The above mechanism also explains the much greater reactivity found for the anions of α,β unsaturated acids.[12] An additional advantage of this mechanism is that it escapes the unstable carbonium ion adjacent to the carboxylate group. Not only would such an intermediate be difficult to form, but it would be expected to react with solvent to produce bromohydrin and no such product is found. Bromohydrins would be less likely from the 1,4 addition mechanism as water is not sufficiently nucleophilic to attack the hypobromite. A similar argument[13] was invoked to explain why dilute HBr, but not dilute H_2SO_4, can isomerize maleic acid.

We therefore suggest that two mechanisms are operating in the aqueous bromination of maleate (and presumably fumarate): (1) the higher energy bromonium ion mechanism which effects a trans addition and (2) the lower energy 1,4 addition which produces primarily meso product. It should be noted that Atkinson and Bell,[14] on the basis of a kinetic study, have postulated that two pathways operate concurrently in the aqueous bromination of olefins. They suggest that the intermediate RBr^+ predominates in the bromination of simple alkenes whereas an intermediate RBr_2 is predominant in the bromination of diethyl fumarate. A later study[3] showed that the aqueous bromination of diethyl maleate and diethyl fumarate both gave the meso dibromide.

A typical experiment was done as follows: Maleic acid (2.9 g, 25 mmol) was dissolved in 25 mL of 2 M NaOH (50 mmol) and 2.0 g of sodium bromide (20 mmol) was added. This solution was mechanically stirred in a constant temperature bath while 25 mL of 1.0 M (25 mmol) bromine in carbon tetrachloride was added. When the bromine color disappeared, the organic layer was removed and the aqueous layer was acidified with 7 mL of concentrated hydrochloric acid and extracted with 2 × 75 mL of ether. The ether extracts were combined, dried over sodium sulfate, and evaporated on a steam bath. After further drying in a desiccator, these mixtures were dissolved in 12 mL of acetone and analyzed by proton NMR. Integration of the two peaks around 260 Hz indicated the proportion of isomers in the mixture (the racemic dibromide absorbing downfield of the meso product). In some cases, mixtures were also analyzed in basic D_2O solution. The identity of the peaks in the NMR spectrum was checked by the addition of authentic samples of each product. In some cases, the products were isolated, purified, and checked with mixture melting points.

The use of bromine in aqueous bromide solution in place of the two-phase addition of bromine in carbon tetrachloride was less convenient but gave similar amounts of products. The bromination using half molar amounts of base (producing sodium hydrogen maleate) appeared to go slower but gave similar data. The bromination using no base went much slower and caused precipitation of fumaric acid.

The stability of the products under reaction conditions was also checked.

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Stereochemistry of the Bromine Cleavage of Organotin Compounds

Sir:

On the basis of experiments with a single compound, optically active *sec*-butyltrineopentyltin,[1] the stereochemistry of bromodestannylation is generally described as involving inversion of configuration at carbon, with all the mechanistic consequences of such a statement.[2] Previously retention of configuration was found only in the case of optically active cyclopropyltin compounds.[3] This was easily rationalized in terms of the known resistance of cyclopropyl derivatives to react with inversion of configuration.[1] We report here some results which demonstrate clearly that inversion is *not* a general trend for *sec*-butyltrialkyltin compounds and, by extension, for other tetraalkyltins. Indeed retention of configuration appears to be the predominant mode of reaction and the steric requirements of the neopentyl group most probably are responsible for the special behavior of *sec*-butyltrineopentyltin.

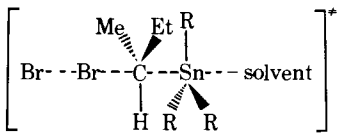
Our bromodestannylation experiments were carried out in the dark with 1:1 stoichiometry. The solution of bromine in methanol was added to the organotin compounds[4] in a 1:1 cyclohexane–methanol mixture at −10 °C and stirred for 12 h at 20 °C.[8]

$$\overset{*}{\text{EtCH(Me)SnR}_3} \xrightarrow[\text{MeOH, } C_6H_{12}]{Br_2} \overset{*}{\text{EtCH(Me)Br}} + \text{RBr} + \text{R}_3\text{SnBr} + \overset{*}{\text{EtCH(Me)SnR}_2\text{Br}}$$

Isopropyl and 3-pentyl (and 2-butyl) were selected as the R groups in *sec*-$BuSnR_3$ in order to ensure a rate of cleavage comparable to that of the *sec*-butyl group.[9] The results obtained, cleavage with predominant retention of configuration at carbon, prompted us to reexamine the cleavage of *sec*-butyltrineopentyltin (Table I).

Our experiments confirmed the experiment reported previously.

It would appear in the brominolysis of R_4Sn that at least two mechanisms, with opposite stereochemistry, are competing,[12] and the following transition states may be considered:



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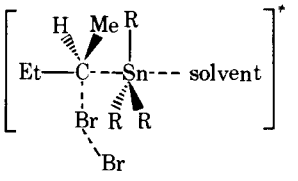
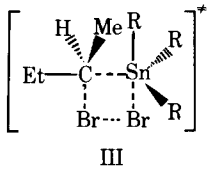


II



III

Transition states I[1] and II,[9] with nucleophilic assistance of methanol at tin, correspond respectively to inversion and re-

