Organotin Hydrides and Organic Free Radicals

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Organotin hydrides are useful intermediates for reduction of organic compounds such as halides, aldehydes, ketones, isocyanates, and isothiocyanates. They also find use for synthesis of other organotin compounds because they add to carbon–carbon double and triple bonds. Certain of these reactions can proceed by free-radical mechanisms in which organic radicals are intermediates. Hydrogen atom transfer from organotin hydrides to these radicals is a very fast process ($k \simeq 10^4$–$10^6\ M^{-1}\ \sec^{-1}$). As a result, it has been possible to trap initially formed radicals before they undergo secondary reactions. Examples discussed involve cyclooct-4-enyl, ω-alkenyl, bicycloheptenyl, tritylmethyl, and β-haloalkoxy radicals, as well as 1-naphthaldehyde triplet states.

Although organotin hydrides have been known for at least four decades, their chemistry received only sporadic attention until about 10 years ago. The current interest in these compounds probably received its greatest impetus from the exploratory investigations carried out by van der Kerk and his collaborators.[1] In the intervening years these compounds have been shown to be of considerable value, particularly as intermediates for the synthesis of organotin compounds and as reducing agents. For reasons which will be made evident below, they have also seen increasing use in the study of organic free radicals. This account will provide a brief survey of the general chemistry of organotin hydrides, followed by a more detailed discussion of two of their reactions, their scopes, mechanisms, and applications in synthetic and mechanistic chemistry.

## Preparation of Organotin Hydrides

The oldest known method, and one of the least used, for preparation of organotin hydrides involves the preparation of an organotin sodium in liquid ammonia, followed by reaction with ammonium bromide (eq 1).[2,3]

$$R_3SnBr + 2Na \longrightarrow NaBr + R_3SnNa \xrightarrow{NH_4Br}$$
$$R_3SnH + NH_3 + NaBr \quad (1)$$
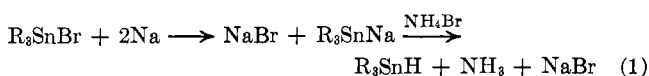
It will be noted that the organotin anion is converted to the hydride by proton abstraction from the ammonium ion.

Halogen bound to tin can be replaced by hydrogen from LiAlH₄,[4] NaBH₄,[5] or dialkylaluminum hydrides.[6]

Oxygen bound to tin can be replaced by hydrogen from hydrosilanes,[7] LiAlH₄,[8] and dialkylaluminum hydrides.[6] LiAlH₄ gives high yields and is the most generally useful. NaBH₄ also gives high yields from organotin halides, but only one of the hydrogens of the borohydride is used, the remainder being "wasted" as diborane (eq 2).

$$2R_3SnCl + 2NaBH_4 \xrightarrow[\text{or monoglyme}]{\text{diglyme}} 2R_3SnH + 2NaCl + B_2H_6 \quad (2)$$
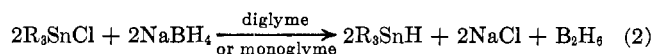
The hydrosilane method, particularly if polymethylhydrosiloxane is used, is perhaps the most convenient for the preparation of lower trialkyl monohydrides, for the reagents need only to be mixed without solvent and the hydride removed by distillation (eq 3). A rather

$$(R_3Sn)_2O + (CH_3SiHO)_n \longrightarrow \longrightarrow R_3SnH + (CH_3SiO_{1.5})_n \quad (3)$$

novel method which appears not to have been explored very extensively involves the thermal decomposition of trialkyltin formates as shown in eq 4.

$$R_3SnOCHO \xrightarrow{\Delta} R_3SnH + CO_2 \quad (4)$$
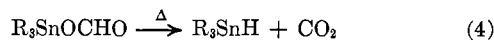
Properties of Organotin Hydrides

The obvious physical characteristics of organotin hydrides are similar to those of the corresponding hydrocarbons with the exception that a carbon atom is replaced by the heavier tin atom. Thus trimethyltin hydride is a liquid boiling at 59°, whereas the carbon analog, isobutane, boils at −12°. The most striking spectroscopic properties of organotin hydrides lie in the location of the Sn–H stretching frequency in the region between 1800 and 1900 cm⁻¹ and the location of the signal from the proton attached to the tin atom in the region around τ 5–6, although higher and lower values have been reported.[1a,9] In addition, protons on carbon atoms attached to tin show three signals in the nmr spectrum. The major signal is a singlet

(1) For recent reviews see: (a) H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 47 (1964); (b) W. P. Neumann, *Angew. Chem.*, **76**, 849 (1964); W. P. Neumann, "Die Organische Chemie des Zinns," Enke Verlag, Stuttgart, 1967.

(2) C. A. Kraus and W. N. Greer, *J. Am. Chem. Soc.*, **44**, 4269 (1922).

(3) Although organotin dihydrides and trihydrides can be prepared, we shall use monohydrides only in this and other illustrations.

(4) A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 2692 (1947).

(5) E. A. Birnbaum and P. H. Javora, *J. Organometal. Chem.* (Amsterdam), **9**, 379 (1967).

(6) W. P. Neumann and H. Niermann, *Ann.*, **653**, 164 (1962).

