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.

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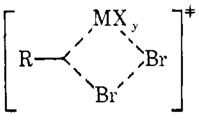
## Stereochemistry and Mechanism of the Bromine Cleavage of Organotin Compounds[1]

*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 SE2 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 SE2 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.

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 compounds 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.



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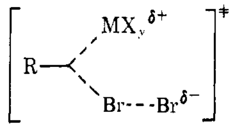
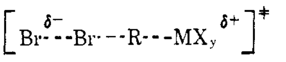


II



III

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.

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

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

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

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°

| $[\alpha]^{22}D$ (*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

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

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[1] Presented at the Twelfth Conference on Reaction Mechanisms, Brandeis University, June 19–21, 1968.

[2] For example, R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, **92**, 5519 (1970).

[3] F. R. Jensen and D. D. Davis, *ibid.*, **93**, 4047 (1971).

[4] Unpublished results with V. S. Krimsley.

followed. Similar rate expressions have been reported for related halogen cleavages or organotin compounds in other systems.[5]

This result requires uniquely the reactions shown in eq 5 and 6.

$$Br_3^- \underset{}{\overset{1/K}{\rightleftharpoons}} Br^- + Br_2 \qquad (5)$$

$$Br_2 + R_4Sn \xrightarrow{k_2} RBr + R_3SnBr \qquad (6)$$

The effect of structure on reactivity is especially illuminating. These results are summarized in Table II and are compared with SE2 retention and SN2 inversion data. A close parallelism exists between these SN2 and SE2 inversion rates, but no relationship exists between the SE2 inversion and the "SE2" retention reaction rates. However, the tabulated "SE2" retention rates are similar to the rates of other "SE2" retention processes. *It is proposed that the stereochemical assignment of an SE2 process can be made by comparison of pertinent rate data with those of SE2 processes known to occur with retention of configuration and with inversion of configuration.*

**Table II.** Effect of Structure on the Relative Rates of Electrophilic and Nucleophilic Substitution on Carbon

| R | Typical SN2 inversion[a] | SE2 inversion[b] ($Br_2 + RSnR_3'$) | SE2 retention[c,d] ($HCl + R_2Hg$) |
|---|---|---|---|
| $CH_3$– | 1 | 1 | 1 |
| $CH_3CH_2$– | 0.03 | 0.144 | 5.95 |
| $CH_3CH_2CH_2$– | 0.013 | 0.0408 | 3.2 |
| $(CH_3)_2CH$– | $8 \times 10^{-4}$ | $7.53 \times 10^{-3}$ | 3.5 |
| $(CH_3)_3CCH_2$– | $3 \times 10^{-7}$ | $5.84 \times 10^{-4}$[e] | |

[a] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 13. [b] This work, obtained from rate constants. In methanol at 45.0°, [NaBr] = 0.366, R′ = neopentyl, $k_{\text{methyl}} = 16.6\ M^{-1}\ \text{sec}^{-1}$. [c] Rates in DMSO by R. E. Dessy and J. Y. Kim, *J. Amer. Chem. Soc.*, **83**, 1167 (1961). [d] Stereochemistry in dioxane is retention: L. H. Gale, J. Landgrebe, and F. R. Jensen, *Chem. Ind. (London)*, 118 (1960). [e] Corrected for a statistical factor of four.

In Figure 1, the log $k_{\text{rel}}$ for the SE2 inversion reaction is plotted *vs.* the log $k_{\text{rel}}$ for the SN2 exchange reaction of bromide ion with alkyl chlorides.[6] This reaction was selected for comparison purposes because in both processes Br–C bonds are being formed. Clearly, a marked similarity between steric factors (and possibly electrical factors) must be present in the two very different processes. Also, the excellent agreement for the neopentyl derivatives strongly suggests that the bromodemetalation reaction for even this compound occurs highly preferentially with inversion of configuration. (In SE2 retention processes, neopentyl cleaves at about the same rate as other alkyl groups.[7])

The data presented herein demonstrate that in the transition state only bromine and tetraalkyltin are involved and that the reaction proceeds with inversion of configuration. These data uniquely require transition state III.

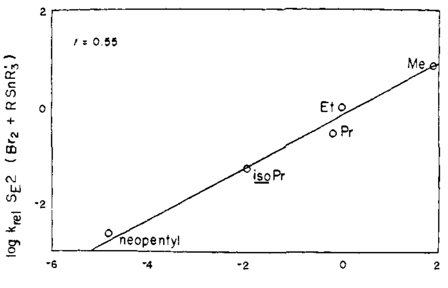

Figure 1. Comparison of the log $k_{\text{rel}}$ for two inversion processes, exchange of bromide ion with alkyl bromides[6] and the bromodemetalation of organotin compounds (this work).

Two previous studies with optically active cyclopropyltin compounds have shown that halodemetalation of these materials occurs with retention of configuration.[8] Because of the very high resistance of cyclopropyl derivatives to react with inversion of configuration, these results are not surprising.

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

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[5] M. Gielen and J. Naszielski, *Ind. Chim. Belg.*, **26**, 1393 (1961); *Bull. Soc. Chim. Belg.*, 71, 32 (1962); *ibid.*, 71, 702 (1962).

[6] P. B. D. De la Mare, *J. Chem. Soc.*, 3180 (1955).

[7] See, for example, E. D. Hughes and H. C. Volger, *ibid.*, 2359 (1961).

[8] K. Sisido, S. Kozima, and K. Takizawa, *Tetrahedron Lett.*, 33 (1967); K. Sisido, T. Miyanisi, and T. Isida, *J. Organometal. Chem.*, 23, 117 (1970); P. Baekelmans, M. Gielen, and J. Naszielski, *Tetrahedron Lett.*, 1149 (1967).

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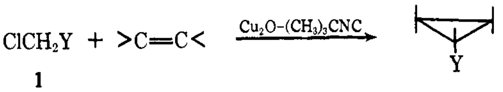
## Synthetic Reactions by Complex Catalysts. XXIII. Cyclopropanes from α-Chloro Ketones, Esters, and Nitriles, Olefins, and a Copper(I) Oxide–Isonitrile Complex

*Sir:*

We wish to report a new synthesis of cyclopropane rings from an olefin, α-chloro compound **1**, and the copper(I) oxide–isonitrile system. Transient α-chloroorganocopper–isonitrile complexes[1] are assumed to be the key intermediates in these reactions; these constitute members of a new class of copper carbenoids. A typical experimental procedure is as follows. Under a nitrogen atmosphere, a mixture of $Cu_2O$ (10 mmol), *tert*-butyl isonitrile (60 mmol), methyl monochloroacetate (20 mmol), and methyl acrylate (30 mmol) was stirred at 80° for 3 hr. The reaction mixture was extracted with ether, the extract was concentrated, and the residue was subjected to glpc analysis. Dimethyl cyclopropane-1,*trans*-2-dicarboxylate (**2**) was isolated by preparative glpc. The structure of the product was established by spectral data and elemental



**1**

Y = $CO_2R$, COR, CN

[1] For previous studies of reactions utilizing copper(I)–isonitrile complexes as intermediates, see (a) T. Saegusa, Y. Ito, S. Tomita, and H. Kinoshita, *J. Org. Chem.*, 35, 670 (1970); (b) T. Saegusa, Y. Ito, H. Kinoshita, and S. Tomita, *Bull. Chem. Soc. Jap.*, 43, 877 (1970).