (d) Reactivities of halides follow a free-radical order. Reduction of γ-chlorobutyrophenone gives a mixture of butyrophenone and α-phenyltetrahydrofuran.

Organotin hydrides have been found to be useful in the selective reduction of alkyl,[2a,4-10] cycloalkyl,[2a,7,9,10] acyl,[5,11,12] and aryl[2a,6,13] halides; see eq. 1 in which Sn is a trisubstituted tin group.

$$R-X + Sn-H \longrightarrow R-H + Sn-X \qquad (1)$$
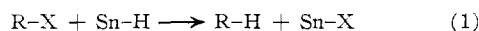
We have been interested in this reaction, particularly from the mechanistic standpoint, and we report in this paper results which point convincingly to a free-radical chain mechanism. A reasonable scheme, in terms of which our results will be discussed, is that shown in eq. 2–6.

$$Sn-H + Q\cdot \longrightarrow Sn\cdot + Q-H \qquad (2)$$

$$Sn\cdot + R-X \longrightarrow Sn-X + R\cdot \qquad (3)$$

$$R\cdot + Sn-H \longrightarrow Sn\cdot + R-H \qquad (4)$$

$$2Sn\cdot \longrightarrow Sn-Sn \qquad (5)$$

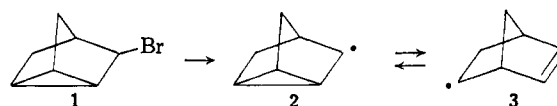$$2R\cdot \longrightarrow R-R \text{ or } R(+H) + R(-H) \qquad (6)$$

Initiation.—The initiation step of eq. 2 is brought about by the abstraction of a hydrogen atom from the tin hydride by some free radical $Q\cdot$. It was shown earlier[10] that small amounts of oxygen exert a definite catalytic effect on the reduction of n-butyl bromide by tri-n-butyltin hydride, although larger amounts

(20% or more) in the atmosphere over the reaction mixture have a profound inhibitory effect. Azobisisobutyronitrile has been shown to be an effective catalyst.[10] As an example, chlorocyclohexane is reduced to the extent of about 1% by tri-n-butyltin hydride in 35 min. at 80°, but in the presence of 1.5 mole per cent of the azo compound 70% reduction occurs under the same conditions. The fact that a small amount of catalyst has such a large effect on the over-all reaction rate supports the postulate of a chain reaction.

Thermal decomposition of the hydride could also lead to formation of $Sn\cdot$. In view of the fact that the hydride can be distilled at 135° without significant decomposition, it is unlikely that this is an important initiation step at room temperature. A further possibility concerning which no information is currently available involves a reaction between halide and hydride to form two free radicals.

Propagation.—Evidence for the formation of free alkyl radicals as intermediates comes from several observations. Reduction of optically active α-phenylethyl chloride by triphenyltin deuteride produced racemic α-deuterioethylbenzene. That this result was not due to racemization of the chloride followed by reduction is shown by the fact that the chloride did not undergo racemization in the presence of triphenyltin chloride under the conditions of the reduction reaction. Since an SN2 mechanism would lead to inversion and a four-center reaction would lead to retention, each of these can be eliminated on the basis of this observation. Reduction of propargyl bromide with tri-n-butyltin hydride led to the formation of a mixture of 84% propyne and 16% allene.[14] Such a product mixture could be formed as a result of either a combination of four-center SN2 and SN2′ reactions

(1) This research was supported by the National Science Foundation under Grant NSF-G-10000 to the University of New Hampshire.

(2) (a) For a preliminary report on a portion of this work see H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Am. Chem. Soc.*, **84**, 3584 (1962); (b) presented at the XIXth International Congress of Pure and Applied Chemistry, London, July, 1963.

(3) (a) Department of Chemistry, State University of New York at Albany, Albany, N. Y.; (b) National Science Foundation Senior Postdoctoral Fellow, California Institute of Technology, 1959–1960.

(4) G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.*, **7**, 356 (1957).

(5) J. G. Noltes and G. J. M. van der Kerk, "Functionally Substituted Organotin Compounds," Tin Research Institute, Greenford, Eng., 1958, p. 72.

(6) J. G. Noltes and G. J. M. van der Kerk, *Chem. Ind.* (London), 294 (1959).

(7) D. H. Lorenz and E. I. Becker, *J. Org. Chem.*, **27**, 3370 (1962).

(8) D. Seyferth, H. Yamazaki, and D. L. Alleston, *ibid.*, **28**, 703 (1963).

(9) E. J. Kupchik and R. E. Connolly, *ibid.*, **26**, 4747 (1961).

(10) H. G. Kuivila and L. W. Menapace, *ibid.*, **28**, 2165 (1963).

