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STUDIES ON ORGANOTIN COMPOUNDS USING THE DEL RE METHOD

VI. TIN–ARYL AND TIN–VINYL BOND CLEAVAGE IN TRIALKYLARYLTIN AND TRIALKYLVINYLTIN COMPOUNDS

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SUMMARY

The application of the reactivity index $Z\mu$ is extended to tin–aryl and tin–vinyl bond cleavage reactions in trialkylaryltin and trialkylvinyltin compounds. The observed reactivity sequence is interpreted, and the relative rates of tin–aryl bond cleavage in polar solvents correlated with the appropriate reactivity index.

INTRODUCTION

In a previous paper[1] a simple reactivity index was developed within the framework of the Del Re approximations, and was successfully applied to the tin–carbon bond cleavage reactions in saturated organotin compounds. In the present communication the application of this reactivity index is extended to the tin–aryl and tin–vinyl bond cleavage reactions in R_3SnAr and R_3SnVi ($R =$ alkyl group) compounds, and an explanation offered for the influence of alkyl groups on the relative rates of destannylation reactions in these compounds in both polar and non-polar solvents.

RESULTS AND DISCUSSIONS

The method of calculation of the reactivity index $Z\mu$ and the approximations involved in its formulation are given in our earlier paper[1]. The present discussion will therefore be restricted to the development of conditions under which the index $Z\mu$ may be applied to the tin–aryl or tin–vinyl bond cleavage reactions.

In aryl- and vinyltin compounds, the total energy of the molecule may be divided into two parts, *viz.*, the π-energy and the σ-energy. Hence the change in the energy of such a system due to attack by a reagent may be considered to be due to changes both in the π-energy and in the σ-energy of the molecule. The total energy change, ΔE, of the molecule may thus be written as in eqn. (1) where ΔE_π and ΔE_σ represents the changes in π- and σ-energy respectively.

$$\Delta E = \Delta E_\pi + \Delta E_\sigma \qquad (1)$$

Using eqn. (14) of our previous paper[1], eqn. (1) may be rewritten as in eqn. (2) where

Z_μ is the reactivity index and $\Delta(\delta_\mu)$ is the change in the Coulomb integral parameter of the atom, μ, being attacked by the reagent.

$$\Delta E = \Delta E_\pi + Z_\mu \cdot \beta \cdot \Delta(\delta_\mu) \tag{2}$$

If we are to use eqn. (2) directly for the study of the reactions, it is necessary to evaluate ΔE_π also. Although ΔE_π may be calculated by the Huckel LCAO MO method, it is not possible to express eqn. (2) in terms of single parameter, since the change in the Coulomb integral $\Delta(\delta_\mu)$ cannot be calculated, and is regarded as a constant for a given reaction of a group of similar compounds with a particular reagent in a given solvent[1]. However considerable simplification results if we restrict our attention to the reactions of a group of compounds containing the same aryl group, *e.g.*, trialkylphenyltin, trialkylnaphthyltin, and trialkylvinyltin compounds, under comparable conditions. In such cases the change in the π-energy ΔE_π, may be regarded as a constant throughout the series. Actual calculations using Del Re approximations for the σ-frame work and Huckel LCAO MO theory for the π-system on R_3SnAr and R_3SnVi type compounds confirm this view. It is thus expected that, in such cases, the variations in the rates of destannylation reactions will be mainly due to the variation in ΔE_σ, and the reactions may be interpreted and correlated by using the reactivity index Z_μ.

The nature of demetallation reactions in trialkylaryltin by different reagent in a number of solvents have been studied and the mechanism of the reactions has been discussed by several authors[2-9]. The reactions are found to be aromatic electrophilic substitutions, but the influence of the alkyl group upon the rate of the reactions is not very clear. The observed reactivity sequence for cleavage of the Ar–Sn bonds in R_3SnAr compounds (where Ar = phenyl, substituted phenyl, 1-naphthyl, 2-naphthyl) is R = Me > n-Bu > i-Pr when the reactions are studied in polar solvents such as methanol, isopropanol, and aqueous alcohol[2-5]. The observed decrease of the rate constants in going from Me to i-Pr has been attributed to the increase of interaction between the incoming and the leaving groups by Buchman *et al.*[2,3]. It is relevant to note that in the destannylation reactions of R_4Sn and R_3SnR' type compounds, where R and R′ are alkyl groups, the observed sequence is R = Me > Et > Bu > Pr > i-Pr > t-