(7) K. Hayashi, J. Iyoda, and I. Shiihara, *J. Organometal. Chem.* (Amsterdam), **10**, 81 (1967).
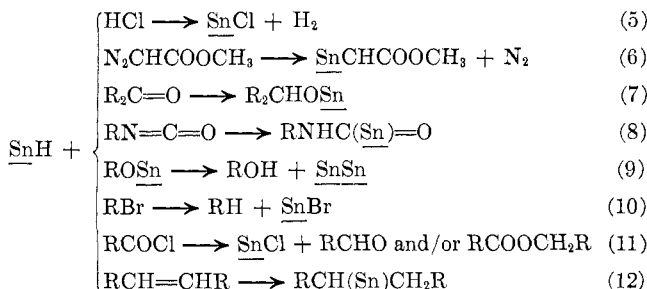
(8) W. J. Considine and J. J. Ventura, *Chem. Ind.* (London), 1683 (1962).

(9) Y. Kawasaki, K. Kawakami, and T. Tanaka, *Bull. Chem. Soc. Japan*, **38**, 1102 (1965).

from those molecules containing ^{118}Sn. There also are two doublets with coupling constants usually between 50 and 60 Hz due to ^{117}Sn and ^{119}Sn, with the value for the latter being larger by about 3 Hz.

Certain organotin hydrides are toxic and should be handled with care, but extreme precautions are not usually necessary. They react readily with oxygen in the air but do not inflame upon exposure. Thermal decomposition, which occurs with increasing ease as the number of hydrogen atoms bonded to tin increases, leads to the formation of hydrogen and compounds containing tin–tin bonds. The most facile reactions, regardless of coreactant, lead to cleavage of the tin–hydrogen bond. This clearly suggests that this bond is weaker than the tin–carbon bond, although no values for its dissociation energy appear to be available in the literature.
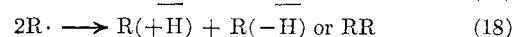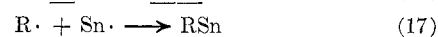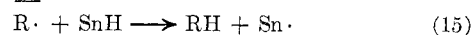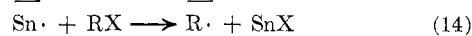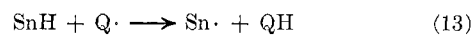
Equations 5 through 12 comprise a list of reactions of organotin hydrides with organic compounds chosen to be illustrative, but not comprehensive. Although mechanisms of all these reactions are not known,

$$SnH + \begin{cases} HCl \longrightarrow SnCl + H_2 & (5) \\ N_2CHCOOCH_3 \longrightarrow SnCHCOOCH_3 + N_2 & (6) \\ R_2C{=}O \longrightarrow R_2CHOSn & (7) \\ RN{=}C{=}O \longrightarrow RNHC(Sn){=}O & (8) \\ ROSn \longrightarrow ROH + SnSn & (9) \\ RBr \longrightarrow RH + SnBr & (10) \\ RCOCl \longrightarrow SnCl + RCHO \text{ and/or } RCOOCH_2R & (11) \\ RCH{=}CHR \longrightarrow RCH(Sn)CH_2R & (12) \end{cases}$$

there is adequate information in the literature to show that (5) and (8), for example, can proceed by polar mechanisms, (7) can proceed by either a polar or a free-radical mechanism, and (10) and (12) usually proceed by free-radical mechanisms. The remainder of this account will be concerned with consideration of the last three reactions of this group with emphasis on mechanisms, synthetic scope, and applications to the study of properties of transient free radicals.

Reduction of Alkyl and Aryl Halides

The original reports on the reduction of alkyl and aryl halides[10] by organotin hydrides have been followed by a number of papers concerning the scope and mechanism of the reaction. It is generally accepted that the reduction of simple halides proceeds by a free-radical chain mechanism[11] involving reactions 14 and 15 as chain-carrying steps and reactions 16–18 as possible termination steps. Several lines of evidence support this formulation. The presence of a tercovalent carbon intermediate can be adduced from the observations that optically active α-phenylethyl chloride with tri-

$$SnH + Q\cdot \longrightarrow Sn\cdot + QH \qquad (13)$$
$$Sn\cdot + RX \longrightarrow R\cdot + SnX \qquad (14)$$
$$R\cdot + SnH \longrightarrow RH + Sn\cdot \qquad (15)$$
$$2Sn\cdot \longrightarrow SnSn \qquad (16)$$
$$R\cdot + Sn\cdot \longrightarrow RSn \qquad (17)$$
$$2R\cdot \longrightarrow R(+H) + R(-H) \text{ or } RR \qquad (18)$$

phenyltin deuteride yields racemic α-deuterioethylbenzene; that α- and γ-methylallyl chlorides each lead to formation of mixtures of 1-butene and cis- and trans-2-butenes; and that reduction of propargyl bromide leads to formation of both propyne (85%) and allene (15%) at 45° in the absence of a solvent.[11] Evidence that the intermediate is a free radical follows from catalysis of the reaction by azobisisobutyronitrile, by oxygen, and by light,[12] and from the fact that it can be retarded by hydroquinone.

