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# MECHANISM OF ELECTROPHILIC SUBSTITUTION WITH PARTICIPATION OF ION PAIRS IN ORGANOMETALLIC CHEMISTRY ($S_E2$ ION PAIR MECHANISM)

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## Summary

A new mechanism ($S_E2$ ion pair) has been suggested for the reaction of organotin compounds with electron-withdrawing groups (R = 9-Me-fluorenyl, indenyl, PhC≡C etc.). It has been shown that some $RSnMe_3$ compounds may undergo ionization or dissociation in polar solvents. In low-polar solvents optically active indenyl derivatives of tin racemize slowly but the rate of racemization is increased by addition of hexamethylphosphoric triamide. This result was explained by the loss of configuration when the ion pair $R^-Sn^+Me_3$ reverts to the covalent form.

The main rules for electrophilic substitution at a saturated carbon atom were established by reactions of organometallic, and in particular organomercury, compounds [1]. At the present time many different organometallic compounds, organotransition metal compounds among them, come within the scope of such studies. Most electrophilic substitution reactions of organometallic compounds proceed by an $S_E2$ mechanism (bimolecular electrophilic substitution). Second order reactions, whose rates increase with increasing nucleophilicity of the organic group R bonded to the metal (according to its position in the Kharasch electronegativity series), and retention of stereochemical configuration when optically active compounds are employed, are characteristics of this mechanism *.

Although attack of the electrophile at the carbon atom bonded to the metal is the rate-determining step, coordination of the nucleophilic part N of an electrophilic agent EN, with the metal atom is the factor which often determines the feasibility of the reaction. This mechanism was labelled $S_Ei$. Nucleophilic coordination may occur simultaneously with or prior to electrophilic attack. The symbols $S_E2i$ and $S_EC$ ** were proposed for these two variations [4]. It should

* The only case of inversion of configuration observed for bromination of *S*-(+)-sec-BuSn(neo-$C_5H_{11})_3$ [2] was found to be due to steric effects of the leaving group [3].

** The $S_EC$ symbol (where C stands for coordination, not carbon) seems confusing and could perhaps be replaced by $S_E2(N)$.

be noted that the $S_E2i$ mechanism is now in question since such a mechanism is forbidden by orbital symmetry [5]. Meanwhile other variations of the $S_E2$ process, e.g. when nucleophilic attack at the metal is the rate-determining step, may be conceived, although no such reaction has been established so far. It should, however, be noted that the effect of the nature of R on the reaction rate in the latter case would be anomalous within the framework of an $S_E2$ mechanism.

$S_E1$ mechanism (monomolecular substitution) is the second type of electrophilic substitution mechanism. It was proposed by Hughes and Ingold in 1935 [6] and established 25 years later [7]. Heterolysis of the C—M bond is the rate-determining step of the $S_E1$ reaction, which is characterized by being zero order in electrophilic agent, having an increase in reaction rate with carbanion $R^-$ stability, and exhibiting racemization when optically active organometallic compounds are used. Several points should be noted concerning the specificity of the mechanism. We assure that the rate-determining step of the reaction does not necessarily involve dissociation of a compound with the formation of free ions: ionization with formation of an R—M ion pair is also possible, which complicates the problem of $S_E1$ reaction stereochemistry. The only example studied so far (isotope exchange of $\alpha$-carboethoxybenzylmercury bromide with $^{203}HgBr_2$ in DMSO) demonstrated that the reaction took place with loss of stereochemical configuration [8] which implies the formation of a free carbanion with change of hybridization of the carbon atom from $sp^3$ to $sp^2$.

The second factor to be taken into account when considering $S_E1$ reactions is the ionization or dissociation of an organometallic compound which may occur either by action of the solvent or as the effect of nucleophilic coordination with the electrophilic agent. Such coordination may change the order of the reaction kinetics and alter the stereochemical result. Thus, the reaction of substituted $\alpha$-carboethoxybenzylmercury bromide with $I_3^-$ exhibited second order kinetics but the substituent effect was anomalous within the framework of an $S_E2$ mechanism [9]. The result is easily justifiable in the case of an $S_E1$ mechanism if ionization of an organomercury compound takes place in the presence of anion $I_3^-$ [10]. A Brønsted-type correlation of $\ln k$ and $pK_a$ values of corresponding CH-acids RH is essential for the identification of an $S_E1$ type of reaction [10].

