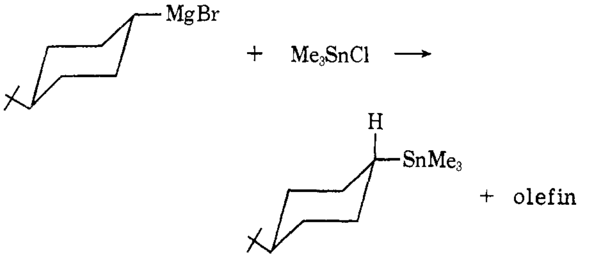
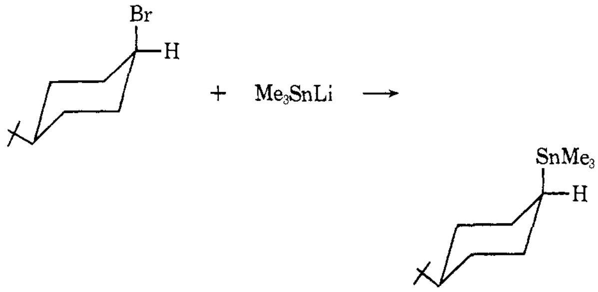
identical with those above except for the trimethyltin singlet which occurred at τ 10.04.

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)



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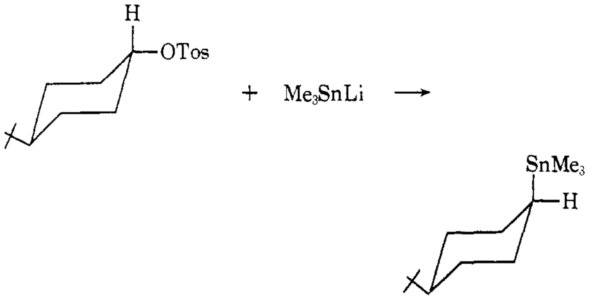

(5)

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

$$RBr + R'_3Sn^- \longrightarrow RSnR'_3 \text{ inversion} \qquad (6)$$

Mechanism 2. SN2 reaction on halogen

$$RBr + R'_3SnLi \longrightarrow RLi + R'_3SnBr \qquad (7)$$

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

Mechanism 3. Radical pair mechanism

$$RBr + R'_3Sn^- \longrightarrow [R\cdot Br^- \cdot SnR'_3]^{cage} \longrightarrow RSnR'_3 + \text{olefin, etc.} \qquad (9)$$

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]

$$BrCH_2CH_2Br + Me_3SnLi \longrightarrow CH_2{=}CH_2 \qquad (10)$$

$$BrCH_2CH_2CH_2Br + 2Me_3SnLi \longrightarrow Me_3SnCH_2CH_2CH_2SnMe_3 \qquad (11)$$

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

$$R_3SnM + R'X \longrightarrow R_3SnR' + MX \qquad (1)$$

inversion,[3] lending credence to the usual implicit assumption that it is of the SN2 type. However,

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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).

retention in configuration has also been observed.[4] We now report that the stereochemistry of this reaction can be profoundly dependent upon the solvent and the alkali metal counterion in R_3SnM.

Trimethyltin alkali was prepared by the reaction of trimethyltin chloride with the appropriate alkali naphthalene, eq 2.[5] *syn*-7-Bromonorbornene was

$$Me_3SnCl + 2M^+C_{10}H_8\cdot^- \longrightarrow Me_3SnM + 2C_{10}H_8 + 2MCl \qquad (2)$$

added to the solution at −20°; the reaction mixture was allowed to come to ambient temperature overnight and analyzed by glpc. Yields of 7-norbornenyltrimethyltins were usually greater than 90%. Norbornene was formed in amounts ranging from 2 to 5%. Comparable amounts of hexamethylditin were also found in some experiments. Stereochemical results are gathered in Table I. When lithium or sodium is the counterion the proportion of *anti*-7-norbornenyltrimethyltin formed by an inversion mechanism increases as the capacity of the solvent for coordinating with cations increases. Thus, by appropriate choice of counterion and solvent, the reaction can be made to proceed predominantly by inversion or retention.[6]

Table I. Stereochemistry of Reaction of Trimethyltin Alkalis with 7-Bromonorbornenes[a]

Isomer	M	% retention in product THF[b]	DME[c]	THF-TG[d]
Syn	Li[e,f]	16	3	3
	Na	90	19	9
	K	53	82	4
Anti	Li	96	98	99
	Na	85	93	96
	K	79	92	96

[a] Concentrations: $[Me_3SnM] = [RBr] \simeq 0.15$ *M*. [b] Tetrahydrofuran. [c] 1,2-Dimethoxyethane. [d] Tetrahydrofuran–tetraglyme $[MeO(CH_2CH_2)_4Me]$ (2:1 v/v). [e] In ethyl ether–THF (2:1, v/v), 46% retention. [f] In tetrahydropyran, 50% retention.