Assuming that the mechanism shown is correct, eq 14 provides a means of determining the relative ease with which an organotin radical abstracts a halogen atom from carbon. This can be determined by placing a halide in competition with another for an insufficient amount of hydride. The results obtained follow a trend expected for the reaction in question assuming that strength of the carbon–halogen bond being broken and stability of the resulting carbon free radicals are prime factors. For bromides reactivity sequences are: tertiary > secondary > primary; alkyl $<$ $C_6H_5CH_2$ $\cong$ $CH_2{=}CHCH_2$ $<$ $CH{\equiv}CCH_2$; Cl_3C > Cl_2HC > ClH_2C > $n\text{-}C_4H_9$. An exception is noted in the observation that propargyl bromide is more reactive than allyl bromide (by a factor of 4.5). This can be rationalized if one considers the organotin radical to be *nucleophilic* relative to a simple carbon radical and that the polar factor plays a role in stabilizing the transition state by way of contributing structures as

$$CH_2{=}CH\overset{\delta-}{CH_2}\text{-}\text{-}Br\text{-}\text{-}\overset{\delta+}{Sn}$$
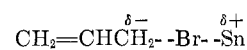
If this is important, the propargyl halide would be expected to be the more reactive because the ethynyl group with its sp hybridization is more electron attracting than the vinyl group with its sp^2 hybridization.

In general, organotin dihydrides are more reactive than the monohydrides, but they are not commonly used because they are considerably less stable. Organotin trihydrides appear not to have been used for the reduction of halides.

From the synthetic standpoint, reduction of geminal polyhalides is one of the more useful applications. It was shown in our initial exploratory work[13] that benzotrichloride could be reduced stepwise to benzal chloride and to benzyl chloride cleanly and in good yields. This characteristic has been exploited in the reduction of adducts of dibromocarbene to simple olefins[14] and

(10) G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.*, **7**, 356 (1957); J. G. Noltes and G. J. M. van der Kerk, "Functionally Substituted Organotin Compounds," Tin Research Institute, Greenford, England, 1956, p 72; J. G. Noltes and G. J. M. van der Kerk, *Chem. Ind.* (London), 294 (1959).

(11) H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Am. Chem. Soc.*, **84**, 3584 (1962); L. W. Menapace and H. G. Kuivila, *ibid.*, **86**, 3047 (1964).

(12) R. J. Strunk, Ph.D. Dissertation, State University of New York at Albany, June 1967.

(13) H. G. Kuivila and L. W. Menapace, *J. Org. Chem.*, **28**, 2165 (1963).

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

allenes[15] to yield successively the monobromo derivatives and the hydrocarbons in high yields. Of special interest here is the reduction of dibromonorcarane to the monobromide (eq 19). Presumably the alkyl radical formed by bromine abstraction undergoes rapid interconversion between the isomer in which the remaining bromine is *exo* and that in which it is *endo*. In the product-forming step the hydrogen may be transferred to either the *exo* or *endo* position, with the former favored because of the steric factor. This is, indeed, the case,
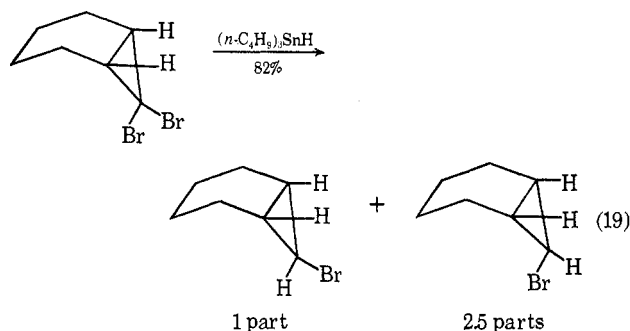
but the *endo* monobromide predominates by a factor of only 2.5. This may be due either to nonbonded interactions between bromine and *endo* hydrogens on the 3 and 4 carbons which would tend to destabilize the *endo* radical, or to a relatively modest steric effect in the hydrogen-transfer step, or both.

Perhaps the most convenient way of carrying out reductions of halides, and other reactions, with organotin hydrides involves generation of the hydride by reacton 3, followed by addition of the substrate to the mixture of hydride and methylpolysiloxane.[16] The reaction between hydride and substrate can then be initiated in any of the conventional ways.
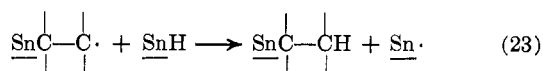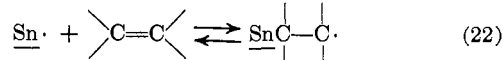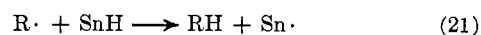
High yields can generally be obtained in thermal or photocatalyzed reactions. Furthermore, the data indicate that reduction of alkyl chlorides, bromides, and iodides occurs more readily than addition to double or triple bonds or reduction of ketones, esters, nitriles, or the pyridine ring.