(11) H. G. Kuivila, *ibid.*, **25**, 284 (1960).

(12) E. J. Walsh, Jr., unpublished observations in this laboratory.

(13) (a) L. A. Rothman and E. I. Becker, *J. Org. Chem.*, **24**, 294 (1959); **25**, 2203 (1960); (b) D. H. Lorenz, P. Shapiro, A. Stern, and E. I. Becker, *ibid.*, **28**, 2332 (1963).

(14) In connection with other work in these laboratories C. R. Warner has observed that reduction of the bromonortricyclene (1) with tri-n-butyltin hydride leads to a mixture of 55% norbornene and 45% nortricyclene. This result is consistent with the formation of radicals **2** and **3** as intermediates.
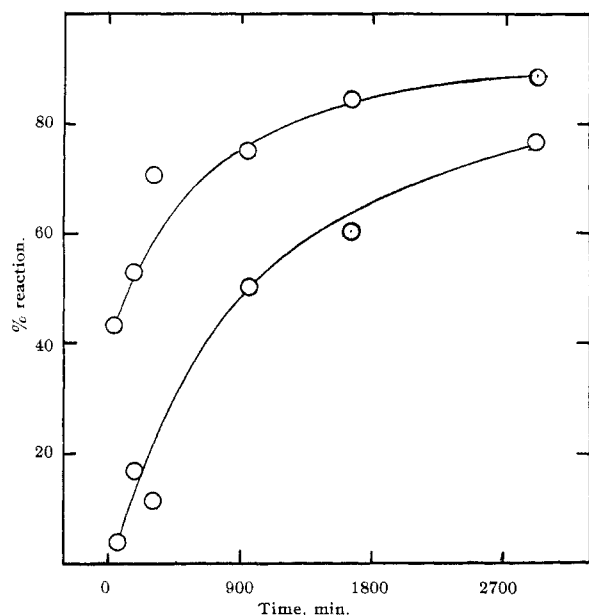
Fig. 1.—Reduction of benzyl chloride with tri-*n*-butyltin hydride; upper curve, without hydroquinone; lower curve, in presence of 1.5 mole % hydroquinone.

or the formation of an intermediate propargyl radical which can react at the methylene carbon to form propyne or at the methine carbon to form allene.

The reduction of α- and γ-methallyl chlorides with triphenyltin hydride was examined as another test for the intermediacy of mesomeric free radicals. Samples enriched in each isomer were analyzed by gas chromatography and infrared spectroscopy to determine the proportions of the α-isomer and the *cis-* and *trans-*γ-isomer. These were then reduced and the composition of the butenes obtained were determined by gas chromatography. Results are gathered in Tables I and II. It is evident that rearrangement has accompanied reduction in each case. Control experiments carried out in the absence of hydride showed that rearrangement of the chlorides did not precede reduction to any significant extent (Table I).

TABLE I

COMPOSITION OF ISOMERIC METHALLYL CHLORIDES

	Reaction I		Reaction II	
Butene chloride	% before start of reaction	% after standing over (C₆H₅)₃SnCl	% before start of reaction	% after standing over (C₆H₅)₃SnCl
3-Chloro-1-	86.0	77.6	9:5	10.7
cis-1-Chloro-2-	2.5	22.4[a]	16.2	89.3[a]
trans-1-Chloro-2-	11.5		74.3	

[a] This figure represents the combined percentage of *cis-* and *trans-*1-chloro-2-butenes.

TABLE II

PERCENTAGE COMPOSITION OF ISOMERIC BUTENES

	Reaction I		Reaction II	
Butene	Obsd.	Calcd.[a]	Obsd.	Calcd.[a]
1-	27.0	30.6	26.9	28.8
cis-2-	13.8	22.4	11.5	12.5
trans-2-	59.2	47.0	61.6	58.7

[a] Calculated on the basis of data in ref. 15; see text.

The stereochemistry of reactants and products are of interest. Since the composition of the mixtures of butenes obtained in the two experiments are substantially identical, it might be concluded that identical radicals are formed from each chloride. However,

