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THE REACTION OF ORGANOTIN COMPOUNDS WITH DERIVATIVES OF TRIARYLMETHANE IN CH_2Cl_2

A.N. KASHIN *, N.A. BUMAGIN, I.P. BELETSKAYA and O.A. REUTOV
Moscow State University, Moscow (U.S.S.R.)
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Summary

The reaction of $RSnMe_3$ with the triarylmethyl salts Ph_3CBF_4, $(C_6Cl_5)_3CSbCl_6$ and $(p\text{-}NO_2C_6H_4)_3CBr$ was studied. It was shown that the reaction of $RSnMe_3$ ($R = CH_3$, $CH_2{=}CHCH_2$, $C_{13}H_9$ (9-fluorenyl), C_9H_7 (indenyl), $PhC{\equiv}C$ and CN) with Ph_3CBF_4 is an electrophilic substitution process and that Ph_3CR is formed quantitatively. The reactions of $PhSnMe_3$ with Ph_3CBF_4 and $RSnMe_3$ ($R = CH_3$, $CH_2{=}CHCH_2$, Ph and $PhC{\equiv}C$) with $(C_6Cl_5)_3SbCl_6$ are redox processes. $(p\text{-}NO_2C_6H_4)_3CBr$ only reacts with $RSnMe_3$ when R is a strong electron withdrawing group (R = 9-fluorenyl, indenyl and cyclopentadienyl) and $(p\text{-}NO_2C_6H_4)_3CR$ and $(p\text{-}NO_2C_6H_4)_3C^{\cdot}$ are formed. It is assumed that the reactions which give $(p\text{-}NO_2C_6H_4)_3CR$ and $(p\text{-}NO_2C_6H_4)_3C^{\cdot}$ are independent.

Introduction

Triarylmethane derivatives are known as oxidizing agents with many organometallic compounds. Thus the reaction of Ph_3CCl with butyllithium gives $(Ph_3CO)_2$ and 1,1,1-triphenylpentane [1]. Trityl radicals were directly observed in the reaction of ethyllithium with Ph_3CCl [2]. Triphenylmethyl radicals are mainly formed in the reaction of Ph_3CCl with PhMgBr; the yield of Ph_4C which is the product of electrophilic substitution is usually 0.5—5% [3] and only under special conditions does it reach 12% *.

Trityl radicals are also formed in the Würtz type reaction between Ar_2Hg and trityl salts [5]. The ratio of the Würtz reaction products and trityl peroxide depends strongly on the nature of the solvents used and the substituent in the benzene ring of Ar_2Hg. On the basis of the correlation of $\log k_2$ and σ^+ the assumption was made that both paths of the reaction are not independent and involve a common ion-radical intermediate formed at the electron transfer stage.

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* p-Phenyltriphenylmethane is also formed in the reaction due to the formation of phenyl radicals [4].

In the present work we studied the reaction of the following triarylmethane derivatives: Ph_3CBF_4, $(C_6Cl_5)_3CSbCl_6$ and $(p\text{-}NO_2C_6H_4)_3CBr$, with organotin compounds $RSnMe_3$ ($R = CH_3$, $PhCH_2$, $CH_2{=}CHCH_2$, Ph, $C_{13}H_9$ (fluorenyl), C_9H_7 (indenyl), $PhC{\equiv}C$, c-C_5H_5 (cyclopentadienyl) and CN) in methylene chloride. The choice of this solvent was determined by its high dissolving ability, the stability of $RSnMe_3$ in it and its high ionization ability with respect to trityl salts. Reactions were carried out at 20°C. Analyses of products were made by TLC, GLC, PMR, UV and mass spectroscopy.

Results

Reaction of $RSnMe_3$ with Ph_3CBF_4

The reaction of $RSnMe_3$ ($R = CH_2{=}CHCH_2$, $C_{13}H_9$, C_9H_7, $PhC{\equiv}C$ and CN) with Ph_3CBF_4 is characterised by a deepening of the colour on mixing the reactants. This phenomenon has been studied in greater detail for the reaction with $PhC{\equiv}CSnMe_3$. The broad band at λ_{max} 571 nm which is absent in the spectra of the reactants is observed in the UV-spectrum of the mixture; the Me_3Sn-group proton signal (0.33 ppm) immediately shifts about 0.4 ppm downfield and the 2143 cm^{-1} band corresponding to the $C{\equiv}C$ bond vibrational frequency in $C_6H_5C{\equiv}CSnMe_3$ disappears.