### Addition to Carbon–Carbon Double Bonds

Hydrostannation (eq 12) is undoubtedly the most useful reaction for the preparation of organotin compounds containing functional groups. Terminal olefins and acetylenes react with particular facility, with the latter being more reactive. An intimation of the scope of the reaction is provided by the range of functional groups which do not interfere with the reaction. Among these are the keto,[17] carbalkoxy,[18] cyano,[18]

hydroxyl, pyridyl and N-carbazyl. Conjugated dienes give 1,2 and 1,4 adducts, with the latter predominating in all cases thus far reported.[19] Allenes give varying proportions of attack by the organotin group at the central carbon: allene, 1,2-butadiene, 3-methyl-1,2-butadiene, and 2,3-pentadiene give 45, 86.5, 100, and 100%, respectively, of such products.[20]

The mechanism generally accepted for olefins not substituted by strongly electron-releasing groups is shown in eq 20–23.[1a,21] Evidence for the free-radical

$$\text{initiator} \longrightarrow 2R\cdot \qquad (20)$$

$$R\cdot + \text{SnH} \longrightarrow RH + \text{Sn}\cdot \qquad (21)$$

$$\text{Sn}\cdot + \underset{}{>}C=C\underset{}{<} \rightleftharpoons \text{SnC}-C\cdot \qquad (22)$$

$$\text{SnC}-C\cdot + \text{SnH} \longrightarrow \text{SnC}-CH + \text{Sn}\cdot \qquad (23)$$

nature of the reaction includes catalysis by free-radical sources such as azobisisobutyronitrile, among others, and ultraviolet irradiation[22] and retardation by the efficient scavenger, galvinoxyl.[21] Evidence for reversibility of reaction 22 with both internal and terminal olefins has been provided by Kuivila and Sommer.[23] In the case of internal olefins, isomerization of *cis*- and *trans*-2-butenes during addition demonstrated reversibility. In the case of the terminal olefins, styrene and 1-hexene, the result could be found by using *cis*- and *trans*-β-deuteriostyrenes and 1-hexenes (eq 24).
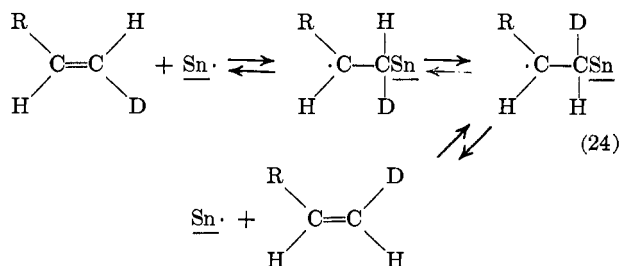
Organotin and Organic Free Radicals

Reaction 14 constitutes, in principle, a reaction in which an organic free radical can be generated at any position in a molecule into which a chlorine, bromine, or iodine atom can be introduced. Similarly, reaction 22 is one which can lead to the generation of an organic free radical from an appropriately located double

(15) W. Raman and H. G. Kuivila, *J. Org. Chem.*, **31**, 772 (1966).

(16) G. L. Grady, unpublished observations in this laboratory.

(17) α,β-Unsaturated ketones generally tend to undergo 1,4 addition to form the organotin analogs of vinyl ethers as major products (M. Pereyre, Ph.D. Dissertation, University of Bordeaux, 1965; M. Pereyre and J. Valade, *Bull. Soc. Chim. France*, 1928 (1967)), contrary to an earlier report that only the carbonyl group is reduced (H. G. Kuivila and O. F. Beumel, Jr., *J. Am. Chem. Soc.*, **83**, 1246 (1961)).

(18) If more than one strongly electron-withdrawing group is attached to the double bond, 1,4 addition may occur. For example, ethylidenemalononitrile yields $CH_3CH_2C(CN)=C=NSn(C_2H_5)_3$ with triethyltin hydride (W. P. Neumann R. Sommer, and E. Muller, *Angew. Chem.*, **78**, 545 (1966)).

(19) W. P. Neumann and R. Sommer, *Ann.*, **701**, 28 (1967); R. H. Fish, H. G. Kuivila, and I. J. Tyminski, *J. Am. Chem. Soc.*, **89**, 5861 (1967).

(20) H. G. Kuivila, W. Rahman, and R. H. Fish, *ibid.*, **87**, 2835 (1965).

(21) W. P. Neumann and R. Sommer, *Ann.*, **675**, 10 (1964).

(22) H. C. Clark, S. G. Furnival, and J. T. Kwon, *Can. J. Chem.*, **41**, 2889 (1963); C. Barnetson, H. C. Clark, and J. T. Kan, *Chem. Ind.* (London), 458 (1964); H. C. Clark and J. T. Kwon, *Can. J. Chem.*, **42**, 1288 (1964).

(23) H. G. Kuivila and R. Sommer, *J. Am. Chem. Soc.*, **89**, 5616 (1967); W. P. Neumann, H. J. Albert, and W. Kaiser (*Tetrahedron Letters*, 2041 (1967)) have also adduced reversibility on the basis of isomerization of *cis*-piperylene under the conditions of addition of an organotin hydride. However, they assumed that an allylic radical underwent isomerization instead of the simple radical formed by attack at C-3 of the diene. The latter appears more likely.

bond. Accordingly, these reactions might be useful for the generation and study of the properties of organic free radicals. In practice, these reactions have proven to be highly useful in free-radical chemistry, and they have been exploited in several laboratories in the past few years. The utility of these reactions has resulted from the fact that organotin hydrides are good hydrogen donors. (They are not the best in the world, for hydrogen bromide and thiophenol and others, perhaps, are better.) This statement has been put into quantitative terms by Carlsson and Ingold.[24] They showed that the absolute rate constants for hydrogen transfer from triphenyl and tri-n-butyltin hydrides to t-butyl radicals, in M^{-1} sec^{-1}, were 5×10^6 and 3×10^5, respectively, and, for chlorine abstraction from t-butyl chloride by triphenyltin and tri-n-butyltin radicals were 3×10^4 and 1.5×10^4, respectively. These rate constants are of considerable significance for they indicate the approximate rates of intramolecular processes of carbon free radicals for which these reactions can be used as probes. This is to say that if the intramolecular process (such as rotation about single bonds) is much faster than the first two values, the intermediates cannot be intercepted, but if the intramolecular process is of the same order of magnitude as $k[R_3SnH]$ or slower, then the reaction will occur more rapidly than this process, and trapping can be effected. Examples of this situation will now be discussed.