The effect of the coordinating capacity of the solvent is shown to be dramatic by the results plotted in Figure 1. Here the percentage of product of retained configuration is plotted as a function of the concentration of tetraglyme in tetrahydrofuran. The stereochemical result of 90% retention is changed to 91% inversion by the presence of 0.053 *M* tetraglyme. In the latter reaction mixture, the initial concentration of trimethyltin sodium is twice that of tetraglyme! This implies that the more "free" trimethyltin sodium ion pair reacts by the inversion mechanism at a tremendously faster rate than does the more tightly bound ion pair, which reacts preferentially by a retention mechanism.[7] A recent report that trimethyltin sodium reacts with *syn*-7-bromonorbornene with inversion in liquid ammonia[8] fits in with these observations.

Experiments similar to those summarized above were also carried out with *anti*-7-bromonorbornene. Results are presented in Table I. They are monotonously similar in showing a great predominance of retention in each of the solvent systems used. It may be inferred that there is present a severe constraint in the anti bromide (relative to the syn isomer) against occurrence of the inversion mechanism. Experiments designed to reveal the nature of the constraint are in progress. That the retention process can occur with considerable ease is further indicated by the fact that 1-bromoadamantane gives a high yield of 1-adamantyltrimethyltin. 2-Bromoadamantane also reacts readily to give the corresponding organotin.[9]

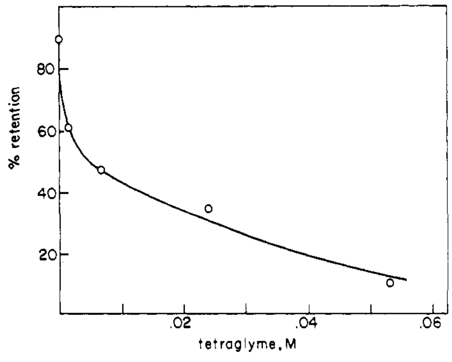

Figure 1.

Although kinetic evidence is still lacking, it seems probable that the S_N2 mechanism is operative in those reactions of organotin alkalis which lead to inversion.

The simplest mechanism that can be envisioned for the retention reaction with *syn*-7-bromonorbornene is a four-center process, eq 3. An alternative is a two-step process involving halogen–alkali exchange, eq 4, followed by coupling of the resulting organotin bromide with the organoalkali, eq 5. This scheme accommodates the formation of hexamethylditin, *via* eq 6, and of norbornene by reaction of the organotin alkali with solvent, eq 7. It also accounts for the formation of substantial amounts of 1-methyl-2,2-diphenylcyclopropane in the reaction of 1-bromo-1-methyl-2,2-diphenylcyclopropane with trimethyltin lithium in THF.[4] The reaction of trimethyltin sodium with cinnamyl chloride in either liquid ammonia[10] or THF yields bicinnamyls and hexamethylditin in high yields, but no cinnamyltrimethyltin. These products can form by reaction 4, followed by reactions 6 and 8. Further

$$Me_3SnM + RBr \longrightarrow Me_3SnR + MBr \qquad (3)$$

$$Me_3SnM + RBr \longrightarrow Me_3SnBr + RM \qquad (4)$$

$$RM + Me_3SnBr \longrightarrow Me_3SnR + MBr \qquad (5)$$

$$Me_3SnM + MeSnBr \longrightarrow Me_3SnSnMe_3 + MBr \qquad (6)$$

$$RM + SH \longrightarrow RH + SM \qquad (7)$$

$$RM + RCl \longrightarrow RR + MCl \qquad (8)$$

evidence for a mechanism involving at least two steps stems from our observation that 3-bromonortricyclene reacts to form 3-nortricyclyltrimethyltin and *exo*-5-norbornenyltrimethyltin; respective proportions were 63:37 with trimethyltin sodium in THF and 43:57 with trimethyltin lithium in DME.

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[4] K. Sisido, S. Kozima, and K. Takizawa, *Tetrahedron Lett.*, 33 (1967).