Walling and Thaler[15] have shown that the allylic radicals formed in the chlorination of butenes by *t*-butyl hypochlorite are configurationally stable. Let us assume that this is true in the tin hydride reduction, and also that a given allylic radical will abstract a hydrogen atom from a tin hydride molecule, or a chlorine atom from *t*-butyl hypochlorite, so as to produce 1-butene, *cis-* and *trans-*2-butenes, or the chlorinated analogs, respectively, in the same proportions. Thus the radical derived from 3-chloro-1-butene would yield 30.9% of 1-butene and 69.1% of a mixture containing 65% *trans-* and 35% *cis-*2-butene. Figures derived on the basis of these assumptions are given in the columns headed "Calculated" in Table II. The agreement between observed and calculated compositions is excellent for the reduction of the mixture rich in 1-chloro-2-butenes. It is not very good for the 3-chloro-1-butene, which yields product containing more *trans-* and less *cis-*2-butene than calculated. This is explicable if we assume with Walling and Thaler that the stereochemistry of the product is determined by the conformation of the chlorobutene at the instant of attack by the radical Sn·. Conformations **4, 5,** and **6** would appear to be the most probable. Conformation **4** yields an ambiguous result, but it is also the least likely to lead to reaction because the p-orbital
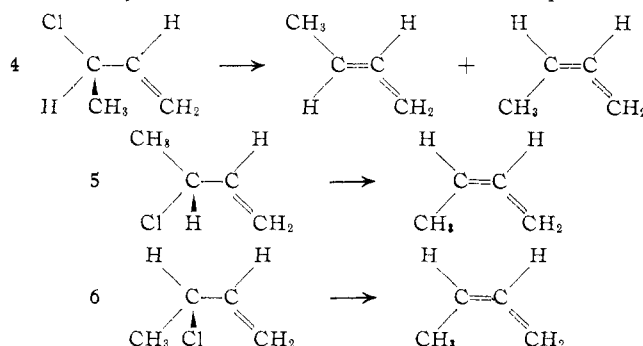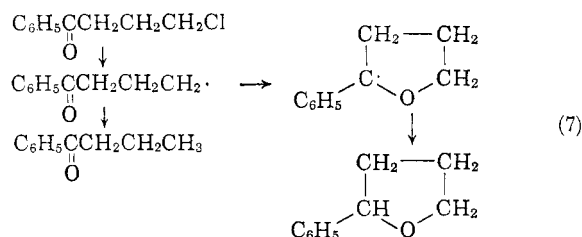

which would develop upon abstraction of the chlorine atom would be perpendicular to the π-orbital already in the molecule, and rotation through 90° would be necessary for maximum overlap of the two. In the other two conformations the stereoelectronic arrangement is more satisfactory. The more probable of the conformations is clearly **5** because the methylene group is staggered between as chlorine and a hydrogen, whereas it is staggered between a chlorine and a methyl group in **6**. Consequently one would expect more *trans-*allylic radical to be formed than in the case in which a *t*-butoxy radical is abstracting a hydrogen atom from 1-butene. We tend toward the view that identical allylic radicals are *not* formed in the tin hydride reductions because the results are consistent with this idea, and because the approximately one-and-a-half bond present in the allylic radical should be strong enough to prevent rapid rotation about it at room temperature.

A chain reaction should be susceptible to inhibition. In preliminary experiments we found that the azobisisobutyronitrile-catalyzed reaction was retarded by hydroquinone. The thermal reaction involving tri-*n*-butyltin hydride and benzyl chloride is also subject to retardation by the addition of 1.5 mole % of hydroquinone to the reaction mixture as shown in Fig. 1.

(15) C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).

The reduction of γ-chlorobutyrophenone was examined in an attempt to trap the intermediate free radical as shown in eq. 7. Driving force for ring closure to the 2-phenyltetrahydrofuryl radical is provided by

$$C_6H_5\underset{O}{\underset{\|}{C}}CH_2CH_2CH_2Cl$$
$$\downarrow$$
$$C_6H_5\underset{O}{\underset{\|}{C}}CH_2CH_2CH_2\cdot \longrightarrow$$
$$\downarrow$$
$$C_6H_5\underset{O}{\underset{\|}{C}}CH_2CH_2CH_3$$

 (7)

formation of the five-membered ring and, particularly, by the formation of a free radical which is stabilized by both the benzene ring and the α-alkoxy group. Isolation of the product obtained upon reduction of the chloroketone with tri-n-butyltin hydride catalyzed by azobisisobutyronitrile provided 65% of reduction product containing 80% 2-phenyltetrahydrofuran and 20% butyrophenone.

Relative Reactivities of Halides.—Twenty-two halides were allowed to compete in pairs for an insufficient amount of tri-n-butyltin hydride at 45 or 80°, usually in chlorobenzene or bromobenzene as solvent. Relative rate constants were calculated using the equation of Ingold and Shaw[16] from the concentrations of unreacted halides or reduction products as determined by gas chromatography. The applicability of the Ingold–Shaw equation which is based on the assumption that both competitors react by the same mechanism and, therefore, have the same kinetic order was tested by determining relative reactivities of bromodichloromethane and benzyl bromide at several concentrations. Results are shown in Table III. No noticeable drift in the relative rates with concentration is present. The variations observed also provide an indication of the precision of the rate determinations.