Octen-5-yl Free Radicals

Dowbenko[25] and Friedman[26] examined the addition of a number of free-radical reagents such as aldehydes and carbon tetrachloride to cis,cis-1,5-cyclooctadiene. In each case they observed as the only product a bicyclo[3.3.0] adduct (eq 25). On the other hand,
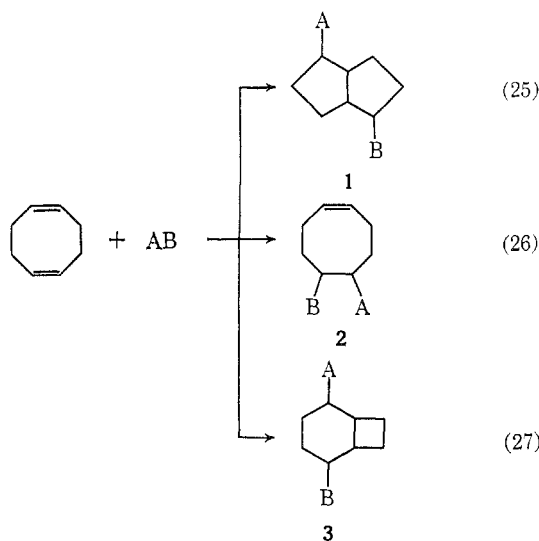
$$\text{(25)}$$
$$\text{(26)}$$
$$\text{(27)}$$

Locke and Duck observed only eq 26 using thiophenol and thiolacetic acids as addends.[27] They suggested the intermediate formation of a free radical, **4**, which could rearrange to radical **5** in the presence of a
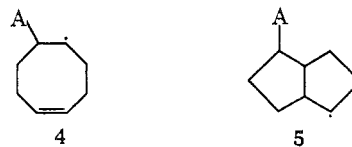
poor atom-transfer agent. However, if a good atom-transfer agent, such as a thiol, were present, the initially formed **4** would abstract hydrogen and form the 1,2 adduct before it rearranged. Trimethyltin hydride is intermediate in reactivity with these reagents.[28] At 150° a mixture of products containing 43% [3.3.0] adduct, 43% 1,2 addition product, and 14% of a third product presumed to be the [4.2.0] adduct is formed. When the temperature is lowered to −78° and the reaction initiated photochemically, the product contains more than 97% of the 1,2-addition product. Thus, whereas the thiols donate hydrogen atoms more rapidly than the cyclooctenyl radical rearranges to a bicyclic isomer, trimethyltin hydride is able to transfer hydrogen less efficiently at high temperatures, but with similar efficiency at low temperatures. These results show clearly that two radicals, at least, are involved in addition to cis,cis-1,5-octadiene but do not answer the question of whether one of these is nonclassical, as **6**. A third possible intermediate is **7**.
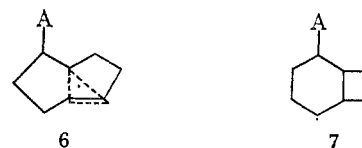
Cyclization of Unsaturated Acyclic Radicals

Walling and his coworkers have generated unsaturated organic radicals by halogen abstraction from appropriate halides and studied the distribution of products formed.[29] Their results can be summarized by the set of equations (28) in which 6-bromo-1-hexene was used as substrate. If the concentration of tri-n-

$$\text{(28)}$$

(24) D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, **90**, 1055 (1968).
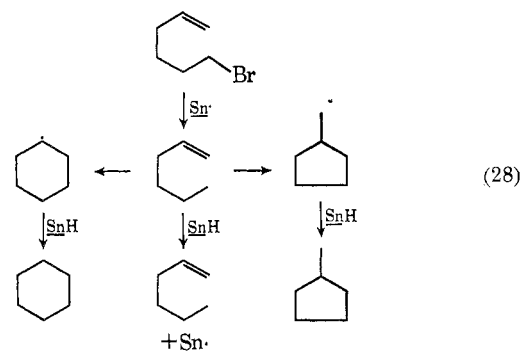
(25) R. Dowbenko, *Tetrahedron*, **20**, 1843 (1964); *J. Am. Chem. Soc.*, **86**, 936 (1964).
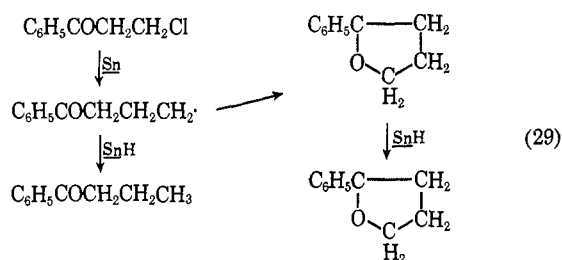
(26) L. Friedman, *ibid.*, **86**, 1885 (1964).