[5] D. Blake, G. E. Coates, and J. M. Tate, *J. Chem. Soc.*, 618 (1961).

[6] The apparently anomalous result with trimethyltin potassium has been checked several times.

[7] The apparent order of reactivity as a function of the counterion is K < Na < Li.

[8] C. H. W. Jones, R. G. Jones, P. Partington, and R. M. G. Roberts, *J. Organometal. Chem.*, **32**, 201 (1971).

[9] Elemental analyses and nmr spectra of these compounds were consistent with the structures.

[10] N. A. Scarpa, Ph.D. Dissertation, State University of New York at Albany, 1970.

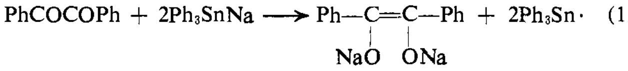
Retention in configuration in the 7-norbornenyl and 1-methyl-2,2-diphenylcyclopropyl systems requires that the coupling reaction, eq 5, be much faster than the rate of epimerization of the corresponding organoalkali intermediates. Walborsky and Impastato have shown that the above cyclopropyllithium does indeed epimerize slowly.[11] On the other hand, reactions proceeding from *syn*-7-bromonorbornene through the Grignard and lithium reagents are not stereospecific.[12] However, it is not known whether the epimerization occurs in the organometallic or at the free-radical stage in its formation. The 7-norbornenyl free radical epimerizes faster than it reacts with tri-*n*-butyltin deuteride.[13]

Triphenyltin sodium reacts with benzoyl chloride to form the dibenzoate of *cis*-stilbenediol and hexaphenylditin.[5] The pathway to this product involves electron transfer processes, eq 9–13. Thus, the possibility that

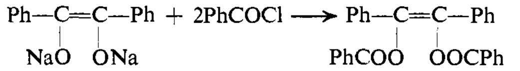
$$\mathrm{Ph_3SnNa + PhCOCl \longrightarrow Ph_3Sn\cdot + Ph\dot{C}O} \qquad (9)$$

$$\mathrm{2Ph_3Sn\cdot \longrightarrow Ph_3SnSnPh_3} \qquad (10)$$

$$\mathrm{2Ph\dot{C}O \longrightarrow PhCOCOPh} \qquad (11)$$



$$\mathrm{PhCOCOPh + 2Ph_3SnNa \longrightarrow Ph{-}\underset{NaO}{\underset{|}{C}}{=}\underset{ONa}{\underset{|}{C}}{-}Ph + 2Ph_3Sn\cdot} \qquad (12)$$



$$\mathrm{Ph{-}\underset{NaO}{\underset{|}{C}}{=}\underset{ONa}{\underset{|}{C}}{-}Ph + 2PhCOCl \longrightarrow Ph{-}\underset{PhCOO}{\underset{|}{C}}{=}\underset{OOCPh}{\underset{|}{C}}{-}Ph} \qquad (13)$$

electron transfer occurs in the reactions of alkyl halides with organotin alkalis cannot be dismissed out of hand. Fortunately, this is subject to test. A carbonium mechanism has also been proposed.[8]

Acknowledgments.[14] This work was supported by the National Science Foundation. Trimethyltin chloride was kindly provided by M & T Chemicals, Inc.

[11] H. M. Walborsky and F. J. Impastato, *J. Amer. Chem. Soc.*, **81**, 5835 (1959).

[12] R. R. Sauers and R. M. Hawthorne, Jr., *J. Org. Chem.*, **29**, 1685 (1964).

[13] G. A. Russell and G. W. Holland, *J. Amer. Chem. Soc.*, **91**, 3968 (1969); S. J. Cristol and A. L. Noreen, *ibid.*, **91**, 3969 (1969).

[14] Observations and conclusions which agree with ours have been made independently by G. S. Koermer, M. L. Hall, and T. G. Traylor, *J. Amer. Chem. Soc.*, **94**, 7205 (1972). We thank Dr. Traylor for open and helpful discussions.