TABLE III

EFFECT OF VARYING CONCENTRATIONS ON THE RELATIVE
RATE CONSTANT BROMODICHLOROMETHANE vs. BENZYL
BROMIDE

Init. concn. BrCHCl₂, mmoles	Init. concn. C₆H₅CH₂Br, mmoles	Init. concn. (n-C₄H₉)₃SnH, mmoles	Volume of solvent, ml.	$k_{BrCHCl_2}/k_{C_6H_5CH_2Br}$
3.70	15.07	3.78	5	3.18
3.87	4.07	3.78	5	3.50
3.75	7.50	3.78	5	3.30
7.40	7.46	3.78	5	3.26
7.59	7.48	3.78	10	3.42
8.86	14.97	7.56	5	3.50

If the thermal reaction and that catalyzed by azobisisobutyronitrile both proceed by a radical chain mechanism, then relative reactivities of halides should be the same for each. This was tested for two pairs: 2-bromobutane–benzyl chloride and bromochloromethane–2-bromooctane. Relative rates for the catalyzed and thermal reactions, respectively, were 32.1 and 34.4 for the first pair and 8.20 and 8.66 for the second. The agreement obtained is taken as further support for a free-radical mechanism for the thermal reaction.

Results of competitive experiments for all of the halides examined are gathered in Table IV. The

reactivity sequence is not that of the SN2 reaction inasmuch as the order for the butyl bromides is 3° > 2° > 1°. Nor is it that of the SN1 reaction: allyl halides solvolyze faster by several powers of ten than propargyl halides,[17] whereas the propargyl halides react faster with tri-n-butyltin hydride by a factor of about four; and t-butyl halides solvolyze faster than benzyl halides by a factor which depends strongly on solvent,[17] whereas the reverse order of reactivity obtains for the tin hydride reduction. If the mechanism of eq. 2–7 is correct, the data provide a measure of relative rates of reaction of halides with the tri-n-butyltin radical. One might therefore expect a rate sequence similar to that obtained by Szwarc and his co-workers[18,19] for the abstraction of halogen atoms from halides by methyl radicals. This is indeed observed as revealed by the data in Table V. The only exception to complete conformity arises in the case of carbon tetrachloride which is more reactive than benzyl bromide toward the organotin radical, but less reactive toward the methyl radical.

Several factors are obviously involved in determining the reactivity sequence. The order I > Br > Cl > F[20] is due primarily to changes in the carbon–halogen bond energy as is the order 3° > 2° > 1°. Resonance stabilization of the incipient free alkyl radical is undoubtedly important in determining the reactivities of the benzyl, allyl, and propargyl halides. A polar factor is also present with electron-withdrawing substituents facilitating reaction. Examples are provided by the greater reactivity of propargyl over allyl halides; facilitation by m-bromo and m-trifluoromethyl in the benzyl halides; and the high reactivity of polyhalomethanes and ethyl bromoacetate. As in the abstraction of halogen by methyl radicals, two explanations for the polar effect are possible.[18,19] In the first the transition state is represented as the resonance hybrid I to which the polar structures make significant contributions because of the ability of the tin atom to accommodate a positive charge. In the second, repulsion be-

I $(R \cdots X \cdots Sn) \longleftrightarrow (R^- \cdot X Sn^+) \longleftrightarrow (R \cdot X^- Sn^+)$

tween the electron in the p-orbital of the attacking tin atom and the outer electrons of the halogen atom is diminished by electron withdrawal on the part of the substituent R. The range of relative rates for halogen abstraction by the organotin radical is tremendously compressed as compared with that for the methyl radical: for example, in the former case bromotrichloromethane reacts about nine times as fast as bromochloromethane, and in the latter case the factor is more than five thousand. Another striking observation is that bromotrichloromethane and carbon tetrachloride differ in reactivity by a factor of only three in the organotin reaction, while the factor is about 1700 in the methyl radical reaction. Yet benzyl bromide reacts 670 times as fast as benzyl chloride with the organotin radical. One implication of these results is that carbon–halogen bond breaking has proceeded to a far smaller degree in the transition state involving the tetrahalomethanes than in that involving the

(16) C. K. Ingold and F. R. Shaw, J. Chem. Soc., 2918 (1927).

(17) A. Streitwieser, Jr., Chem. Rev., **56**, 616 (1956).

(18) F. W. Evans, R. J. Fox, and M. Szwarc, J. Am. Chem. Soc., **82**, 6414 (1960).

(19) R. J. Fox, R. W. Evans, and M. Szwarc, Trans. Faraday Soc., **57**, 1915 (1961).

(20) Benzotrifluoride reacts very slowly with tri-n-butyltin hydride at 80°, whereas benzotrichloride reacts exothermally at room temperature.