(27) J. M. Locke and E. W. Duck, *Chem. Commun.*, 151 (1965).

(28) I. J. Tyminski, Ph.D. Dissertation, University of New Hampshire, 1967.

(29) C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *J. Am. Chem. Soc.*, **88**, 5361 (1966).

butyltin hydride was large, 1-hexene and methyl-cyclopentane were formed in comparable amounts. if the concentration of hydride was low, methylcyclopentane predominated in a ratio 11:1. Somewhat surprisingly, little or no cyclohexane was formed in these experiments. Here again the time scale for ring closure is similar to that for hydrogen transfer from hydride to carbon free radical.

Cyclization of the intermediate radical was also observed in the reduction of γ-chlorobutyrophenone. Reaction with tri-*n*-butyltin hydride provided a 65% yield of product containing 80% 2-phenyltetrahydrofuran and 20% butyrophenone (eq 29).[11] The driving force for the ring closure is undoubtedly the formation

$$C_6H_5COCH_2CH_2Cl$$

$$\downarrow Sn$$

$$C_6H_5COCH_2CH_2CH_2 \cdot \quad \longrightarrow$$

$$\downarrow SnH$$

$$C_6H_5COCH_2CH_2CH_3 \qquad\qquad (29)$$

of a species which is both a benzylic and an α-alkoxy radical.

The norbornenyl–nortricyclyl radical system (8 ⇌ 9) is another one in which ring closure of an unsaturated radical, as well as the reverse process, is of interest. Perhaps the most clear-cut evidence for a discrete norbornenyl radical was obtained by Cristol and


8   **9**
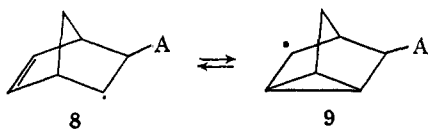
Davies,[30] who showed that the amount of 2,3 adduct obtained in the addition of arenesulfonyl halides depended on the nature and concentration of the halide (I > Br > Cl).

Another way of generating the radicals 8 ⇌ 9 is by the reaction of the norborn-2-en-5-yl and 3-nortricyclyl halides with organotin hydrides.[31] When tri-*n*-butyltin hydride was used, the product from each had the same proportions of norbornene and nortricyclene, indicating rapid equilibration of intermediate radicals. On the other hand, reduction of nortricyclyl bromide with triphenyltin hydride, neat, yielded a hydrocarbon mixture containing 56.5 ± 3% nortricyclene, whereas dilution with pentane yielded a mixture containing only 45.5 ± 2%. Thus, partial trapping of initially formed nortricyclyl radicals was effected. The relative rates of reduction of these and other cyclic halides fall within a relatively narrow range and indicate that anchimeric assistance does not attend the halogen-abstraction step in these reductions.[31] Although the results cited require the existence of at least two intermediate

radicals, they do not rule out the possibility that one of these may be nonclassical (**10**) or that a third, presumably nonclassical, radical exists in equilibrium with the two classical ones.


10
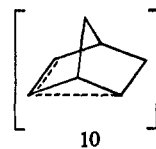
Still other possible processes have been suggested by a study of the addition of trimethyltin hydride to norbornadiene. The reaction, thermal or photocatalyzed, provided a mixture of *endo*- and *exo*-norborn-2-en-5-yltrimethyltin and 3-nortricyclyltrimethyltin.[32] In a typical experiment carried out photochemically at 65°, the product mixture contained 35% *endo*-norborn-2-en-5-yltrimethyltin, 43% *exo* isomer, 11% nortricyclyl isomer, and 11% of a fourth product whose analytical and spectroscopic data are consistent with structure **11**, norborn-2-en-7-yltrimethyltin. The large

11
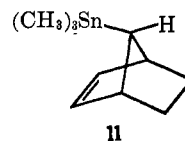
proportion of *endo*-norbornenyltrimethyltin was unexpected and is tentatively attributed to the intermediacy of species **12** in which norbornadiene is functioning as a bidentate ligand in coordinating with vacant d orbitals on the organotin free radical. Another piece of evidence which makes this reasonable is the observation made by Fish that, in the addition of trimethyltin hydride to butadiene, the 1,4 adduct contained 1.47 times as much *cis* isomer as *trans*.[19] Radical **13** may play a role directing the course of the reaction.

12   **13**

Formation of **11** can be rationalized either by rearrangement of the initially formed radical by migration of the vinyl from C-1 to C-6 in the *endo* radical or by its conversion to a nortricyclyl radical, followed by cleavage of another bond of the cyclopropane ring (eq 30).
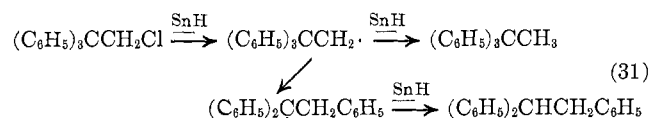

$$(30)$$
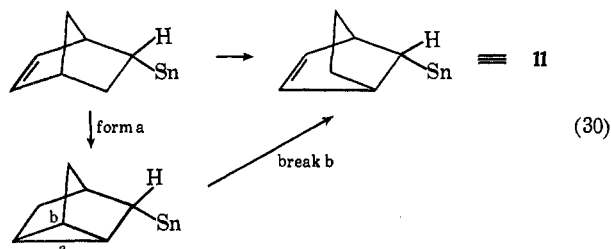
(30) S. J. Cristol and D. I. Davies, *J. Org. Chem.*, **29**, 1282 (1964).
(31) C. R. Warner, R. J. Strunk, and H. G. Kuivila, *ibid.*, **31**, 3381 (1966).