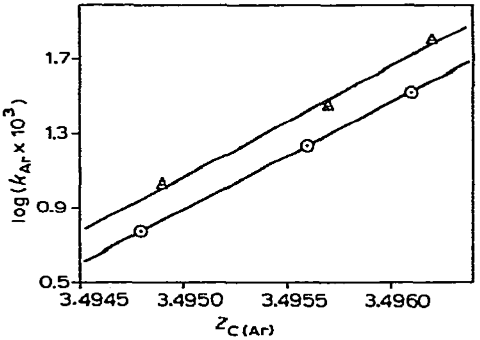
TABLE 1

REACTIVITY INDEX $Z_{C(Ar)}$ AND THE EXPERIMENTAL RATE OF CLEAVAGE OF THE GROUP Ar IN R_3SnAr TYPE COMPOUNDS BY HCl AND IODINE IN METHANOL

Compounds R_3SnAr		$Z_{C(Ar)}$	$K_2 \times 10^2$ (*HCl in methanol*)	K_2 (*I_2 in methanol*)
R	*Ar*			
Methyl	Phenyl	3.4961	3.24	437
n-Butyl	Phenyl	3.4956	1.70	107
Isopropyl	Phenyl	3.4948	0.576	15.9
Methyl	1-Naphthyl	3.4854	6.31	1100
n-Butyl	1-Naphthyl	3.4849	3.80	398
Isopropyl	1-Naphthyl	3.4841	2.24	64.6
Methyl	2-Naphthyl	3.4962	6.31	1020
n-Butyl	2-Naphthyl	3.4957	2.76	257
Isopropyl	2-Naphthyl	3.4949	1.07	28.8

Bu when the reactions are carried out in polar solvents. In our previous communication it has been shown that this sequence is mainly due to the electronic effects, the steric effects being relatively unimportant. It is therefore reasonable to expect that also in the case of R_3SnAr or R_3SnVi type compounds the steric factors will not be important in determining the sequence of the reactions.

If the mechanism of destannylation for trialkylaryltin compounds is an aromatic electrophilic substitution at the carbon atom bonded directly to the tin atom, and if we consider the reactions of the compounds having the same aryl group but different alkyl groups then the appropriate reactivity index will be $Z_{C(Ar)}$ where C(Ar) is the aryl carbon atom bonded to the tin atom. The calculated values of $Z_{C(Ar)}$ for R_3SnAr type compounds (where R = Me, n-Bu, and i-Pr and Ar = phenyl, 1-naphthyl and 2-naphthyl) are given in Table 1 along with the reported second order rate constants for iodo- and proto-destannylation reactions in methanol[2,3]. Figs. 1–4 show the



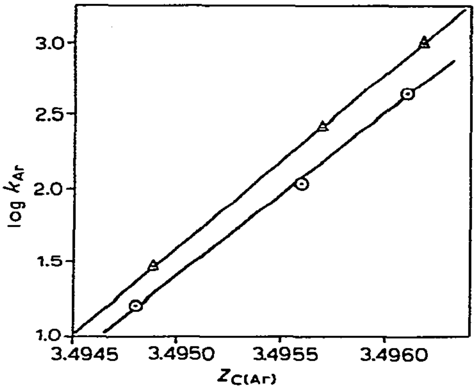
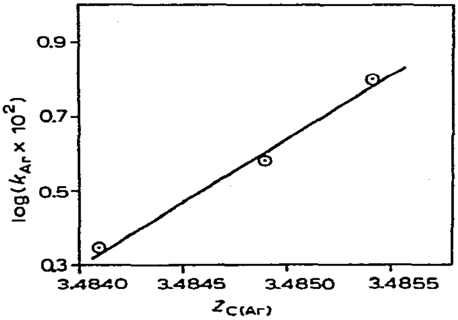


Fig. 1. Correlation between the reactivity index $Z_{C(Ar)}$ and the logarithm of rate of proto-demetallation of R_3SnAr type compounds in methanol; ⊙-Ar = phenyl; △-Ar = 2-naphthyl.

Fig. 2. Correlation between the reactivity index $Z_{C(Ar)}$ and the logarithm of rate of iodo-demetallation of R_3SnAr type compounds in methanol; ⊙-Ar = phenyl; △-Ar = 2-naphthyl.



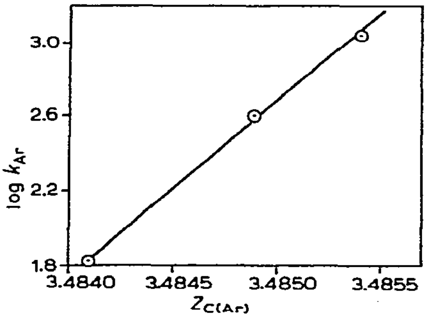


Fig. 3. Correlation between the reactivity index $Z_{C(Ar)}$ and the logarithm of the rate of proto-demetallation of R_3SnAr (Ar = 1-naphthyl) type compounds in methanol.