TABLE IV

RELATIVE RATES OF REDUCTION OF ORGANIC HALIDES BY TRI-n-BUTYLTIN HYDRIDE

No.	Halide	Rel. rate[b]	No.	Halide	Rel. rate[b]
	—At 45°—			—At 80 ± 2°[a]—	
1	$C_6H_5CH_2Cl$	0.05	19	$C_6H_5CH_2Cl$	1.00
2	n-C_4H_9Br	1.00	20	C_6H_5Br	0.72 ± 0.07
3	1-BrC_8H_{17}	1.10	21	m-$CF_3C_6H_4CH_2Cl$	1.64 ± 0.04
4	Cyclo-$C_6H_{11}Br$	1.46	22	$H_2C{=}CHCH_2Cl$	1.83
5	Cyclo-C_6H_9Br	2.37	23	$HC{\equiv}CCH_2Cl$	6.11 ± 0.77
6	2-BrC_8H_{17}	2.63	24	2-BrC_8H_{17}	30.0 ± 3.8
7	2-BrC_4H_9	2.99	25	2-BrC_4H_9	33.3 ± 1.28
8	t-C_4H_9Br	7 ± 1	26	$BrCH_2Cl$	250 ± 22
9	$BrCH_2Cl$	25.8 ± 1.4			
10	$CH_2{=}CHCH_2Br$	30.5 ± 1.6			
11	$C_6H_5CH_2Br$	33.5 ± 1.8			
12	m-$BrC_6H_4CH_2Br$	36.2 ± 4.6			
13	$BrCH_2COOC_2H_5$	60.4 ± 3.3			
		42.9 ± 2.3			
14	1-IC_7H_{15}	61.1 ± 5.7			
15	CCl_4	75.1 ± 4.7			
16	$BrCHCl_2$	112 ± 6			
17	$HC{\equiv}CCH_2Br$	139 ± 7			
18	$BrCCl_3$	226 ± 12			

[a] Competitive reactions conducted at 80 ± 2° were all initiated by approximately 1.7 mole % azobisisobutyronitrile except for numbers 20, 25, and 26. For numbers 20 and 25, four experiments were carried out, two with and two without azobisisobutyronitrile. For number 26, three experiments were carried out, two with and one without azobisisobutyronitrile. [b] Relative rate constants which are the result of more than one competitive experiment include the standard deviation.

TABLE V

RELATIVE RATE CONSTANTS FOR HALOGEN ATOM ABSTRACTION

R	Methyl radical[a]			Tin hydride reduction		
	I	Br	Cl	I	Br	Cl
CH_3	45	6 × 10^{-3}				
C_2H_5	180					
n-C_4H_9					1.00	
n-C_7H_{15}				61.1		
i-C_3H_7	870					
s-C_4H_9					2.99	
t-C_4H_9	1680				7	
$C_6H_5CH_2$	7560	6.5			33.5	0.05
CH_2Cl	6400	1.4			25.8	
$CHCl_2$		131			112	
CCl_3		7400	4.4		226	75.1
CF_3	20,000					

[a] Relative rate constants for reactions $RX + CH_3{\cdot} \rightarrow R{\cdot} + CH_3X$ (k_2) expressed as a ratio k_2/k_1, where k_1 refers to the reaction $CH_3{\cdot} + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2{\cdot}$ (ref. 18).

benzyl halides and the organotin radical, probably as a consequence of the relatively high nucleophilic character of the latter. More detailed discussion should await the accumulation of additional data on the relationship between reactivity and structure, as well as other reaction parameters, now being gathered.

Experimental

All reactions involving organotin hydrides were conducted in ordinary laboratory apparatus under an atmosphere of prepurified nitrogen (Matheson).

Materials.—Organotin hydrides were prepared by previously described methods.[21,22] The organic halides which were commercially available were redistilled before use if discolored or shown to contain more than 5% of impurities. m-Trifluoromethylbenzyl chloride was prepared from m-trifluoromethylbromobenzene according to well-established procedures.[23]

Reduction of Propargyl Bromide.—Propargyl bromide (3.8 mmoles) was added to an equimolar amount of tri-n-butyltin

hydride contained in a flask connected to a gas buret. Reaction occurred readily and the infrared spectrum of the gas which was collected was found to contain all bands expected for allene and propyne.[24] Gas chromatography using an 11-ft. column packed with 17% silicone nitrile on Chromosorb P (42–60 mesh) showed that the mixture contained 84% propyne and 16% allene.