Table I. Stereochemistry of the Bromodemetalation of *sec*-Butyltrialkyltin Compounds in Methanol–Cyclohexane

sec-$BuSnR_3$ (% optical purity)	*sec*-BuBr[a] (% optical purity)	Predominant stereochemistry (% stereospecificity)
(*R*)-(−)-*sec*-$BuSn(i\text{-}Pr)_3$ (75)	*R* (−) (34)	Retention (45)
(+)-$(sec\text{-}Bu)_4Sn$[b]	*S* (+) (7.5)	Retention (ca. 35[c])
(*R*)-(−)-*sec*-$BuSn(3\text{-pentyl})_3$ (25)	*R* (−) (2)	Retention (8)
(*S*)-(+)-*sec*-$BuSn(neopentyl)_3$ (25)	*R* (−) (7)	Inversion (28)

[a] The maximum optical rotation has been taken as $[\alpha]^{22}D$ 34.2°.[10] [b] Obtained from (*S*)-(+)-*sec*-butyltriphenyltin (86% optical purity) as a mixture of three diastereoisomers.[11] [c] See note[11] for the significance of this value, which might be not very accurate.

tention of configuration, while the closed transition state III,[9] in which bond-making and breaking are not necessarily synchronous[15] (therefore developing charges and possible stabilization by solvent), will lead to retention.

Molecular models show clearly that front-side approach to the carbon by the halogen (II) is progressively hindered when R groups on tin are made bulkier.[16] Moreover, due to its steric requirements, a neopentyl group is much more reluctant to occupy an apical position (III) than a *sec*-butyl group (I). It is thus understandable that *sec*-butyltrineopentyltin will lead to a predominant inversion of configuration at carbon. With smaller R groups, the interactions are less severe and retention of configuration could be preferred on energetics grounds. Methyl or ethyl groups, too easily cleaved to be used in this study, should induce even more predominant retention mechanisms.

The data presented herein suggest that retention of configuration probably is the main stereochemical course of the bromodemetalation of tetraalkyltins in the presence of methanol.[17] In special cases, steric requirements would induce a predominant inversion mechanism.

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(8) The initial concentration was about 0.9 M for the tetraalkyltin to which a stoichiometric amount of 0.8 M bromine was added. ^{13}C and ^{119}Sn NMR spectra showed that the cleavages were quantitative. No residual tetraalkyltin or dihalogenated organotins were detected (amounts over 3% would have been observed). Quantitative yields for alkyl bromides were confirmed by GLC of the crude mixtures. Alkyl bromides were distilled together with solvents, then the methanol was removed with $CaCl_2$. Optical rotations were measured in cyclohexane after further GLC determination.
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(11) Symbolizing the chiral centers as *R* and *S*, Ph_3SnS should lead,[4] in absence of asymetric induction, to a mixture of three diastereoisomers: SnS_4 (0.125), optically inactive SnR_2S_2 (0.375), and both enantiomers $SnRS_3$ (0.375) and $SnSR_3$ (0.125). ^{119}Sn NMR analysis shows that the isomers are present in the above ratio, before and after limited brominolysis, indicating that the diastereoisomers react at very similar rates. With the likely hypothesis that bromine would remove R or S from $SnRS_3$ (and $SnSR_3$) at similar rates, the cleavage of a mixture obtained from optically pure Ph_3SnS should lead to *sec*-butylbromide with a 25% maximum optical purity.
(12) Control experiments have shown that under the conditions of the demetalation (in the presence of trialkyltin bromide[13] and methanol) as well as during the workup, *sec*-butyl bromide does not undergo racemization. Moreover the presence of methanol and the absence of light is intended to prevent major contribution by a radical cleavage mechanism.[3,14]
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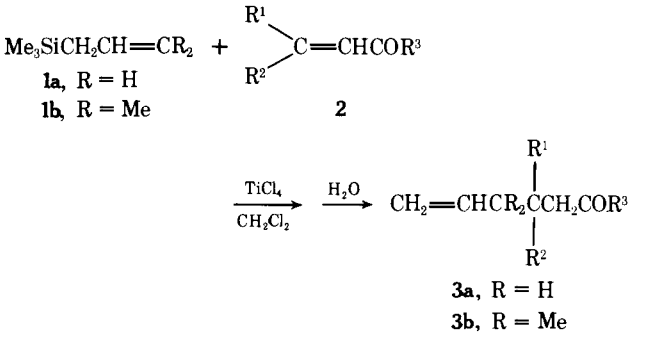
Conjugate Addition of Allylsilanes to α,β-Enones. A New Method of Stereoselective Introduction of the Angular Allyl Group in Fused Cyclic α,β-Enones[1]

Sir:

Allylsilanes are interesting synthetic intermediates with highly nucleophilic double bonds,[2] and recently we have demonstrated that the allyl transfer reaction takes place very smoothly from allylsilanes to carbonyl compounds[3a] and acetals,[3b] with regiospecific transposition of the allylic part, to afford homoallyl alcohols and homoallyl ethers, respectively. Titanium chloride is the most effective activator of the reaction among various Lewis acids.

In this paper, we show the allylation reaction can be applied successfully to α,β-enones to give δ,ε-enones. The most important fact of the findings may be that the allyl group can be introduced at the angular position of a fused cyclic α,β-enone, selectively in high yield.



The results are listed in Table I. As a general procedure, to a solution of an α,β-enone (2 mmol) in dry dichloromethane (3 mL) under nitrogen was added titanium tetrachloride (2 mmol) dropwise with a syringe. After additional stirring for 5 min, an allylsilane (2.2 mmol) in dichloromethane (3 mL) was added from a dropping funnel at a temperature indicated in the table and the mixture was stirred for 3 h. Water was added to the mixture which was subsequently extracted with ether. The organic layer was washed with water, dried over sodium sulfate, and concentrated at reduced pressure. The residue was subjected to silica gel column chromatography, yielding a δ,ε-enone. The products were mostly pure enough to give correct analyses and were characterized by GLC,