(32) O. R. Khan, I. J. Tyminski, F. L. Pelczar, and R. Y. Tien, unpublished observations.

The Tritylmethyl Radical

A number of investigators have examined reactions in which this radical might be generated. Most observed complete rearrangement of this radical to the 1,1,2-triphenylethyl system. This raised the question of whether rearrangement accompanied radical formation. A suggestion that the tritylmethyl radical has a discrete lifetime was the observation that decomposition of 3,3,3-triphenylpropanoyl peroxide led to the formation of up to 4.9% 1,1,1,4,4,4-hexaphenylbutane.[33] A more clear-cut demonstration for the discrete existence of the tritylmethyl radical was realized when tritylmethyl chloride was subjected to reduction with triphenyltin hydride.[34] If the concentration of the hydride was high enough, as much as 90% of the product was 1,1,1-triphenylethane, the remainder being 1,1,2-triphenylethane. Equation 31 describes the probable course of events in this reaction.

$$(C_6H_5)_3CCH_2Cl \xrightarrow{SnH} (C_6H_5)_3CCH_2 \cdot \xrightarrow{SnH} (C_6H_5)_3CCH_3$$
$$\swarrow \qquad\qquad (31)$$
$$(C_6H_5)_2\dot{C}CH_2C_6H_5 \xrightarrow{SnH} (C_6H_5)_2CHCH_2C_6H_5$$

Free-Radical β Eliminations

In contrast to geminal halides, vicinal dibromides formed by the addition of bromine to ethylene, propylene, isobutylene, *trans*-stilbene, and *cis*- and *trans*-2-butenes undergo dehalogenation with organotin hydrides according to eq 32.[35] If triethylamine is added

$$Br\overset{|}{C}-\overset{|}{C}Br + 2SnH \longrightarrow 2SnBr + H_2 + \underset{}{>}C=C\underset{}{<} \quad (32)$$
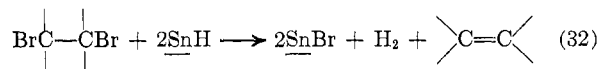
to the reaction mixture, only 1 mole of organotin hydride need be used. Organotin bromide, olefin, and triethylammonium bromide are formed, but hydrogen is not. Thus, it is concluded that hydrogen bromide is an intermediate which reacts with 1 mole of hydride to generate the hydrogen and organotin bromide. The results obtained in a study of the stereochemistry of the reaction as a function of concentration of reactants are shown in Table I. The first point to be noted is that the reaction is a partially stereospecific *anti* elimination. Secondly, the degree of stereospecificity depends upon the concentration of organotin hydride. By contrast to these two dibromides, the corresponding chlorides undergo reduction to butane as the major reaction, and the small amounts of butenes formed contain the same amounts of *cis* and of *trans* regardless of the stereochemistry of the starting dichloride.

These results can be accounted for in terms of eq 33. Organotin radical abstracts a halogen atom leading to formation of the bridged radical **14** which can establish an equilibrium with the open-chain radical **15**. If X is bromine, the bridged radical is relatively stable and

Table I
Effect of Concentration on the Stereochemistry of Dehalogenation of 2-Butenes by Tri-*n*-butyltin Hydride

	Temp, °C	SnH/Br	Concn	—Butene— % *trans*	% *cis*
meso	25	1	Neat	90	10
dl	25	1	Neat	34	66
meso	25	5	Neat	90	10
dl	25	5	Neat	24	76
meso	25	1	1.9 *M* ethyl ether	84	16
dl	25	1	1.9 *M* ethyl ether	41	59

can react with organotin hydride to give over-all *anti* elimination, the extent of which depends on the hydride concentration. If hydride concentration is low, **15** can form and close up again to give either the original *trans* bridged radical or the *cis* diastereomer (not shown). If X is chlorine, the bridged radical is much less stable, and **15** is the predominating species. Reaction with hydride is not fast enough to intercept any **14** before it has become equilibrated with **15**. Furthermore, **15** reacts with hydride at the carbon bearing the unpaired electron to give 2-chlorobutane, which is further reduced to butane.
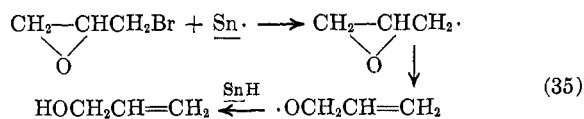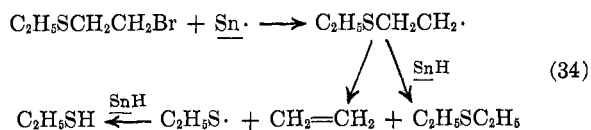

