CBr_4 is formed slowly from $CHBr_3$. V could be formed from III by either (1) hydrolysis of III to acetoin (VII) followed by successive halogenations at C-1 and hydrolytic cleavage to V or (2) successive enolizations and brominations at C-1, hydrolytic cleavage to $CH_3CHBrCO_2^-$, and hydrolysis to V. The second possibility requires that enolization of III at C-1 be faster than hydrolysis of III. However, after 57% of III was hydrolyzed to VII in the absence of NaOBr, none (<5%) of the remaining III had enolized, as shown by lack of deuterium incorporation by nmr. Hence V is formed *via* VII.

$$\begin{tikzcd}
{}^{-}\mathrm{CH_2COCH_2CH_3} \arrow[r] & \underset{\mathrm{II}}{\mathrm{BrCH_2COCH_2CH_3}} \arrow[r] & \underset{\mathrm{IV}}{{}^{-}\mathrm{O_2CCH_2CH_3}} \\
\underset{\mathrm{I}}{{}^{-}\mathrm{OH} + {}^{-}\mathrm{OBr} + \mathrm{CH_3COCH_2CH_3}} \arrow[u] \arrow[d] & & \underset{\mathrm{V}}{{}^{-}\mathrm{O_2CCHOHCH_3}} \\
\mathrm{CH_3COCH^{-}CH_2} \arrow[r] & \underset{\mathrm{III}}{\mathrm{CH_3COCHBrCH_3}} \arrow[r] & \underset{\mathrm{VII}}{\mathrm{CH_3COCHOHCH_3}} \arrow[u]
\end{tikzcd}$$

Thus, in the NaOH-induced bromination of I in aqueous solution at 25°, each hydrogen on C-1 and C-3 of I is attacked *equally* fast (±5%) to form a sodium enolate, and the resulting II and III rapidly give bromoform, plus sodium propionate and sodium lactate (*via* acetoin), respectively.

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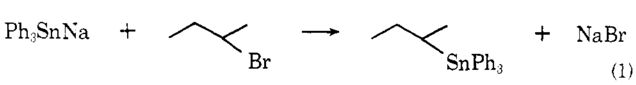
Stereochemistry of Metal Anion Substitutions on Carbon[1]

Sir:

The reaction of alkali metal salts of various metal anions with alkyl halides and tosylates has become a standard method of preparing carbon–metal bonds as illustrated by reaction 1.[2,3]



(1)

The extremely rapid reaction rate of anions of Sn, Ge, Pb, Co (cobalamine), and others with alkyl halides has prompted the name "supernucleophile."[4-6] In almost all cases studied this reaction has been found to proceed with inversion of configuration.[4,7,8]

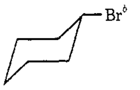
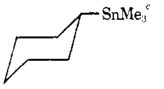
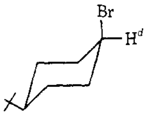
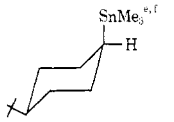
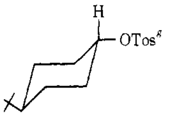
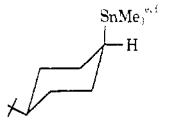
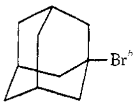
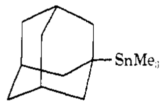
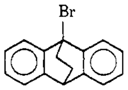
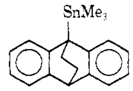
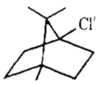
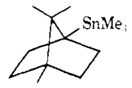
However, the observation that 1-bromo-1-methyl-2,2-diphenylcyclopropane reacted with trimethyltin lithium with retention of configuration[9] and the ready reaction of certain metal anions with bromobenzene[2] suggests that a mechanism other than the assumed S_N2 reaction could be occurring in some cases.[10]

We have studied the reaction of trimethyltin lithium with some alkyl halides and tosylates to test for other stereochemistry and possibly other mechanisms. The

$$\mathrm{Me_3SnLi + RX \longrightarrow RSnMe_3 + LiX} \qquad (2)$$

results are shown in Table I.