Reduction of γ-Chlorobutyrophenone.—Into a 100-ml. flask fitted with a stirrer, a pressure-equalizing addition funnel, a condenser, and an inlet tube for nitrogen were placed 35.7 mmoles of γ-chlorobutyrophenone and 25 ml. of anhydrous ether. The flask was placed in a bath at 80° and a solution containing 37.8 mmoles of tri-n-butyltin hydride and 0.061 mmole of azobisisobutyronitrile in 25 ml. of ether was added over a period of 10 hr. After an additional 34 hr. at 80° the reaction mixture was distilled providing 65% of product, b.p. 66–74° at 0.25 mm. Treatment with excess Girard T reagent removed 20% of the material and the residual product had an infrared spectrum identical with that of authentic 2-phenyltetrahydrofuran kindly provided by Dr. R. L. Letsinger.

Retardation by Hydroquinone.—The reaction flasks used were fitted with two stopcocks so that the contents could be sampled with rigorous exclusion of air. To each of two flasks was added 3.78 mmoles of benzyl chloride. Then 0.6 mmole of hydroquinone was added to one flask, followed by 10 ml. of solvent, and 3.75 mmoles of tri-n-butyltin hydride added to each. At intervals, samples were removed from each flask, quenched by addition of sulfuric acid, washed with water, and dried over potassium carbonate. Gas chromatographic analysis followed, a 4-ft. column packed with 20% paraffin oil on Chromosorb P (80–100 mesh) being used. Results are presented graphically in Fig. 1.

Reduction of Isomeric Methallyl Chlorides by Triphenyltin Hydride.—The composition of mixtures of 1-chloro-2-butene and 3-chloro-1-butene were determined by gas chromatography using an 11 ft. by 0.25 in. column of 17% silicone nitrile on Chromosorb P (42-60 mesh). The ratios of $trans$- to cis-1-chloro-2-butene were approximated on the basis of infrared spectra given by Hatch and Nesbitt.[25] Results are given in Table I. To test for isomerization of the chlorides each was allowed to stand in contact with excess triphenyltin chloride at room temperature for 40 days and analyzed with results given in Table I.

To 8.46 mmoles of triphenyltin hydride was added 7.74 mmoles of the allylic chloride. The mixture was sealed in an ampoule and allowed to stand for 40 days, whence the butenes were collected and analyzed by gas chromatography using a 15-ft. col-

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(23) "Organic Syntheses," H. Gilman, Ed., John Wiley and Sons, Inc., New York, N. Y., Coll. Vol. I, 1932, p. 188; Coll. Vol. III, 1955, p. 698.

(24) R. C. Lord and P. Vankateswarlu, J. Chem. Phys., **20**, 1237 (1952); R. H. Pierson, A. N. Fletcher, and E. St. Clair Gantz, Anal. Chem., **28**, 1218 (1956).

(25) L. W. Hatch and S. S. Nesbitt, J. Am. Chem. Soc., **72**, 727 (1950).