Electrophilic substitution and other reactions of ionic organometallic compounds which form ions and ion pairs [11] in solution take place with participation of these ionic species. In analogy with the symbol for nucleophilic substitution the symbol $S_E2C^-$ is proposed for these reactions *: it would imply that electrophilic attact is directed at the ionic species. The observed rate constant, in accordance with Acree's equation, is equal to the sum of contributions of the species of each type: $k_{obs} = \alpha k_i + (1 - \alpha)k_{ip}$, where $\alpha$ is the degree of dissociation. This mechanism is quite important for determining the reactivity of carbanions and work in this area has been yielding good results [12].

We thus have considered the three mechanisms of electrophilic substitution

* It is quite possible that $S_N2C^+$ and $S_E2C^-$ processes which involve participation of carbonium ions and carbanions should not be considered as substitution reactions.

which have been recognized so far, each being a part of the whole spectrum of mechanism modifications.

However, a study of the reactivities of organotin compounds has made it necessary for us to introduce a new electrophilic substitution mechanism. In the study of the reactions of halogen- and mercury-destannylation [13—16] we have found that in accordance with an $S_E2$ mechanism the reaction rate decreases on going from $C_6H_5SnMe_3$ to $C_6F_5SnMe_3$; but in the case of organotin compounds with stronger electron-withdrawing groups as substituents (R = PhC≡C, fluorenyl, indenyl) the reaction rate sharply increased although the reaction was of the second order (eqn. 1):

$$RSnMe_3 + I_2 \xrightarrow{DMSO} RI + Me_3SnI \qquad (1)$$

$k_2$ 25°C (l mol$^{-1}$ s$^{-1}$) [14,17]: All, 2.3 × 10$^7$; $C_9H_7$, 9.6 × 10$^6$; PhC≡C, 3.4 × 10$^6$; $CH_2$=CH, 620; Ph, 420; Me, 52.5; $C_6F_5$, 46.7.

$$RSnMe_3 + Br_2 \xrightarrow{DMF/CCl_4} RBr + Me_3SnBr \qquad (2)$$

$k_2$ 25°C (l mol$^{-1}$ s$^{-1}$) [16]: $C_9C_7$, 1.2 × 10$^8$, 9-$CH_3C_{13}H_8$, 4.1 × 10$^4$; Ph, 1.35 × 10$^4$. Halogenation of $RSnMe_3$ (where R = cyclo-$C_5H_5$, $CH_3COCH_2$ and CN) in DMSO was a first order reaction which was zero order in $Hal_2$, i.e. an $S_E1$ mechanism operated [17].

$$RSnMe_3 + I_2 \xrightarrow{DMSO} RI + Me_3SnI \qquad (3)$$

$k_1$ 20°C (s$^{-1}$): CN, 0.33; $CH_3COCH_2$, 0.25; cyclo-$C_5H_5$, 4.1 *. Many of the reactions studied were so rapid that their rates could only be studied by the stopped flow technique. Similar patterns in the effects of substituents were observed in the reactions of organogermanium compounds [18]. It should be noted that all the reactions considered only proceeded with cleavage of the R—Sn (or R—Ge) bond. We have assumed that the increased reactivity of organotin compounds with sufficiently strong electron-withdrawing substituents is due to the participation of ion pairs formed in the pre-equilibrium stage rather than to the covalent-structured forms of an organometallic compound, i.e. the reaction proceeds by an ion pair $S_E2$ mechanism ($S_E2ip$) (eq. 4).

$$RSnMe_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^{-+}SnMe_3 \xrightarrow[k_2]{EN} RE + Me_3SnN \qquad (4)$$

In our opinion, this mechanism must occur when the nucleophility of R is too low for direct electrophilic attack as in an $S_E2$ mechanism, while the carbanion, $R^-$, stability is too low for an $S_E1$ mechanism to operate. In this case the situation may arise when electrophilic attack at the ion pair as the rate-determining step will prove to be the most effective mechanism.