Table I. Products[a] and Stereochemistry of Reaction 2 in Tetrahydrofuran at 25°

Structure of RX	Reaction time, hr	Yield, %	Product	Stereo-chemistry
	1–2	51		
	3.5	30		Retention
	12	63		Inversion
	3.5	57		Retention
	2.5	85		Retention
	5	66		Retention

[a] All new compounds had analyses and nmr consistent with the indicated structures. [b] From Aldrich Chemical Co. [c] See R. C. Putnam and H. Pu, *Can. J. Chem.*, **44**, 1343 (1966). [d] Prepared from 66% trans, 34% cis alcohol. The nmr indicated that the bromide was 78–80% axial (cis). See ref 7. [e] See text for structure proof. [f] Greater than 95% was of the indicated configuration. [g] Pure *trans*-tosylate was prepared by the method of S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, **77**, 5574 (1955). A mixture of *cis*- and *trans*-tosylates afforded mostly cis tin compound and much olefin. [h] Identical with structure prepared by H. J. Berwin, Thesis, University of California, San Diego, 1970. See also W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 7476 (1970). [i] Prepared in a previous investigation: S. Winstein and T. G. Traylor, *ibid.*, **78**, 2597 (1956).

The products of reaction of *trans*-4-*tert*-butylcyclohexyl tosylate and *cis*-4-*tert*-butylcyclohexyl bromide with Me_3SnLi have almost identical nmr spectra having an Me_3Sn singlet at τ 9.87. However, the reaction of the 4-*tert*-butylcyclohexyl Grignard with Me_3SnCl produced a compound whose nmr spectrum was

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(1) Supported by the Air Force Office of Scientific Research (Grant No. AFOSR-69-1639C).

(2) C. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. I, Methuen, London, 1967, p 457.

(3) F. R. Jensen and D. D. Davis, *J. Amer. Chem. Soc.*, **93**, 4047 (1971).

(4) R. E. Dessy, R. L. Pohl, and R. B. King, *ibid.*, **88**, 5121 (1966).

(5) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **7**, 311 (1967).

(6) G. N. Schrauzer and E. Deutsch, *J. Amer. Chem. Soc.*, **91**, 3341 (1969).

(7) F. R. Jensen, V. Madan, and D. H. Buchanan, *ibid.*, **92**, 1414 (1970).

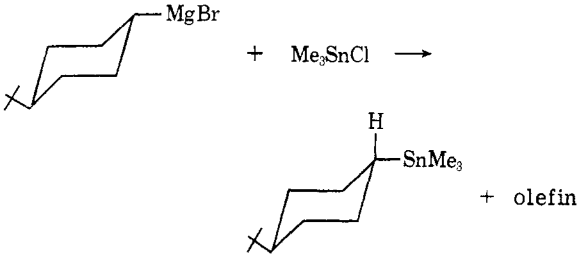
(8) G. M. Whitesides and D. J. Boschetto, *ibid.*, **91**, 4313 (1969).

(9) K. Sisido, S. Kozima, and K. Takizaiva, *Tetrahedron Lett.*, 33 (1967).

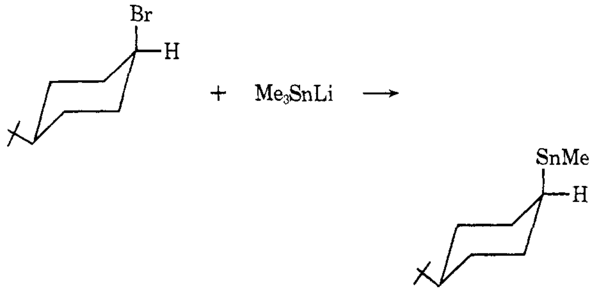
(10) See also R. E. Dessy and P. M. Weissman, *J. Amer. Chem. Soc.*, **88**, 5124 (1966).

identical with those above except for the trimethyltin singlet which occurred at τ 10.04.

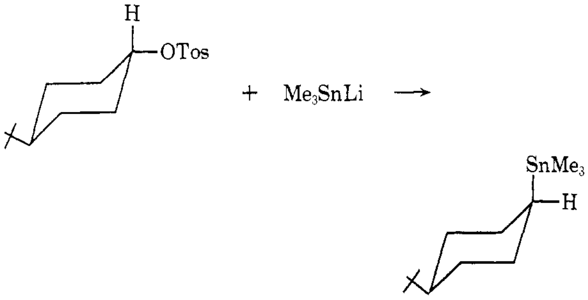
Jensen and Nakamaye[11] have shown that this Grignard reagent gives >95% trans product upon reaction with reagents such as $HgCl_2$ or CO_2 and on this basis we assign this product the trans configuration. Further evidence comes from the position of the cyclohexyltrimethyltin Me_3Sn singlet at τ 9.97. This position must be nearest that of *trans*-4-*tert*-butylcyclohexyltrimethyltin because the Me_3Sn group is not likely to be predominantly axial.[12]



(3)



(4)



(5)

In contrast to its reaction with the tosylate, trimethyltin lithium may react with bromides with retention of configuration and in reaction 4 prefers to do so.