TABLE VI

RELATIVE RATES OF REDUCTION OF ORGANIC HALIDES BY TRI-n-BUTYLTIN HYDRIDE AT 45°

Expt.	Competitor A	Competitor B	Solvent	k_B/k_A
1	n-C$_4$H$_9$Br	2-BrC$_8$H$_{17}$	C$_6$H$_5$CH$_3$	2.63
2	1-BrC$_8$H$_{17}$	2-BrC$_8$H$_9$	C$_6$H$_5$CH$_3$	2.72
3	n-BrC$_4$H$_9$	1-BrC$_8$H$_{17}$	C$_6$H$_5$CH$_3$	1.10
4	n-C$_4$H$_9$Br	t-C$_4$H$_9$Br	C$_6$H$_4$(CH$_3$)$_2$	7.56
5	n-C$_4$H$_9$Br	t-C$_4$H$_9$Br	C$_6$H$_4$(CH$_3$)$_2$	6.79
6	n-C$_4$H$_9$Br	Cyclo-C$_6$H$_{11}$Br	Cyclo-C$_6$H$_{12}$	1.46
7	n-C$_4$H$_9$Br	Cyclo-C$_5$H$_9$Br	Cyclo-C$_6$H$_{12}$	2.37
8	BrCH$_2$Cl	C$_6$H$_5$CH$_2$Br	C$_6$H$_5$Cl	1.30
9	BrCH$_2$Cl	C$_6$H$_5$CH$_2$Br	C$_6$H$_5$Cl	1.30
10	C$_6$H$_5$CH$_2$Br	CCl$_4$	C$_6$H$_5$Cl	2.16
11	C$_6$H$_5$CH$_2$Br	CCl$_4$	C$_6$H$_5$Br	2.38
12	C$_6$H$_5$CH$_2$Br	CCl$_4$	C$_6$H$_5$Br	2.14
13	C$_6$H$_5$CH$_2$Br	BrCHCl$_2$	C$_6$H$_5$Br	3.18
14	C$_6$H$_5$CH$_2$Br	BrCHCl$_2$	C$_6$H$_5$Br	3.50
15	C$_6$H$_5$CH$_2$Br	BrCHCl$_2$	C$_6$H$_5$Br	3.30
16	C$_6$H$_5$CH$_2$Br	BrCHCl$_2$	C$_6$H$_5$Br	3.26
17	C$_6$H$_5$CH$_2$Br	BrCHCl$_2$	C$_6$H$_5$Br	3.42
18	C$_6$H$_5$CH$_2$Br	BrCHCl$_2$	C$_6$H$_5$Br	3.50
19	CH$_2$=CHCH$_2$Br	C$_6$H$_5$CH$_2$Br	C$_6$H$_5$Cl	1.15
20	CH$_2$=CHCH$_2$Br	C$_6$H$_5$CH$_2$Br	C$_6$H$_5$Cl	1.09
21	CH$_2$=CHCH$_2$Br	C$_6$H$_5$CH$_2$Br	C$_6$H$_5$Cl	1.04
22	CH$_2$=CHCH$_2$Br	C$_6$H$_5$CH$_2$Br	C$_6$H$_5$Cl	1.13
23	C$_6$H$_5$CH$_2$Br	BrCH$_2$CO$_2$C$_2$H$_5$	C$_6$H$_5$Cl	1.28
24	C$_6$H$_5$CH$_2$Br	BrCH$_2$CO$_2$C$_2$H$_5$	(CH$_3$)$_2$CHCH(CH$_3$)$_2$	1.80
25	2-BrC$_4$H$_9$	C$_6$H$_5$CH$_2$Br	C$_6$H$_5$Br	10.4
26	2-BrC$_4$H$_9$	C$_6$H$_5$CH$_2$Br	C$_6$H$_5$Br	11.1
27	2-BrC$_4$H$_9$	C$_6$H$_5$CH$_2$Br	C$_6$H$_5$Br	11.3
28	2-BrC$_4$H$_9$	C$_6$H$_5$CH$_2$Br	C$_6$H$_5$Br	12.0
29	C$_6$H$_5$CH$_2$Br	1-IC$_7$H$_{15}$	C$_6$H$_5$Br	1.95
30	C$_6$H$_5$CH$_2$Br	1-IC$_7$H$_{15}$	C$_6$H$_5$Br	1.70
31	C$_6$H$_5$CH$_2$Cl	2-BrC$_4$H$_9$	C$_6$H$_5$Br	54.6
32	m-BrC$_6$H$_4$CH$_2$Br	CH$_2$=CHCH$_2$Br	C$_6$H$_5$Cl	1.01
33	C$_6$H$_5$CH$_2$Br	m-BrC$_6$H$_4$CH$_2$Br	C$_6$H$_5$Cl	1.21
34	C$_6$H$_5$CH$_2$Br	m-BrC$_6$H$_4$CH$_2$Br	C$_6$H$_5$Cl	1.18
35	BrCHCl$_2$	BrCCl$_3$	C$_6$H$_5$Br	1.97
36	BrCHCl$_2$	BrCCl$_3$	C$_6$H$_5$Br	2.06
37	C$_6$H$_5$CH$_2$Br	HC≡CCH$_2$Br	C$_6$H$_5$Br	3.96
38	C$_6$H$_5$CH$_2$Br	HC≡CCH$_2$Br	C$_6$H$_5$Br	3.98
39	C$_6$H$_5$CH$_2$Br	HC≡CCH$_2$Br	C$_6$H$_5$Br	4.33
40	C$_6$H$_5$CH$_2$Br	HC≡CCH$_2$Br	C$_6$H$_5$Br	4.34

TABLE VII

RELATIVE RATES OF REDUCTION BY TRI-n-BUTYLTIN HYDRIDE AT 80 ± 2° CATALYZED BY 1.6% AZOBISISOBUTYRONITRILE[a]

