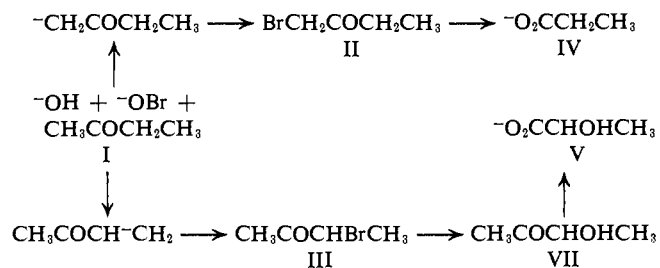


$\text{CBr}_4$  is formed slowly from  $\text{CHBr}_3$ . V could be formed from III by either (1) hydrolysis of III to acetoin (VII) followed by successive halogenations at C-1 and hydrolytic cleavage to V or (2) successive enolizations and brominations at C-1, hydrolytic cleavage to  $\text{CH}_3\text{-CHBrCO}_2^-$ , 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  $\text{NaOBr}$ , none (<5%) of the remaining III had enolized, as shown by lack of deuterium incorporation by nmr. Hence V is formed *via* VII.



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

C. Gardner Swain,\* Richard P. Dunlap

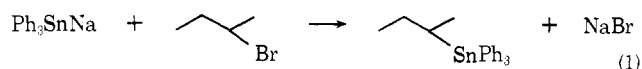
Department of Chemistry, Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

Received July 15, 1972

### Stereochemistry of Metal Anion Substitutions on Carbon<sup>1</sup>

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.<sup>2,3</sup>

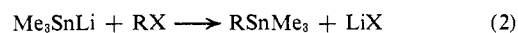


The extremely rapid reaction rate of anions of Sn, Ge, Pb, Co (cobalamine), and others with alkyl halides has prompted the name "supernucleophile."<sup>4-6</sup> In almost all cases studied this reaction has been found to proceed with inversion of configuration.<sup>4,7,8</sup>

However, the observation that 1-bromo-1-methyl-2,2-diphenylcyclopropane reacted with trimethyltin lithium

with retention of configuration<sup>9</sup> and the ready reaction of certain metal anions with bromobenzene<sup>2</sup> suggests that a mechanism other than the assumed  $\text{S}_\text{N}2$  reaction could be occurring in some cases.<sup>10</sup>

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



results are shown in Table I.

Table I. Products<sup>a</sup> and Stereochemistry of Reaction 2 in Tetrahydrofuran at  $25^\circ$

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

<sup>a</sup>All new compounds had analyses and nmr consistent with the indicated structures. <sup>b</sup>From Aldrich Chemical Co. <sup>c</sup>See R. C. Putnam and H. Pu, *Can. J. Chem.*, **44**, 1343 (1966). <sup>d</sup>Prepared from 66% trans, 34% cis alcohol. The nmr indicated that the bromide was 78-80% axial (cis). See ref 7. <sup>e</sup>See text for structure proof. <sup>f</sup>Greater than 95% was of the indicated configuration. <sup>g</sup>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. <sup>h</sup>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). <sup>i</sup>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  $\text{Me}_3\text{SnLi}$  have almost identical nmr spectra having an  $\text{Me}_3\text{Sn}$  singlet at  $\tau$  9.87. However, the reaction of the 4-*tert*-butylcyclohexyl Grignard with  $\text{Me}_3\text{SnCl}$  produced a compound whose nmr spectrum was

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

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

(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).

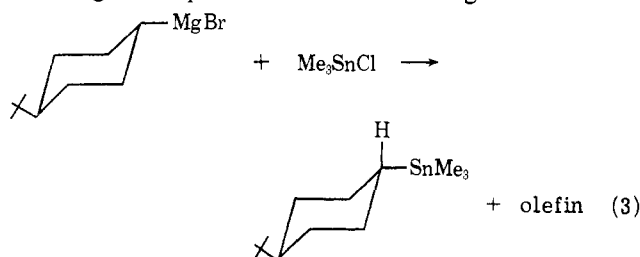
(6) G. N. Schrauzer and E. Deutsch, *J. Amer. Chem. Soc.*, **91**, 3341 (1969).