Fig. 4. Correlation between the reactivity index $Z_{C(Ar)}$ and the logarithm of the rate of iodo-demetallation of R_3SnAr (Ar = 1-naphthyl) type compounds in methanol.

correlation between $Z_{C(Ar)}$ and $\log k_{Ar}$. The existence of such linear correlation between $Z_{C(Ar)}$ and $\log k_{Ar}$ strongly supports the validity of the assumptions regarding the constancy of ΔE_π in a series of R_3SnAr type compounds having the same aryl group and confirms the suggestion that the reactions are electrophilic substitutions at the carbon atom bonded to the tin atom without any appreciable nucleophilic assistance by the reagent at the tin atom. Similar arguments may be applied to the tin–vinyl bond cleavage reactions in trialkylvinyltin compounds by iodine in methanol. The calculated values of $Z_{C(Vi)}$, where C(Vi) indicates the vinyl carbon atom bonded to the tin atom, are given in Table 2. The $Z_{C(Vi)}$ values in R_3SnVi type compounds (R = Me, Et, n-Bu, i-Pr) decrease in the order Me > Et ~ n-Bu > i-Pr, which is in essential agreement with the observed reactivity sequence, *viz.*, Me ~ Et > n-Bu > i-Pr[10].

TABLE 2

VALUES OF THE REACTIVITY INDEX $Z_{C(Vi)}$ FOR SOME R_3SnVi TYPE COMPOUNDS

R in R_3SnVi	$Z_{C(Vi)}$
Methyl	3.8353
Ethyl	3.8346
Isopropyl	3.8340
n-Butyl	3.8347

In non polar solvents the demetallation reactions are difficult to interpret because of the possibility of nucleophilic assistance at the tin atom by the reagent. In such cases Z_C is no longer a valid reactivity index. As discussed in our previous paper[1], the change in the σ-energy in such cases is given by eqn. (3) and no general correlation is possible without the evaluation of actual changes in the Coulomb integrals of the carbon and the tin atoms.

$$\Delta E_\sigma = \beta \cdot [Z_c \cdot \Delta(\delta_c) + Z_{Sn} \cdot \Delta(\delta_{Sn})] \tag{3}$$

However the relative importance of the electrophilic at the carbon atom and the nucleophilic attack at the tin atom may be qualitatively evaluated in such cases by comparing the observed reactivity sequence with the two calculated extreme sequences, one for the electrophilic attack at the carbon atom, given by Z_C and the other for the nucleophilic attack at the tin atom, given by Z_{Sn}. In the iodine cleavage of $R_3SnC_6H_4X$

TABLE 3

REACTIVITY INDICES $Z_{C(Ph)}$ AND Z_{Sn} AND THE RELATIVE RATES OF IODO-DEMETALLATION OF R_3SnPh (R = Me, Et AND CYCLOHEXYL) TYPE COMPOUNDS IN CARBON TETRACHLORIDE

Compound	$Z_{C(Ph)}$	Z_{Sn}	*k(relative)* *I_2 in CCl_4*
$(CH_3)_3SnC_6H_5$	3.4961	3.9946	1
$(C_2H_5)_3SnC_6H_5$	3.4955	3.9173	5.1
$(Cyclo\text{-}C_6H_{11})_3SnC_6H_5$	3.4951	3.8581	5.4

compounds (R = cyclohexyl, Et, Me or Ph) in carbon tetrachloride, studied in detail by Bott *et al.*[7], the observed reactivity sequence is cyclohexyl > Et > Me > Ph. In Table 3 the calculated values Z_C and Z_{Sn} for some trialkylphenyltin compounds are given, along with the relative rates of tin–phenyl bond cleavage reaction. The expected sequence for purely electrophilic attack at the carbon atom in these compounds is Me > Et > cyclohexyl while that for purely nucleophilic attack at the tin is cyclohexyl > Et > Me. Since the observed reactivity sequence is the same as that expected for nucleophilic attack at the tin atom, considerable nucleophilic assistance at the tin atom by iodine is suggested in these reactions. It must however be pointed out that the observed rates do not correlate with the Z_{Sn} values, and the observed rate of cleavage of the tricyclohexyltin group is much less than what would be expected on the basis of purely nucleophilic attack (linear correlation between Z_{Sn} and log k). This suggests that the reaction is actually electrophilic in nature as suggested by Bott *et al.*, though strongly modified by the nucleophilic assistance at the tin atom by the reagent due to the non-polar nature of the solvent.

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