All the reactions proceed with cleavage of the R—Sn bond and in every case except for $PhSnMe_3$ the products of electrophilic substitution, Ph_3CR are formed quantitatively (Table 1). The signal of $Ph_3C^{\cdot}$ is absent in EPR spectra during the reactions.

The reaction of $PhSnMe_3$ with Ph_3CBF_4 proceeds via another route. To determine the extent of this reaction the reaction mixture was treated with iodine after 27 h and the quantity of PhI (16%) was determined. C_6H_6 (53%), $CHCl_3$, Ph_3COH (96%) and, unexpectedly, Me_4Sn (31%) were found in the products of the reaction. Tetraphenylmethane was not formed, as has been shown by mass spectroscopy *.

Reaction of $RSnMe_3$ with $(C_6Cl_5)_3CSbCl_6$

The quantitative formation of $(C_6Cl_5)_3C^{\cdot}$ in the reaction of $RSnMe_3$ ($R = CH_3$, $CH_2{=}CHCH_2$, Ph and $PhC{\equiv}C$) with $(C_6Cl_5)_3CSbCl_6$ was shown by UV spectroscopy. The band at λ_{max} 691 nm (ϵ 30000) for $(C_6Cl_5)_3CSbCl_6$, and two bands at λ_{max} 510 (ϵ 1190) and 562 nm (ϵ 1200) for $(C_6Cl_5)_3C^{\cdot}$ are in the visible range of the UV-spectrum [7]. In a 50-fold excess of $SbCl_5$ radical $(C_6Cl_5)_3C^{\cdot}$ is transformed to the original salt $(C_6Cl_5)_3CSbCl_6$ and the concentration of the salt formed is the same as the original one. The results are given in Table 2.

Reaction of $RSnMe_3$ with $(p\text{-}NO_2C_6H_4)_3CBr$

The reaction of 9-fluorenyltrimethyltin with $(p\text{-}NO_2C_6H_4)_3CBr$ takes place with formation of 9-tris(*p*-nitrophenyl)methylfluorene (90%), tris(*p*-nitrophenyl)methyl radical (7%) and bis(9-fluorenyl). The rate of the reaction is very low; 89% yield is reached only after 600 h. However, the rate increases sharply in the presence of Et_4NCl and the reaction is over in 1.5 h. 9-Tris(*p*-

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* The characteristic peaks with *m/e* 320, 244, 243, 165 are absent in the mass spectrum [6].

TABLE 1

YIELD OF THE PRODUCTS OF THE REACTION OF $RSnMe_3$ WITH Ph_3CBF_4 AND CH_2Cl_2 AT 20°C

R	c (M)	t (h)	Conversion [a] (%)	Yield of Ph_3CR (%)
CH_3	0.20	336	58	90
$CH_2{=}CHCH_2$	0.57	72	100	96
$C_{13}H_9$ (9-Fluorenyl)	0.20	2	100	98
C_9H_7 (indenyl)	0.35	1	87	96
$PhC{\equiv}C$	0.20	20	77	99
CN	0.10	0.2	90	96
C_6H_5	0.54	27	84	—

[a] Conversion was determined by measuring the quantity of RH and Ph_3COH formed from the initial reactants upon treatment of the reaction mixture with water.

nitrophenyl)methylfluorene (94%) and $(p\text{-}NO_2C_6H_4)_3C^{\cdot}$ (6%) were found in the mixture of products.

The yield of the product of electrophilic substitution, tris(p-nitrophenyl)-indene, decreases to 68% as the yield of the product of the redox process, $(p\text{-}NO_2C_6H_4)_3C^{\cdot}$, increases to 32% in the reaction with indenyltrimethyltin.

The redox reaction is even more important in the reaction with $c\text{-}C_5H_5SnMe_3$: the yield of $(p\text{-}NO_2C_6H_4)_3C^{\cdot}$ is 50%. This latter reaction was only allowed to proceed for a short time in order to avoid the influence of side reactions on the yield of $(p\text{-}NO_2C_6H_4)_3C^{\cdot}$. It is known that dienes [8], and in particular cyclopentadiene derivatives, react with $Ph_3C^{\cdot}$ to yield the 1,4 addition product. In fact, the yield of $(p\text{-}NO_2C_6H_4)_3C^{\cdot}$ was about only 15% if the reaction was allowed to go to completion (after 48 h). The results are shown in Table 3.