Expt.	Competitor A	Competitor B	k_B/k_A
41	C$_6$H$_5$Br	C$_6$H$_5$CH$_2$Cl	1.21
42	C$_6$H$_5$Br	C$_6$H$_5$CH$_2$Cl	1.26
43[b]	C$_6$H$_5$Br	C$_6$H$_5$CH$_2$Cl	1.48
44[b]	C$_6$H$_5$Br	C$_6$H$_5$CH$_2$Cl	1.55
45	C$_6$H$_5$CH$_2$Cl	2-BrC$_4$H$_9$	34.4
46	C$_6$H$_5$CH$_2$Cl	2-BrC$_4$H$_9$	34.5
47[b]	C$_6$H$_5$CH$_2$Cl	2-BrC$_4$H$_9$	32.2
48[b]	C$_6$H$_5$CH$_2$Cl	2-BrC$_4$H$_4$	32.0
49	CH$_2$=CHCH$_2$Cl	2-BrC$_8$H$_{17}$	15.4
50	CH$_2$=CHCH$_2$Cl	2-BrC$_8$H$_{17}$	17.3
51	C$_6$H$_5$CH$_2$Cl	CH$_2$=CH$_2$—CH$_2$Cl	1.83
52	HC≡C—CH$_2$Cl	2-BrC$_8$H$_{17}$	4.71
53	HC≡C—CH$_2$Cl	2-BrC$_8$H$_{17}$	5.57
54	HC≡C—CH$_2$Cl	2-BrC$_8$H$_{17}$	4.46
55	C$_6$H$_5$CH$_2$Cl	m-CF$_3$C$_6$H$_4$CH$_2$Cl	1.60
56	C$_6$H$_5$CH$_2$Cl	m-CF$_3$C$_6$H$_4$CH$_2$Cl	1.68
57	2-BrC$_8$H$_{17}$	BrCH$_2$Cl	7.95
58[c]	2-BrC$_8$H$_{17}$	BrCH$_2$Cl	8.40
59[b]	2-BrC$_8$H$_{17}$	BrCH$_2$Cl	8.66

[a] In cumene as solvent. [b] Reactions conducted without the addition of azobisisobutyronitrile. [c] In bromobenzene as solvent.

umn of 40% dimethyl sulfolane on firebrick (40 mesh) with results shown in Table II.

Reduction of Optically Active α-Phenylethyl Chloride by Triphenyltin Deuteride.—To 17.5 mmoles of α-phenylethyl chloride, α^{27}D +40.18° (neat), was added 19.2 mmoles of triphenyltin deuteride, prepared by reduction of the chloride with lithium aluminum deuteride, and the mixture was allowed to stand at room temperature for 23 hr., during which time crystals of triphenyltin chloride formed in the flask. After heating on the steam bath for 4 hr. to ensure complete reaction the product was distilled yielding 1.41 g. of α-deuteriophenylethane, b.p. 65–67° at 77–80 mm., α^{27}D 0.02° ± 0.03° (neat). A control experiment showed no detectable racemization of the optically active chloride by the organotin chloride under the conditions of the reduction reaction.

Determination of Relative Reactivities of Halides.—The relative rate constants were determined by allowing the halides

to compete in pairs for an insufficient amount of hydride. Usually a half-mole of hydride was used per mole of halide. The competitors and an internal standard were placed in the reaction flask or ampoule followed by solvent and organotin hydride. The reaction vessel was kept in a constant temperature bath until all of the hydride was consumed as indicated by the absence of hydrogen evolution upon treatment with an ethereal solution of sulfuric acid. Analysis for unreacted halide and/or reduction product was made by gas chromatography using the internal standard method described by Keulemans.[26] A 4-ft. column packed with 20% paraffin oil on Chromosorb P (80–100 mesh) was used in most experiments. When m-trifluoromethylbenzyl chloride and benzyl chloride were the competitors a 4-ft. column packed with 17% silicone nitrile on Chromosorb P (60–80 mesh) was used. Relative rate constants were computed by the method of Ingold and Shaw.[16] In most cases the solvent was chlorobenzene or bromobenzene. For analytical convenience other solvents were used on occasion; these included toluene, cumene, cyclohexane, and 2,3-dimethylbutane. When using bromochloromethane and 2-bromooctane as competitors, the same relative rate constants were obtained with cumene and bromobenzene as solvents, indicating that the relative rates would vary little among the solvents used. Results of the individual competition experiments are given in Tables VI and VII.

(26) A. I. M. Keulemans, "Gas Chromatography," Reinhold Publishing Corp., New York, N. Y., 1957, p. 32.

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The Nature of Chromium(VI) in Acid Solution and Its Relation to Alcohol Oxidation[1]

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A spectroscopic investigation of the variation of the pK_a of chromic acid with changes in the identity of the mineral acid solvents has been made, and the results have been applied to explain observed variations in the rate of oxidation of isopropyl alcohol in solutions of different mineral acids. Protonation of the acid chromate ion is accompanied by incorporation of the mineral acid anion into the chromium(VI) species and this markedly affects the latter's oxidizing ability. The mechanism of the chromium(VI)–alcohol reaction in moderately concentrated aqueous solutions of mineral acid, HA, is believed to occur by a cyclic, unimolecular decomposition of the chromate ester, R$_2$CHOCrO$_2$AH$^+$.

Introduction

The mechanism of chromic acid oxidations of organic substrates has been extensively investigated by a large number of workers. Most commonly mechanistic

deductions have been drawn from the observation of changes in kinetic rate data that occurred when the