The mechanism suggested is directly analogous to a nucleophilic substitution where an $S_N2$ ion pair mechanism is proposed by Sneen as a "unified" nucleophilic substitution mechanism [19]. In nucleophilic substitution reactions this

* This is the rate constant for reaction with bromine in DMF/$CCl_4$ 1/1 [15].

mechanism is most likely to occur with secondary compounds: for primary and tertiary derivatives $S_N2$ and $S_N1$ mechanisms, which are extreme cases of the $S_N2$ ion pair mechanism are more common. At present, however, arguments in favour of the $S_N2$ ion pair mechanism are nearly outbalanced by the arguments against. No direct evidence of the existence of such a mechanism has been obtained [20,21] but this concept does not contradict theoretical calculations and is generally appealing [22]. The essential feature of Sneen's mechanism is the assumption of that a contact ion pair is formed in the pre-equilibrium stage with resulting inversion of configuration on substitution. An $S_N1$ mechanism would require the transformation of a contact ion pair into a solvent-separated ion pair, or free ions, as the rate-determining step. Generally, however, this limitation is unnecessary. The kinetics observed may be accounted for by the following simple scheme for the relation of $k_2$ and $k_1$ constants:

$k_{-1} \gg k_2$ [EN] $\quad k_{obs} = Kk_2$[EN] $\quad (S_E2ip)$

$k_{-1} \ll k_2$[EN] $\quad k_{obs} = k_1 \quad (S_E1)$

Organometallic chemistry is a rewarding field for such studies and, since both the polarity of the R—M bond may vary widely with change in the nature of the carbanion and metal, and the solvent too has an effect on ionization of organometallic compounds, a variety of reaction mechanisms are observed.

We found it quite unexpected that the latter factor (solvent effect) affected most strongly the state of organotin compounds in solutions. We have shown earlier that some σ-bonded organotin compounds containing electron-withdrawing groups are capable of ionization or even dissociation in sufficiently polar solvents [23]. UV spectroscopy and conductometry were employed to study the process. The electronic spectra of 9-substituted fluorenyl and indenyl derivatives of tin in heptane are very similar to the spectra of corresponding hydrocarbons which indicates that they have a covalent form. The spectrum of 9-$CNC_{13}H_8SnMe_3$ in hexamethylphosphoric triamide (HMPTA) is, however, identical to the spectrum of the corresponding caesium salt. The positions of adsorption maxima ($\lambda_{max}$ 458, 432, 407 nm) and the ratios of extinction coefficients do not change on dilution which points to the formation of free ions or solvent-separated ion pairs in solutions of organotin compounds because the spectral characteristics of these species are practically identical. Conductometric studies showed that free ions were formed since the equivalent conductivity remained unchanged over a range ($2 \times 10^{-3}$—$8 \times 10^{-3}$ $M$) of concentrations ($\lambda$ 108 $\Omega^{-1}$ $mol^{-1}$ $cm^2$). Complete dissociation of 9-$CNC_{13}H_8SnMe_3$ in HMPTA is also confirmed by the similarity of the rate constants for alkylation of the 9-cyanofluorenyl derivatives of caesium ($k_2$ 10°C) $7.8 \times 10^{-2}$ $M^{-1}$ $s^{-1}$ [24]) and tin ($k_2$ (20°C) $3.1 \times 10^{-2}$ $M^{-1}$ $s^{-1}$).

9-$CNC_{13}H_8SnMe_3$ may also dissociate into free ions in acetonitrile and pyridine, although dissociation is not complete. The degree of dissociation in MeCN is only 1.2% at $c$ $6.8 \times 10^{-3}$ $M$. Dissociation is inhibited by the addition of $Me_3SnBF_4$ which forms a common ion, $Me_3Sn^+$.