The electrochemical reduction of Ar_3CX

We have studied the polarographic reduction of $(p\text{-}NO_2C_6H_4)_3CBr$ and Ph_3CBF_4 as well as the oxidation and reduction of $(C_6Cl_5)_3C^{\cdot}$ over a platinum disk electrode (0.5 cm^2). A 0.2 *M* solution of Bu_4NClO_4 in methylene chloride was used as the supporting electrolyte. Polarographic data are given in Table 4.

Discussion

As may be seen from the above, the product of electrophilic substitution, Ph_3CR, is formed quantitatively in the reactions of $RSnMe_3$ (R = CH_3, CH_2=

TABLE 2

YIELD OF $(C_6Cl_5)_3C^{\cdot}$ IN THE REACTION OF $RSnMe_3$ WITH $(C_6Cl_5)_3CSbCl_6$ AND CH_2Cl_2 AT 20°C

R	Yield of $(C_6Cl_5)_3C^{\cdot}$ (%)
CH_3	88
$CH_2{=}CHCH_2$	100
C_6H_5	100
$C_6H_5C{\equiv}C$	91

TABLE 3

YIELD OF THE PRODUCTS IN THE REACTION OF $RSnMe_3$ WITH $(p\text{-}NO_2C_6H_4)_3CBr$ AND CH_2Cl_2 AT 20°C

R	t (h)	Conversion (%)	Yield of $(p\text{-}NO_2C_6H_4)_3CR$ (%)	Yield of $(p\text{-}NO_2C_6H_4)_3C^{\cdot}$ (%)
$C_{13}H_9$	600	90	90	7
C_9H_7	120	73	68	32
$c\text{-}C_5H_5$	3	34		50

TABLE 4

THE RESULTS OF POLAROGRAPHIC REDUCTION OF TRIARYLMETHYL DERIVATIVES ON A PLATINUM DISK ELECTRODE, CH_2Cl_2, 0.2 M Bu_4NClO_4, 25°C

Compound	c (mmol/l)	w (rev/min)	i (μA)	$i \times 10^2/w^{1/2}$, ($\mu A \cdot rad^{-1/2} \cdot s^{1/2}$)	$E_{1/2}$ (V) vs. SCE	αn_a
$(C_6H_5)_3CBF_4$	1	1350	1.80	15	0.335	
		3000	2.44	14	0.330	0.70
		7550	2.72	10	0.350	
$(p\text{-}NO_2C_6H_4)_3CBr$		1350	4.00	35	−0.790	
		2000	5.90	33	−0.740	0.28
		5750	8.00	33	−0.790	
	1	1350	4.09	35	−0.170 [a]	
		3000	5.64	31	−1.150	0.97
		5750	7.64	31	−1.190	
$(C_6Cl_5)_3C^{\cdot}$		2080	0.67	4.5	1.680 [b]	
		3000	0.85	4.8	1.685	
	1	3960	0.73	3.6	1.684	0.91
		3000	0.90	5.1	−0.125	
		7450	1.05	3.8	−0.125	0.90

[a] May be the wave due to the reduction of the NO_2 group. [b] The wave due to the oxidation of the radical.

$CHCH_2$, $C_{13}H_9$, C_9H_7, $PhC{\equiv}C$ and CN) with Ph_3CBF_4. No $Ph_3C^{\cdot}$ was observed using EPR spectroscopy *, thus we may conclude that the majority of the reactions studied are electrophilic substitutions of the type shown in eq. 1.

$$RSnMe_3 + Ph_3CBF_4 \rightarrow Ph_3CR + Me_3SnBF_4 \quad (1)$$

The absence of radicals and radical transfer products rules out the possibility of a redox mechanism.