In addition to the stereochemical results we also observe hexamethyldistannane and olefin as byproducts. Because inversion of configuration had been reported in the reaction of triphenyltin sodium with bromides[3] and because we find retention of configuration and olefin in the reactions of some bromides, we suggest that several mechanisms are available for the reaction of metal anions with halides (eq 6–9).[10]

Mechanism 1. SN2 reaction on C

$$\text{RBr} + \text{R}'_3\text{Sn}^- \longrightarrow \text{RSnR}'_3 \text{ inversion} \qquad (6)$$

Mechanism 2. SN2 reaction on halogen

$$\text{RBr} + \text{R}'_3\text{SnLi} \longrightarrow \text{RLi} + \text{R}'_3\text{SnBr} \qquad (7)$$

$$\text{(retention) RSnR}' + \text{LiBr} \xleftarrow{\text{fast}} \qquad (8)$$

Mechanism 3. Radical pair mechanism

$$\text{RBr} + \text{R}'_3\text{Sn}^- \longrightarrow [\text{R}\cdot\text{Br}^-\cdot\text{SnR}'_3]^{\text{cage}} \longrightarrow \text{RSnR}'_3 + \text{olefin, etc.} \qquad (9)$$

Other evidence in support of the interchange mechanism 7 is the reaction of 1,2-dibromoethane to produce ethylene (eq 10). Yet 1,3-dichloro- or 1,3-dibromopropanes afford good yields of the ditin product[13]

$$\text{BrCH}_2\text{CH}_2\text{Br} + \text{Me}_3\text{SnLi} \longrightarrow \text{CH}_2\!=\!\text{CH}_2 \qquad (10)$$

$$\text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br} + 2\text{Me}_3\text{SnLi} \longrightarrow \text{Me}_3\text{SnCH}_2\text{CH}_2\text{CH}_2\text{SnMe}_3 \qquad (11)$$

We suggest that, where there is a driving force to bring about attack on halogen, this reaction will predominate instead of SN2 reaction at carbon.

Either the direct interchange (reaction) or the radical pair mechanism would explain the formation of hexamethylditin and olefin. However, radical pairs of the stability of R_3Sn would rotate in the cage and this should produce some of the more stable equatorial tin compound in reaction 4.[14] We therefore prefer the combination of SN2 on C and Br to explain our findings.

These results make the use of halogen displacement to produce stereochemically known metal compounds questionable and suggest that the displacement of "hard" leaving groups like tosylate be used for this purpose.

The independent study of Kuivila, Considine, and Kennedy[15,16] agrees with this conclusion and indicates how stereochemistry might be controlled in some cases.

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[11] F. R. Jensen and K. L. Nakamaye, *J. Amer. Chem. Soc.*, **90**, 3248 (1968).

[12] The conformations of cyclohexyltrimethylmetal compounds will be discussed elsewhere.

[13] J. Jerkuniča and T. G. Traylor, *J. Amer. Chem. Soc.*, **93**, 6278 (1971).

[14] That 1-bromodibenzbicyclooctadiene reacts much faster than 1-bromoadamantane also argues against a free-radical mechanism.

[15] H. G. Kuivila, J. L. Considine, and J. D. Kennedy, *J. Amer. Chem. Soc.*, **94**, 7206 (1972).

[16] We are grateful to Professor Henry Kuivila for a full exchange of information prior to publication and for helpful advice.

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Solvent and Counterion Control of Stereochemistry in a Formal Nucleophilic Displacement Reaction. Mechanisms of Reaction of Trimethyltin Alkalis with Alkyl Halides

Sir:

Since the first observation a half-century ago[1] the literature has contained scattered reports on the reactions of organotin alkalis, R_3SnM (M = Li, Na, K), with organic halides to form tetrasubstituted organotins, eq 1.[2] The reaction has been shown to proceed with inversion,[3] lending credence to the usual implicit assumption that it is of the SN2 type. However,

$$\text{R}_3\text{SnM} + \text{R}'\text{X} \longrightarrow \text{R}_3\text{SnR}' + \text{MX} \qquad (1)$$

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[1] C. A. Kraus and R. H. Bullard, *J. Amer. Chem. Soc.*, **48**, 2131 (1926).

[2] For recent reviews see: (a) W. P. Neumann, "The Organic Chemistry of Tin," Wiley, New York, N. Y., 1970; (b) J. G. A. Luijten and G. J. M. van der Kerk in "The Bond to Carbon," A. G. MacDiarmid, Ed., Marcel Dekker, New York, N. Y., 1968, Chapter 4; (c) D. D. Davis, *Organometal. Chem. Rev., Sect. A*, **6**, 283 (1970).

[3] F. R. Jensen and D. D. Davis, *J. Amer. Chem. Soc.*, **93**, 4047 (1971).