In Table 1 the values of dissociation constants for 9-$CNC_{13}H_8SnMe_3$ in a number of solvents are given. These constants show that dissociation is determined by the donor ability of the solvent, characterized by the Gutmann donor

TABLE 1

VALUES OF DISSOCIATION CONSTANTS FOR 9-$CNC_{13}H_8SnMe_3$ IN VARIOUS SOLVENTS

| Solvent | $K$ (18°C) (mol · $l^{-1}$) | DN($SbCl_5$) [a] | $\epsilon$ (20°C) |
|---|---|---|---|
| DME | [b] | 19.2 | 4.3 |
| MeCN | $(3 \pm 1) \times 10^{-5}$ | 14.1 | 38 |
| Py | $(1.2—0.4) \times 10^{-3}$ | 33.1 | 12.4 |
| HMPTA | [c] | 38.8 | 30 |

[a] Gutman donor number [25]. [b] Conductances of solution and pure solvent are identical. [c] Completely dissociated at concentrations below $10^{-2}$ *M*.

number [25], rather than by its dielectric constant. The ability of $RSnMe_3$ to dissociate and ionize is also determined by the nature of group R: unsubstituted fluorenyl and indenyl derivatives of tin under the conditions studied are not capable of undergoing ionization or dissociation. In general the ability to dissociation (or ionization) is determined by carbanion $R^-$, stability. For $RSnMe_3$ with R = $C_{13}H_9$, 9-$MeC_{13}H_8$ * and $C_9H_7$ p$K_a$ of RH [26] = 21.1, 21.8 and 20.2 respectively, and dissociation does not occur. For $RSnMe_3$ with R = 9-$PhC_{13}H_8$, 1-Me-3-$PhC_9H_5$ and 9-$CNC_{13}H_8$ p$K_a$ of RH [26] = 18.6, 16 and 11.4, respectively, and complete dissociation occurs. Some compounds, however, dissociate more readily than might be expected from their p$K_a$ values. Thus, 9-phenylfluorenyltrimethyltin dissociates completely although the p$K_a$ values for indene and 9-phenylfluorene are identical on the MSAD scale [27]. This is likely to be connected with steric factors and reduction of tension upon dissociation.

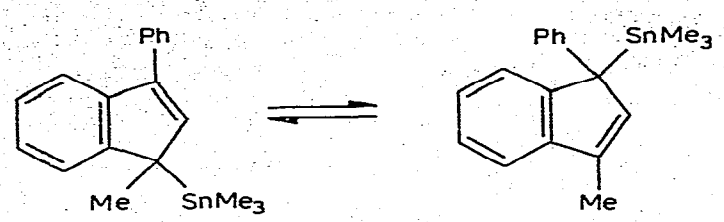
The ability of the organotin compounds under study to ionize and dissociate is a strong argument in favour of an ion pair mechanism in cases when ions and ion pairs are not detected in reactions in measurable amounts. Direct proof of ion pair formation in solutions of organotin compounds at steady concentrations was obtained by stereochemical studies. We used optically active *S*-(+)-(3-methylindenyl)trimethyltin ($[\alpha]_D^{18}$ +232°, $C_6H_6$, *c* 2.4) and (+)-(1-methyl-3-phenylindenyl)trimethyltin ($[\alpha]_D^{18}$ +24°, $C_6H_6$, *c* 4.4), which were synthesised by stannylation of optically active hydrocarbons using diethylaminotrimethyltin on *S*-(+)-1-methylindene ($[\alpha]_D^{18}$ +189°, $C_6H_6$, *c* 1.2) and *R*-(—)-1-methyl-3-phenylindene ($[\alpha]_D^{18}$ —55°, $C_6H_6$, *c* 2.2) in benzene [28,29] (eq. 5). A study of the

$$R_3CH + Et_2NSnMe_3 \rightarrow R_3CSnMe_3 + Et_2NH \quad (5)$$

temperature dependence of $^{13}C$ NMR spectra showed that together with (1-methyl-3-phenylindenyl)trimethyltin another isomer (1-phenyl-3-methylindenyl)-trimethyltin, was present in the equilibrium mixture at room temperature. Fast metallotropic rearrangement takes place between these isomers.
The metallotropic equilibrium is displaced to the left and the proportion of (1-phenyl-3-methylindenyl)trimethyltin is 10—15% [29]. The retention of optical activity shows that migration is intermolecular (eq. 6).

