making known his experimental results before publication and Dr. William Movius for valuable discussions.

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The Synthesis of Optically Active Organo Derivatives of Group IV Elements[1]

Sir:

Considerable evidence has accumulated indicating the electrophilic cleavages of organometallic compounds, in which vacant orbitals are available on the metal, occur with retention of configuration. For example, the electrophilic cleavage of organomercurials by bromine occurs with retention of configuration apparently through a closed transition state.[2] The observed retention of configuration is forced by the mechanism. One method of investigating the stereochemistry of electrophilic substitution which occurs by an open transition state would be to use a system in which the metal has no low lying unfilled orbitals for complexation.

Reported here is the first general procedure for obtaining compounds of the type, R_3MR', M = Si, Ge, Sn, and Pb, where R′ is a simple alkyl group such as *sec*-butyl, containing an asymmetric carbon directly bonded to the metal atom. A single optically active derivative of a group IV element, [(−)-2,2-diphenyl-1-methylcyclopropyl]trimethyltin, has been reported.[3] However, this preparation was carried out by the unusual reaction of the trimethylstannyl anion with active 2,2-diphenyl-1-methylcyclopropyl bromide[4] and occurred with retention of configuration.

A well-known method for the preparation of unsymmetrical group IV organometallic compounds utilizes the reaction of triphenylmetal anions with alkyl halides.[5] This reaction has now been utilized to prepare optically active derivatives of the group IV metals.

$$(C_6H_5)_3M^- + (S)\text{-}(+)\text{-}sec\text{-BuBr} \longrightarrow (R)\text{-}(-)\text{-}sec\text{-Bu}M(C_6H_5)_3$$
M = Si, Ge, Sn, or Pb

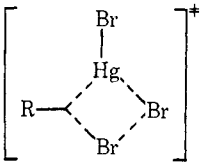
This reaction has all the features of an SN2 process which apparently always occurs with inversion of configuration. However, the assignment of stereochemistry as inversion of configuration is made with confidence utilizing the correlations of Brewster[6] and Davis and Jensen.[7] For *sec*-butyl compounds, all derivatives (except the deuterio compounds) which are dextrorotatory have the *S* configuration. Other examples of the reactions of organometallic anions with alkyl ha-

Table I. Synthesis and Properties of Ph_3M(*sec*-butyl)

M	Conditions	$[\alpha]^{22}D$ obtained,[a] deg	$[M]^{22}D$ cor to opt purity,[b] deg	% yield[c]	Mp, °C	$[M]D$ calcd BR–MR,[d] deg	% inversion
Si	$Ph_3SiSiPh_3$, Li, THF, (*S*)-(+)-*sec*-butyl chloride, $[\alpha]^{22}D$ +5.43 (neat)	−1.23	−26.5	34	68–69.5	−51.5	51
Ge	Ph_3GeBr, Na, NH_3, (*S*)-(+)-*sec*-butyl bromide, $[\alpha]^{22}D$ +8.31 (neat)	−2.33	−34.6	39	71–71.8	−53.9	67
Sn	Ph_3SnCl, Na, DME,[e] (*S*)-(+)-*sec*-butyl chloride, $[\alpha]^{22}D$ +5.43 (neat)	−2.20	−61.0	46	70.5–71.5	−67.4	90
Sn	Ph_3SnCl, Na, DME,[e] (*S*)-(+)-*sec*-butyl bromide, $[\alpha]^{22}D$ +8.31 (neat)	−3.54	−59.3	55	70.5–71.5		88
Sn	Ph_3SnCl, Na, DME,[e] (*R*)-(−)-*sec*-butyl iodide, $[\alpha]^{22}D$ −26.8 (neat)	+9.39	+47.8	58	70.5–71.5	+67.4	71
Pb	Ph_3PbCl, Na, NH_3, ether, (*S*)-(+)-*sec*-butyl bromide, $[\alpha]^{22}D$ +8.31 (neat)	−4.16	−84.8	26	79.5–81	−126	67.5

[a] (*c* 5–8 *M*, benzene). [b] The specific rotations of optically pure *sec*-butyl chloride, bromide, and iodide were taken to be 37, 34.2, and 33.5, respectively, ref 6. [c] No attempt was made to determine optimal conditions. [d] Based upon values predicted by the BR–MR method, ref 7. [e] With a few per cent added naphthalene.

$$RHgBr + Br_2 \longrightarrow$$



$$\longrightarrow RBr + HgBr_2$$

(1) Presented at the Twelfth Conference on Reaction Mechanisms, Brandeis University, June 19–21, 1968.
(2) F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968, p 96.
(3) K. Sisido, S. Kozima, and K. Takizawa, *Tetrahedron Lett.*, 33 (1967).
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(6) J. H. Brewster, *J. Amer. Chem. Soc.*, **81**, 5475 (1959).
(7) D. D. Davis and F. R. Jensen, *J. Org. Chem.*, **35**, 3410 (1970).

lides with inversion of configuration utilize π-cyclopentadienyldicarbonyliron(0)[8] and pyridine[bis(dimethylglyoximato)]cobalt(I).[9]

The results are summarized in Table I. Magnitudes of the molecular rotations calculated by an empirical extension of the Brewster method,[6] the bond refraction–molecular rotation correlation (BR–MR),[7] are also reported.