(33)
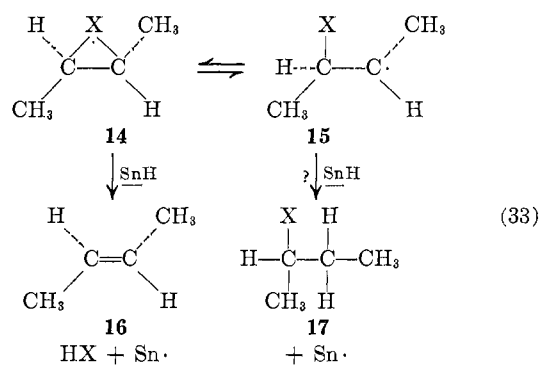
If this rationale be sound, it would be of interest to seek the possible occurrence of anchimeric assistance in the formation of the intermediate radicals. To test this, experiments were conducted with dibromides and the configurationally related chlorobromides from *trans*-2-butene and styrene. Results obtained, after correction for the statistical factor of two for the dibromides, were in the right direction for anchimeric assistance but not as dramatic as might be hoped: the dibromide from *trans*-2-butene reacted 64% faster than the chlorobromide, and for the styrene adduct the factor was 30%.

Further examples of eliminations induced by organotin hydrides are shown in eq 34 and 35. In the former, when the reactants were mixed neat at ambient temperature the product contained equimolar amounts of diethyl sulfide, the product of simple reduction, and of ethyl mercaptan and ethylene, the products of a β elimination. The reduction of epibromohydrin

(33) D. B. Denney, R. L. Ellsworth, and D. Z. Denney, *J. Am. Chem. Soc.*, **86**, 1116 (1964).
(34) L. Kaplan, *ibid.*, **88**, 4531 (1966).
(35) H. G. Kuivila and R. J. Strunk, unpublished observations.

$$C_2H_5SCH_2CH_2Br + \underline{Sn}\cdot \longrightarrow C_2H_5SCH_2CH_2\cdot$$

$$C_2H_5SH \overset{SnH}{\rightleftarrows} C_2H_5S\cdot + CH_2{=}CH_2 + C_2H_5SC_2H_5 \qquad (34)$$

$$CH_2{-}CHCH_2Br + \underline{Sn}\cdot \longrightarrow CH_2{-}CHCH_2\cdot$$

$$HOCH_2CH{=}CH_2 \overset{SnH}{\rightleftarrows} \cdot OCH_2CH{=}CH_2 \qquad (35)$$

yields as the main product allyl alcohol, formed, as depicted, by another β elimination. No propylene oxide was observed.

Vinyl Free Radicals

For several years chemists have been seeking ways in which to determine, on the one hand, whether vinyl radicals have the unpaired electron in an sp^2 orbital, in which case two equilibrating radicals shown below might be expected. On the other hand, the electron might be in a p orbital, in which case only one radical would exist, and questions regarding isomeric radicals would be irrelevant. The two cases are depicted below.
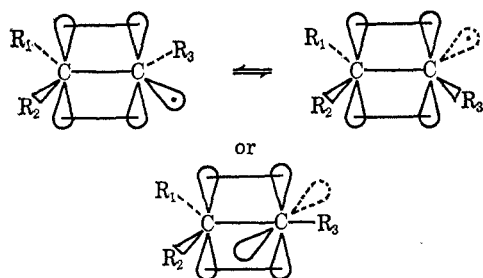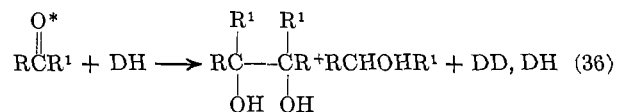

Evidence for the former case has been obtained from decompositions of α-substituted cinnamyl peroxy

esters[36] and cinnamoyl peroxides[37] and from reduction of 3-chloro-3-hexenes with sodium naphthalenide.[38] We have found similar evidence upon reduction of 2-bromo-2-butenes with tri-n-butyltin hydride. At $-75°$ the 2-butenes obtained from the *cis* bromide contained 57% of the *cis* isomer, whereas that from the *trans* isomer contained only 15%. The latter figure increased upon dilution of the reaction mixture. Thus, both the *cis*- and *trans*-but-2-en-2-yl radicals can be partially trapped by the hydride before complete equilibration.

Photoreduction

Many ketones react photochemically in the presence of secondary alcohols or alkyl benzenes (DH) to form the reduction products, alcohol or pinacol (eq 36), in which $RR^1C{=}O^*$ is the triplet state of the ketone.

$$\overset{O^*}{\underset{\|}{R\overset{}{C}R^1}} + DH \longrightarrow \overset{R^1 \quad R^1}{\underset{\underset{OH \ OH}{|}}{R\overset{}{C}{-}{-}\overset{}{C}R} {+} RCHOHR^1} + DD, DH \quad (36)$$

It was observed that neither 1-naphthaldehyde nor 2-acetonaphthone underwent reduction with the usual hydrogen donors. It was postulated that triplet energies for these compounds are not high enough to lead to hydrogen abstraction. This could be tested, and was found to be correct, by the use of the excellent hydrogen donor, tri-n-butyltin hydride.[39]

(36) L. A. Singer and N. P. Kong, *Tetrahedron Letters*, 643 (1967); *J. Am. Chem. Soc.*, **89**, 5251 (1967).

(37) O. Simmamura, K. Tokumaru, and H. Yui, *Tetrahedron Letters*, 5141 (1966).

(38) G. D. Sargent and M. W. Browne, *J. Am. Chem. Soc.*, **89**, 2788 (1967).

(39) G. S. Hammond and P. Leermakers, *ibid.*, **84**, 207 (1962).