It is known that the CN group may be considered as a pseudohalogen and that it participates in anion exchange reactions. For example, tritylcyanide and tritylisocyanide are formed in the reaction of Ph_4AsCN with Ph_3CCl [9], and the reaction of Me_3SnCN with Ph_3CBF_4 where tritylcyanide is formed quantitatively is a similar process. This latter reaction must be reversible since in the UV-spectrum of the mixture of colourless Me_3SnBF_4 and Ph_3CCN in CH_2Cl_2 there appear bands at λ_{max} 435 and 412 nm corresponding to the absorptions of the trityl cation. However, the position equilibrium shifts strongly towards

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* Only 0.01% $Ph_3C^{\cdot}$ was registered by EPR spectroscopy in the reaction of $C_{13}H_9SnMe_3$ with Ph_3CBF_4.

formation of Ph_3CCN. Me_3SnCN may be regarded as a cyanide in nonpolar solvents [10,11], but in theory the reaction of Me_3SnCN with Ph_3CBF_4 may bring about the formation of both trityl cyanide and trityl isocyanide owing to the ambivalent character of the cyano group. GLC and IR spectroscopy revealed only trityl cyanide in the reaction, nevertheless the formation of $Ph_3CN{=}C$ initially cannot be excluded as we have shown that it isomerises rapidly (when obtained separately) to Ph_3CCN, even in the presence of 1% Ph_3CBF_4.

We have mentioned above a deepening of the colour upon mixing the reagents. This may be connected with the formation of complexes of organotin compounds with Ph_3CBF_4. It is known that organotin compounds such as Alk_4Sn form charge transfer complexes with tetracyanoethylene [12]. But in our case the change of colour is observed only for organotin compounds which contain a π-electron system. Thus we may postulate that $RSnMe_3$ forms π-type complexes with Ph_3CBF_4. This assumption is confirmed by the formation of π-complexes of trityl salts and aromatic hydrocarbons [13,14]. If this is the case these complexes may take part in the reaction under consideration.

The reactivity of the series of organotin compounds $RSnMe_3$ in trityldestannylation reactions varies in practically the same way as for other reactions of electrophilic substitution [15]: $CH_3 < CH_2{=}CHCH_2 < PhC{\equiv}C < C_{13}H_9 < C_9H_7 <$ CN. Thus Me_4Sn reacts with Ph_3CBF_4 extremely slowly (58% after 336 h) and $PhCH_2SnMe_3$ does not react at all (see ref. 16). The high reactivity of allyltrimethyltin towards Ph_3CBF_4 agrees with the behaviour of this compound in other reactions, and the explanation is usually as S_E2' or S_Ei' mechanism with attack at the "tail" of the molecule [15].

Organotin compounds containing strong electron-withdrawing groups ($R = PhC{\equiv}C$, $C_{13}H_9$, C_9H_7 and CN) are especially active in trityldestannylation reactions which also agrees with their behaviour in mercury- and iodo-destannylation reactions [17,18]. It is possible that in this as well as in other reactions of these compounds the ionized form of $RSnMe_3$ participates in the reaction, i.e. an S_E2 ion pair mechanism takes place [18].

The reaction of $PhSnMe_3$ with Ph_3CBF_4, where steric factors prevent electrophilic attack, follows a different path. In our opinion, benzene is formed as the result of a redox reaction between the phenyl radical and the solvent. The latter reaction also leads to formation of $CHCl_3$ (eqs. 2—4). Although eq. 2 is a

$$PhSnMe_3 + Ph_3CBF_4 \rightarrow Ph^{\cdot} + Ph_3C^{\cdot} + Me_3SnBF_4 \qquad (2)$$

$$Ph^{\cdot} + CH_2Cl_2 \rightarrow C_6H_6 + CHCl_2^{\cdot} \qquad (3)$$

$$CHCl_2^{\cdot} + CH_2Cl_2 \rightarrow CHCl_3 + CH_2Cl^{\cdot} \qquad (4)$$

redox process we were unable to show the presence of $Ph_3C^{\cdot}$ in it by using EPR. Moreover Ph_3COH (96%) was found among the reaction products after treating the reaction mixture with water. These results may be explained by the decomposition of Me_3SnBF_4 formed in the reaction into BF_3 *, and by the reaction

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* Partial decomposition of $Me_2Sn(BF_4)_2$ into Me_2SnF_2 and BF_3 has already been shown [19].

of the latter with $Ph_3C^{\cdot}$ to form a trityl cation (eq. 5) [20]. Actually it has been

$$Ph_3C^{\cdot} \xrightarrow{BF_3} Ph_3C^+ \quad (5)$$

established that the trityl radical disappears fairly quickly in the presence of BF_3 during EPR spectroscopy. This readily explains why these radicals are not detected by EPR in the reaction of $PhSnMe_3$ with Ph_3CBF_4, which takes place very slowly.