Optically active indenyl derivatives of tin in low-polar aprotic solvents ($C_6H_6$,

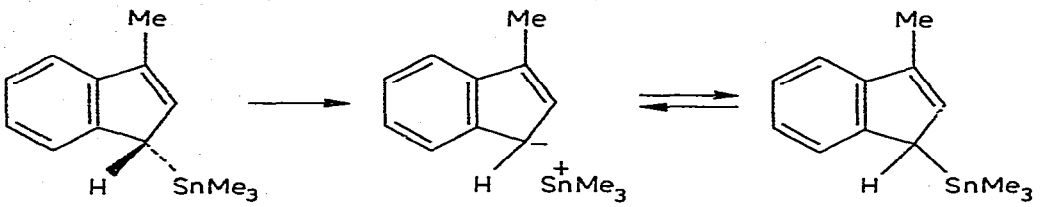
* 2% ionized (or dissociated) at [$RSnMe_3$] $8.5 \times 10^{-3}$ *M*.




(6)

dimethoxyethane) are quite stable stereochemically. However, they quickly racemize in pure form or in solution in HMPTA (Table 2). The rate of racemization of the two organotin compounds studied is related to their ability to ionize. Thus, (1-methyl-3-phenylindenyl)trimethyltin, which ionises more readily, exhibits markedly decreased optical activity even in benzene ($k_1$ (20°C) 3.2 × $10^{-5}$ $s^{-1}$, $c$ 0.2 $M$); in $CH_2Cl_2$ it is even faster. Racemization of (1-phenyl-3-methylindenyl)trimethyltin under these conditions is extremely slow.

We assume that loss of stereochemical configuration occurs as the result of ionization (facilitated by coordination of the tin atom with the solvent) with the formation of an ion pair, the return of which into the initial state takes place with racemization (eq. 7).




(7)

The type of this ion pair remains unknown. The reversion from a contact ion pair in nucleophilic substitution reactions was found to occur with retention of configuration, yet in the case of carbanion ion pairs nothing is known about the nature of migration of the cation moiety around the anionic centre in the various types of ion pairs. The formation of solvent-separated ion pairs in the presence of HMPTA seems probable but their existence in benzene is unlikely.

The ability of the organotin compounds studied to ionize and to follow an

TABLE 2

EFFECT OF ADDED HMPTA ON RACEMIZATION RATE CONSTANTS FOR *S*-(+)-(3-METHYLINDENYL)TRIMETHYLTIN IN DME AT 18°C

| [$RSnMe_3$] × $10^2$ ($M$) | [HMPTA] × $10^2$ ($M$) | $\tau_{1/2}$ × $10^{-2}$ (min) | $k_1$ × $10^5$ ($s^{-1}$) |
|---|---|---|---|
| 4.98 | 0 | 34.0 | 0.34 [a] |
| | 1.18 | 13.8 | 0.83 |
| | 1.88 | 9.7 | 1.2 |
| | 2.30 | 6.8 | 1.7 |
| 3.72 | 4.24 | 1.9 | 6.0 |
| | 7.77 | 0.97 | 12.9 |
| | 12.9 | 0.60 | 19.3 |

[a] In 1/5 DME/THF.

$S_E2$ ion pair mechanism in their reactions may be used for synthetic purposes. We have carried out the reaction of organotin compounds, $RSnMe_3$ (R = fluorenyl, 3-methylindenyl, indenyl, 9-cyanofluorenyl), with alkylating agents (MeI, MeOTs, $(MeO)_2SO_2$) in HMPTA and a mixture of tetrahydrofuran/ether (1/1) at 20°C to demonstrate this aspect of the probelm [30]. Alkyldestannylation is known to be a non-specific reaction for organotin compounds. It has been shown by GLC that the presence of excess alkylating agent and with sufficient reaction time the yields of alkyldestannylation products were quantitative (eq. 8). The reactivities of organotin compounds in this reaction from a series

$$RSnMe_3 + CH_3X \rightarrow RCH_3 + Me_3SnX \qquad (8)$$

corresponding to the decrease in electron-withdrawing properties of the substituent group: $9\text{-}CNC_{13}H_8SnMe_3 \gg C_9H_7SnMe_3 > 3\text{-}CH_3C_9H_6SnMe_3 \gg C_{13}H_9SnMe_3$.