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

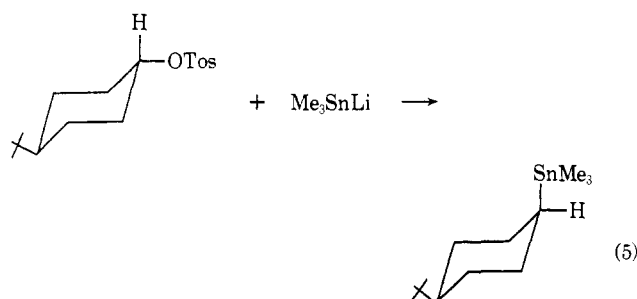
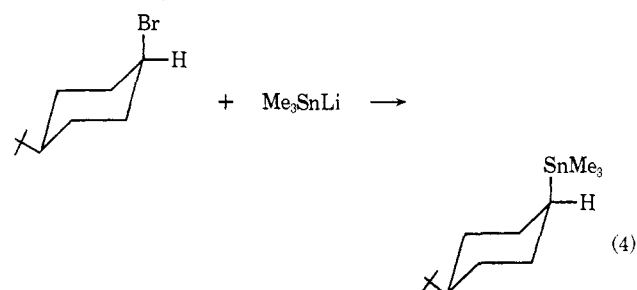
(8) G. M. Whitesides and D. J. Boschetto, *ibid.*, **91**, 4313 (1969).

identical with those above except for the trimethyltin singlet which occurred at  $\tau$  10.04.

Jensen and Nakamaye<sup>11</sup> have shown that this Grignard reagent gives >95% trans product upon reaction with reagents such as HgCl<sub>2</sub> or CO<sub>2</sub> and on this basis we assign this product the trans configuration. Fur-



ther evidence comes from the position of the cyclohexyltrimethyltin Me<sub>3</sub>Sn singlet at  $\tau$  9.97. This position must be nearest that of *trans*-4-*tert*-butylcyclohexyltrimethyltin because the Me<sub>3</sub>Sn group is not likely to be predominantly axial.<sup>12</sup>



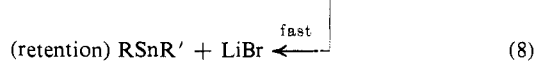
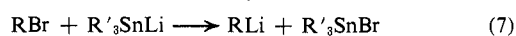
In contrast to its reaction with the tosylate, trimethyltin lithium may react with bromides with retention of configuration and in reaction 4 prefers to do so.

In addition to the stereochemical results we also observe hexamethyldistannane and olefin as by-products. Because inversion of configuration had been reported in the reaction of triphenyltin sodium with bromides<sup>3</sup> and because we find retention of configuration and olefin in the reactions of some bromides, we

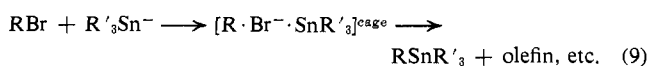
Mechanism 1. S<sub>N</sub>2 reaction on C



Mechanism 2. S<sub>N</sub>2 reaction on halogen



Mechanism 3. Radical pair mechanism

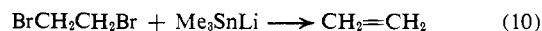


(11) F. R. Jensen and K. L. Nakamaye, *J. Amer. Chem. Soc.*, **90**, 3248 (1968).

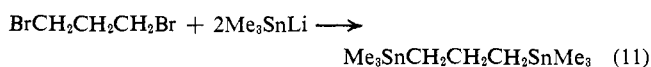
(12) The conformations of cyclohexyltrimethylmetal compounds will be discussed elsewhere.

suggest that several mechanisms are available for the reaction of metal anions with halides (eq 6-9).<sup>10</sup>

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-dibromo-



propanes afford good yields of the ditin product<sup>13</sup>



We suggest that, where there is a driving force to bring about attack on halogen, this reaction will predominate instead of S<sub>N</sub>2 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<sub>3</sub>Sn would rotate in the cage and this should produce some of the more stable equatorial tin compound in reaction 4.<sup>14</sup> We therefore prefer the combination of S<sub>N</sub>2 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<sup>15,16</sup> agrees with this conclusion and indicates how stereochemistry might be controlled in some cases.

(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.

G. S. Koerner, M. L. Hall, T. G. Traylor\*

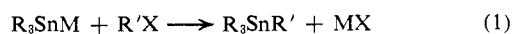
Department of Chemistry, Revelle College  
University of California, San Diego  
La Jolla, California 92037

Received May 22, 1972

### 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<sup>1</sup> the literature has contained scattered reports on the reactions of organotin alkalis, R<sub>3</sub>SnM (M = Li, Na, K), with organic halides to form tetrasubstituted organotins, eq 1.<sup>2</sup> The reaction has been shown to proceed with



inversion,<sup>3</sup> lending credence to the usual implicit assumption that it is of the S<sub>N</sub>2 type. However,

(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).