Me_4Sn may be formed in the exchange reaction between $PhSnMe_3$ and Me_3SnBF_4 (eq. 6). This exchange is confirmed in the PMR spectra of the reaction mixture.

$$PhSnMe_3 + Me_3SnBF_4 \rightarrow Me_4Sn + PhMe_2SnBF_4 \quad (6)$$

The signal due to Me_4Sn protons (δ 0.06 ppm) and the signal at δ 0.51 ppm probably corresponding to $PhMe_2SnBF_4$, appear in the NMR spectrum during the course of the reaction together with signals of $PhSnMe_3$ (δ 0.28 ppm) and Me_3SnBF_4 (δ 0.70 ppm). The ratio of integral intensities is 2/1 for the signals at δ 0.06 and δ 0.51 ppm. The exchange process is rapid because when $PhSnMe_3$ is 53% oxidised which gives 53% Me_3SnBF_4, 31% of $PhSnMe_3$ has taken part in the exchange process. Indeed in the PMR spectrum the signals at δ 0.06 and 0.51 ppm appear immediately upon mixing $PhSnMe_3$ and Me_3SnBF_4 in CH_2Cl_2. It is also possible that $PhMe_2SnBF_4$ decomposes into $PhMe_2SnF$ and BF_3.

At the same time we established that signals similar to the Me_3Sn proton signals which appear in the reaction of $PhSnMe_3$ with Ph_3CBF_4, also appear in the reaction of $PhSnMe_3$ with BF_3 or $BF_3 \cdot Et_2O$, where cleavage of the Ph—Sn bond leads to formation of $PhBF_2$ and Me_3SnBF_4 [21]. This then reacts with $PhSnMe_3$ to form Me_4Sn and $PhMe_2SnBF_4$. However, the reaction with BF_3 proceeds rapidly in excess BF_3 and may probably be neglected when considering the reaction of $PhSnMe_3$ with Ph_3CBF_4.

Thus Ph_3CBF_4 may react with organotin compounds both as an electrophilic agent and as an oxidant. When the oxidative activity of Ar_3C salts is greater than their electrophilic activity they will react only as oxidants. The strongest oxidizing agent of the triarylmethyl salts is $(C_6Cl_5)_3CSbCl_6$, which oxidizes many organic compounds, for example, 9,10-diphenylanthracene, cycloheptatriene [7] and triethylsilane [22] with formation of $(C_6Cl_5)_3C^{\cdot}$. We have shown that $(C_6Cl_5)_3CSbCl_6$ reacts as an oxidant with organotin compounds $RSnMe_3$ ($R = CH_3$, $CH_2{=}CHCH_2$, Ph, $PhC{\equiv}C$) in CH_2Cl_2 giving $(C_6Cl_5)_3C^{\cdot}$ quantitatively. Benzene (87%) and chlorobenzene (7%), which are the products of reaction of the phenyl radical and CH_2Cl_2 (eq. 7), are also detected by GLC in the reaction of $PhSnMe_3$. Thus the reaction of organotin compounds with tris(pentachlorophenyl)methylhexachloroantimony is a redox process and may be described by eq. 8.

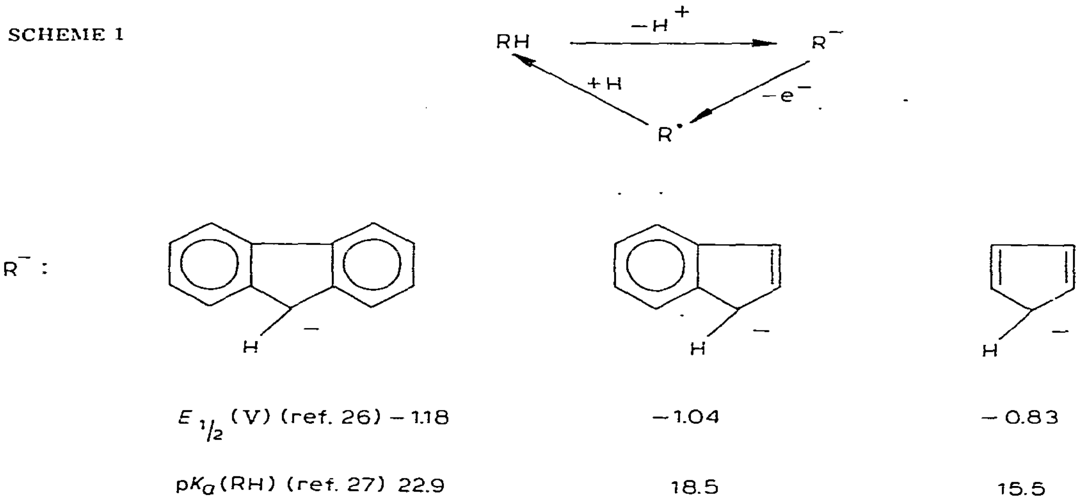
$$CH_2Cl^{\cdot} + PhCl \leftarrow Ph^{\cdot} + CH_2Cl_2 \rightarrow C_6H_6 + CHCl_2^{\cdot} \quad (7)$$