These materials may be conveniently converted to other alkyl derivatives by cleavage of the phenyl groups with bromine followed by reaction with Grignard or lithium reagents. The *sec*-BuSn(neopentyl)$_3$ compounds used in the accompanying paper[10] were prepared as follows.

$$R'Sn(C_6H_5)_3 + 2Br_2 \longrightarrow R'Sn(C_6H_5)Br_2 + 2C_6H_5Br$$

$$R'Sn(C_6H_5)Br_2 + 2RMgBr \longrightarrow R'Sn(C_6H_5)R_2 + 2MgBr_2$$

$$R'Sn(C_6H_5)R_2 \xrightarrow{Br_2} \xrightarrow{RMgBr} R'SnR_3$$

The availability of these compounds will facilitate a wide variety of mechanistic studies of alkyl group IV compounds. Investigations of several electrophilic and free-radical substitution reactions of these compounds are in progress. In the accompanying paper, the stereochemistry and mechanism of the electrophilic bromine cleavage of alkyltin compounds are reported.[10]

Acknowledgments. Grateful acknowledgment is made to the National Institutes of Health for partial support of this research under Grant No. 15373.

(8) G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **91**, 4313 (1969).
(9) F. R. Jensen, V. Madan, and D. H. Buchanan, *ibid.*, **92**, 1414 (1970).
(10) F. R. Jensen and D. D. Davis, *ibid.*, **93**, 4048 (1971).

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Stereochemistry and Mechanism of the Bromine Cleavage of Organotin Compounds[1]

Sir:

It is generally assumed that the stereochemistry of electrophilic substitution is retention of configuration and in fact this assumption has even been used to assign stereochemistry to substrate.[2] This paper provides stereochemical and kinetic evidence for the cleavage of tetraalkyltin compounds by bromine. *These data allow a definitive description of the transition state for this bimolecular electrophilic reaction and demonstrate that the reaction occurs with inversion of configuration.*

As was noted in the previous paper in this series,[3] the commonly observed stereochemistry for S$_E$2 reactions of retention of configuration might result as a consequence of mechanism, *i.e.*, a closed or four-center transition state I can only give retention of configuration. Of more interest would be the stereochemistry of S$_E$2 reactions which occur by open transition states, II and III, *i.e.*, where there is no attachment, even through ligand, between the electrophile and the leaving group.

(1) Presented at the Twelfth Conference on Reaction Mechanisms, Brandeis University, June 19–21, 1968.
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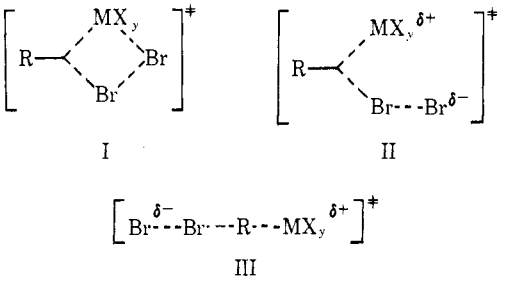
It seemed reasonable that open transition states, such as II and III, would be favored over a closed transition state I when there are no readily accessible, empty low-lying orbitals on the leaving group. Satisfactory com-



I II

III

pounds to test this hypothesis would be tetraalkyltin compounds. Optically active *sec*-butyltrineopentyltin was synthesized using the procedure previously described.[3] Preliminary experiments had demonstrated that neopentyl groups cleave slowly and therefore highly preferential cleavage of the *sec*-butyl group was expected.

Unfortunately, the optical purity of the *sec*-butyltrineopentyltin compound is not known and therefore only the accumulated stereospecificity is known for reactions 1–3. The results are summarized in Table I.

$$(R)\text{-}(-)\text{-}sec\text{-BuBr} + (C_6H_5)_3Sn^- \longrightarrow (S)\text{-}(+)\text{-}sec\text{-BuSn}(C_6H_5)_3 \quad (1)$$

$$(S)\text{-}(+)\text{-}sec\text{-BuSn}(C_6H_5)_3 \xrightarrow[\text{steps}]{\text{four}} (S)\text{-}(+)\text{-}sec\text{-BuSn(neopentyl)}_3 \quad (2)$$

$$(S)\text{-}(+)\text{-}sec\text{-BuSn(neopentyl)}_3 \xrightarrow[MeOH]{Br_2,\ Br^-} (R)\text{-}(-)\text{-}sec\text{-BuBr} + (\text{neopentyl})_3SnBr \quad (3)$$

These results indicate a minimum overall stereospecificity of 37%. However, these cleavages were carried out in dilute solution under the conditions of the kinetic experiments (see below), and racemization of the product *sec*-BuBr by bromide ion was occurring. In more concentrated solution, the amount of racemization can be diminished with a resulting overall stereospecificity of 80%.[4] Since step 1 occurs with inversion[3] and step 2 does not involve the asymmetric center, it follows that the *sec*-butyl group is cleaved with predominant inversion of configuration (step 3).

Table I. Stereochemistry of the Bromodemetalation (Br_3^-) of *sec*-Butyltrineopentyltin in Methanol at 45°

[α]^{22}D (*c* 6, benzene)		
Starting *sec*-BuBr (eq 1)	Product *sec*-BuBr (eq 3)	% accumulated stereospecificity
+6.50	+1.95	30
+6.50	+2.29	35
+7.85	+2.44	37

Kinetic experiments add strength to these beliefs. In methanol as solvent, over a wide variation of bromine, bromide, and tetraalkyltin compound concentrations, the kinetic expression shown in eq 4 is rigorously

$$\text{rate} = \frac{k_2[Br_3^-][R_3SnR']}{K[Br^-]} \quad (4)$$

(4) Unpublished results with V. S. Krimsley.