The reactivities of methylating agents decrease in the series: MeI > MeOTs > $(MeO)_2SO_4$. Such an effect of the nature of the leaving group is characteristic of nucleophilic substitution reactions when weak nucleophilic agents are used.

In the future we hope to carry out a number of other reactions which are usually carried out with ionic type organometallic compounds.

## Experimental

HMPTA was purified by double distillation over $CaH_2$ under reduced pressure ($<10^{-1}$ mmHg). DME and THF were treated with KOH, boiled and distilled over sodium in the presence of benzophenone. Acetonitrile was purified according to the literature method [31]. Pyridine was dried and distilled over anhydrous BaO.

Organotin compounds were prepared by the action of $Et_2NSnMe_3$ on the corresponding hydrocarbon in anhydrous benzene [32]. $9\text{-}CNC_{13}H_8SnMe_3$ and $9\text{-}PhC_{13}H_8SnMe_3$ were obtained for the first time, as viscous oils, which were purified by distillation at 120—160°C/0.01 mmHg). The structure and purity of compounds obtained were acertained by NMR spectroscopy and elemental analysis.

$9\text{-}CNC_{13}H_8SnMe_3$, NMR ($CCl_4$) ($\delta$, ppm): 7.2 (m, 8H, aromatic). 0.29 (s, 9H, $Me_3Sn$); analysis Found: C, 57.6; H, 4.87. $C_{17}H_{17}NSn$ calcd.: C, 57.4; H, 4.80%.

$9\text{-}PhC_{13}H_8SnMe_3$, NMR ($CCl_4$) ($\delta$, ppm): 7.7 and 7.2 (m, 13H, aromatic), 0.18 (s, 9H, $Me_3Sn$); analysis found: C, 64.5; H, 5.31. $C_{22}H_{22}Sn$ calcd.: C, 65.3; H, 5.43%.

$1\text{-}Me\text{-}3\text{-}PhC_9H_5SnMe_3$, NMR ($CCl_4$) ($\delta$, ppm): 7.8 (m, 9H, aromatic), 6.72 (s, H, —CH=CPh—) 1.85 (s, 3H, Me), 0.06 (s, 9H, $Me_3Sn$); analysis found: C, 62.3; H, 5.90. $C_{19}H_{22}Sn$ calcd.: C, 61.7; H, 5.95%.

The others organotin compounds exhibited physical constants agreeing with those reported elsewhere ($C_9H_7SnMe_3$ [33], $9\text{-}MeC_{13}H_8SnMe_3$ [16]). The preparation of $Me_3SnBF_4$ was described in ref. 34.

*S*-(+)-$3\text{-}MeC_9H_6SnMe_3$ ($[\alpha]_D^{18}$ +232°; PhH, *c* 2.4 *M*) was prepared from *S*-(+)-$1\text{-}MeC_9H_7$ ($[\alpha]_D^{18}$ +189°, PhH, *c* 1.2 *M*) [28]. The same method was used in the preparation of *S*-(+)-$1\text{-}Me\text{-}3\text{-}PhC_9H_5SnMe_3$ ($[\alpha]_D^{18}$ +24°, PhH, *c* 4.4 *M*) from *R*-(—)-$1\text{-}Me\text{-}3\text{-}PhC_9H_6$ ($[\alpha]_D^{18}$ —55.1°, PhH, *c* 2.2 *M*). *R*-(—)-$1\text{-}Me\text{-}3\text{-}PhC_9H_6$ was prepared by treatment of *R*-(—)-1-methylindanone with phenylmagnesium

bromide followed by dehydration with 15% $H_2SO_4$ (43% yield), b.p. 153—155°C/15 mmHg). NMR ($CCl_4$) δ ppm: 7.6 (m, 9H, aromatic), 6.3 (d, H, —CH=CPh—), 3.5 (q, H, CHMe), 1.3 (d, 3H, Me).

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