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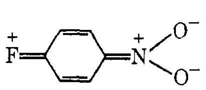
Regarding Aprotic Solvent Effects on the Fluorine Nuclear Magnetic Resonance Shifts of Para-Substituted Fluorobenzenes[1]

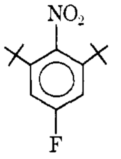
Sir:

We wish to report two new critical lines of evidence which define the origin of the effects of aprotic polar solvents on the F nmr shifts of para-substituted fluorobenzenes. The two previous interpretations which have been made of these solvent effects are shown to be invalid. Taft and students have attributed the increasing downfield shifts of +R para-substituted fluorobenzenes relative to fluorobenzene with increasing polarity of the aprotic solvent to increased contribution of the trans quinoidal resonance forms,[2] *e.g.*

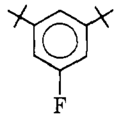


Emsley and Phillips[3] have attributed these solvent effects to the reaction field shielding contribution to the total shielding which they have related to the relative size of the solute's dipole moment.

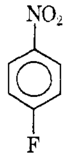
Compounds I and II have been prepared[4] and their F nmr solvent shifts compared with those of compounds III and IV. The results are recorded in Table I. The



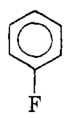
I



II



III



IV

downfield shift for the coplanar NO_2 group, $f_{\mathrm{IV}}^{\mathrm{III}}$, as expected, is markedly larger than the corresponding shift for the twisted NO_2 group, $f_{\mathrm{II}}^{\mathrm{I}}$. However, the solvent effects on $f_{\mathrm{IV}}^{\mathrm{III}}$ are not markedly smaller as expected,[2] but instead essentially identical solvent effects are observed. Further, in cyclohexane, $f_{\mathrm{II}}^{\mathrm{I}}$ is essentially the same as $f_{\mathrm{H}}^{m\text{-}\mathrm{NO_2}}$ (the substituent shift for *m*-nitrofluorobenzene, −3.43 ppm).[5] This identity is expected on the basis that (a) the *tert*-butyl groups force the NO_2 group perpendicular to the plane of the benzene ring giving rise to complete steric inhibition of resonance[6] and (b) the polar effect of the twisted NO_2 is essentially the same as that for the coplanar NO_2 substituent in *m*-nitrofluorobenzene.[7] Previous evidence[2b,5,8] has indicated generally that the effects of meta substituents (a) involve little or no resonance or π delocalization effects and (b) the polar effects are nearly equal from the meta and para positions.

Since both solvent and polar effects are the same for the completely twisted p-NO_2 as for the coplanar p-NO_2 group, it is clear that the polar *not* the resonance effect[2] of the NO_2 group governs the solvent effect. Since NO_2 twisting markedly alters the molecular dipole moment,[9] the equal solvent effects on $f_{\mathrm{II}}^{\mathrm{I}}$ and $f_{\mathrm{IV}}^{\mathrm{III}}$ also clearly do not support the Emsley and Phillips explanation of polar solvent effects.

We have reexamined the previously reported[2] F nmr shifts for a critical selection of both −R and +R para-substituted fluorobenzenes obtained in a graded series of aprotic polar solvents. By the choice[2] of both solvents and substituents, the formation of specific complexes, *e.g.*, hydrogen-bonded complexes, or Lewis

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[1] This work was supported in part by the National Science Foundation. We also gratefully acknowledge the support of the National Science Foundation which made available the nmr spectrometer to the Chemistry Department.

[2] (a) R. W. Taft, R. E. Glick, I. C. Lewis, I. R. Fox, and S. Ehrenson, *J. Amer. Chem. Soc.*, **82**, 756 (1960); (b) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 3146 (1963).

[3] J. W. Emsley and L. Phillips, *Mol. Phys.*, **11**, 437 (1966).

[4] Prepared by the Schiemann reaction from the corresponding amino compounds. We are indebted to Professor B. M. Wepster for samples of the latter; *cf.* J. Burgers, W. Van Hartingsveldt, J. Van Kowen, P. E. Verkade, H. Visser, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, 75, 1327 (1956).

[5] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 709 (1963).

[6] (a) B. M. Wepster, *Progr. Stereochem.*, **2**, 99 (1958); D. H. Geske and J. L. Rugle, *J. Amer. Chem. Soc.*, **83**, 3532 (1961).

[7] Further evidence is obtained from the fact that $3\text{-NO}_2\text{-}4\text{-}t\text{-BuC}_6\text{H}_3\text{F}$ is downfield shifted (−3.50 ppm) from $4\text{-}t\text{-BuC}_6\text{H}_4\text{F}$ in cyclohexane solution by essentially the same amount as $f_{\mathrm{H}}^{m\text{-}\mathrm{NO_2}}$.

[8] R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960).

[9] C. E. Ingham and G. C. Hampson, *J. Chem. Soc.*, 981 (1939).