

INTERACTION OF THE CARBON-TIN BOND WITH BETA POSITIVE CHARGE
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Abstract: Participation of the C-Sn bond in the development of beta positive charge in aqueous trifluoroethanol does not depend on solvent nucleophilicity but does depend on Sn-C-C-X stereochemistry. These observations favor a hyperconjugative interaction and predict a phenomenal acceleration in the antiperiplanar arrangement.

Positive charge is strongly stabilized by a beta bond between carbon and a lower Group IV (14) atom, as in M-C-C⁺. When M is silicon, the interaction has been described in terms of strong hyperconjugation.¹ Production of the carbocation from Si-C-C-X can occur with an acceleration of at least 10¹² in comparison with the H-C-C-X system.¹ Analogous accelerations involving tin have also been studied, but no general explanation has been agreed upon. Eaborn and Pande originally explained the effect of tin in terms of induction and the strength of the C-M bond.² Davis and co-workers³ concluded that attack by a hydroxylic solvent on tin was the rate-determining step and hence the source of the acceleration. Traylor and co-workers⁴ favored hyperconjugation, as did Eaborn in later papers. Because solvents with different nucleophilicities were used in these studies, these conclusions are not necessarily in contradiction.

To resolve the question of how the carbon-tin bond interacts with developing beta positive charge, we have studied the rate as a function of the stereochemistry about the Sn-C-C-X fragment in solvents of low nucleophilicity. Induction, Sn-C bond strength, and solvent nucleophilicity

should not depend on the dihedral angle, but hyperconjugation varies with the square of the cosine of the Sn-C-C-X dihedral angle.⁵ Consequently, we have prepared and studied compounds 1 and 2; the dihedral angle in 1 is about 60°,



in 2 about 180° when R = *tert*-butyl.⁶ We report herein solvolytic studies of these systems.

Treatment of 1-chlorocyclohexene with sodium and chlorotrimethyltin produced 1-(trimethyltin)cyclohexene, which was epoxidized. Ring opening with lithium aluminum hydride gave 1-OH. For 2-OH (R = H), cyclohexene oxide was opened with trimethyltinlithium. The synthesis of 2-OH (R = *tert*-butyl) was analogous to that used for the silicon substrate.¹

Use of trifluoroacetate as leaving group was found to provide a convenient rate for kinetic studies of the silicon substrates, but the trifluoroacetates of 1 and 2 could not even be isolated. Elimination to cyclohexene occurred instantaneously. In contrast to silicon, even the 3,5-dinitrobenzoates were not isolable. We were able to isolate the *cis* form as its acetate, 1-OAc. The rate of 1-OAc in 97% trifluoroethanol, a solvent of very low nucleophilicity, was measured to be $6.52 \times 10^{-5} \text{ s}^{-1}$ at 25°C. Dilution with water to 80% and 60% TFE changed the rate by very little. Because aqueous trifluoroethanol has variable nucleophilicity but constant ionizing power as the water concentration is changed, the insensitivity of the rate to solvent nucleophilicity is consistent with a carbocation mechanism rather than attack by water on tin.¹

To convert the rate of the acetate to that of trifluoroacetate,⁷ we have multiplied by 1.5×10^6 , but this factor may be too small. The so-calculated

rate is 90 s^{-1} . This value is about 10^{11} times faster than that of cyclohexyl trifluoroacetate and more than 10^6 times faster than that of the analogous silicon substrate under the same conditions.¹

We also measured the rate of the acid-catalyzed elimination of the parent cis alcohol (1-OH) in 91% aqueous CD_3OD : $1.78 \times 10^{-3} \text{ s}^{-1}$ for 0.1 M DCl at 25°C . This value is about 2000 times faster than that for the cis silicon alcohol under the same conditions, so that the rate acceleration of tin over silicon is somewhat moderated in this more nucleophilic solvent.

The acetates of the trans structures (2) reacted much too rapidly to be isolated. We estimate that the trans acetate therefore must react at least a thousand times more rapidly than the cis acetate, and probably much more. Similarly, the rate of acid-catalyzed alcohol eliminations was too fast to measure even at -50°C . Converted to the trifluoroacetate basis, the rate of trifluoroethanolysis of 2-OAc had to be at least 10^5 s^{-1} at 25°C , that is, more than 10^{14} times faster than cyclohexyl trifluoroacetate.

By direct but not quantitative observation, the trans substrates react much more rapidly than the cis substrates, both as the acetate in trifluoroethanol and as the alcohol in aqueous methanol. This stereochemical dependence of the rate supports a hyperconjugative mechanism of interaction between the C-Sn bond and the developing positive charge, as suggested by others.⁴ Explanations based on induction, C-Sn bond strength, or nucleophilic involvement of solvent are not in agreement with the much greater reactivity of the trans substrates. Dilution of the tin effect compared with silicon as solvent nucleophilicity increases, however, suggests that a nucleophilic component may become important in solvents other than 97% trifluoroethanol.

Since 1 appears to react by a k_C mechanism, the 10^{11} acceleration indicates a remarkable stabilization of positive charge by the skew β tin group (the analogous factor for β silicon is 10^5). If the 10^{11} acceleration for

this *cis* trifluoroacetate (60° dihedral angle) may be partitioned¹ into an inductive effect of 10^3 (as an upper limit) and a hyperconjugative effect of 10^8 , we may calculate the expected rate for the 180° axial-axial dihedral angle by the Sunko-Hehre equation⁵ used to analyze the analogous accelerations for silicon.¹ The cosine-squared dependence requires a logarithmic factor of four between 180° and 60° , so that the 10^8 hyperconjugative factor for *cis* translates into a 10^{32} factor for *trans*. We are exploring the ramifications of this extraordinary reactivity of β tin compounds.

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