$$(C_6Cl_5)_3CSbCl_6 + RSnMe_3 \rightarrow [(C_6Cl_5)_3C^{\cdot}SbCl_6^{-}R^{+\cdot}SnMe_3] \rightarrow (C_6Cl_5)_3C^{\cdot} + R^{\cdot} \quad (8)$$

The data obtained show that there are two possible pathways for the reaction of Ar_3CX with $RSnMe_3$ (redox and electrophilic substitution) depending upon the nature of reagents. The absence of a radical and the products of its transformation in S_E2-reactions suggests that these two routes are independent.

It may be expected that for a triarylmethyl salt with different oxidative and electrophilic activities a reaction is possible when the same organotin compound reacts via two routes simultaneously. $(n\text{-}NO_2C_6H_4)_3CBr$ could be a suitable compound for investigation since its reactions with organomercury compounds as both an electrophile [23] and an oxidant [24] are known. However, we have found that tris(*p*-nitrophenyl)methyl bromide does not react with organotin compounds which contain a nucleophilic radical R (as regards their position in the Kharash series [7]). The reaction will not take place even with allyl- and phenyl-trimethyltins, which are particularly reactive in electrophilic substitution reactions [25]. Yet organotin compounds with electron-withdrawing groups (R = 9-fluorenyl, indenyl, cyclopentadienyl) do react with $(p\text{-}NO_2C_6H_4)_3CBr$. In these cases, as we expected, the products of both electrophilic substitution and oxidation are formed in amounts whose ratio depends upon the nature of R in $RSnMe_3$. We believe that the reactions which give $(p\text{-}NO_2C_6H_4)_3CR$ and $(p\text{-}NO_2C_6H_4)_3C^{\bullet}$ are independent, although some $(p\text{-}NO_2C_6H_4)_3CR$ could be formed as a result of recombination of the corresponding radicals after their formation in the solvent. The yield of the oxidation products must rise with increasing stability of radicals so long the escape of radicals from the cage increases. The stability of radicals increases in the series cyclopentadienyl < indenyl < 9-fluorenyl, which may be demonstrated by means of a thermodynamic cycle using electrochemical oxidation potentials of the carbanion R^- and values $pK_a(RH)$ (Scheme 1). However a contradictory picture is observed:

SCHEME 1



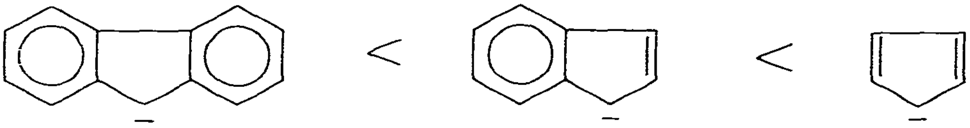
the part played by the redox process in the reaction increases in the series 9-fluorenyl- < indenyl- < cyclopentadienyl-trimethyltin.

As we have noted above the route of the reaction of $RSnMe_3$ with triarylmethyl salts is determined by the ratio between the oxidative and electrophilic activities of Ar_3CX. We cannot compare the electrophilic activities of Ar_3CX quantitatively, but their oxidative activities can be compared from data obtained in electrochemical reduction reactions. We have studies the polarographic reduction of $(p\text{-}NO_2C_6H_4)_3CBr$ and Ph_3CBF_4, and the oxidation and reduction of $(C_6Cl_5)_3C^{\cdot}$. As follows from the dependence of the limiting current on the rate of rotation of electrode, all polarographic waves are diffuse and all of them except those of $(p\text{-}NO_2C_6H_4)_3CBr$ are reversible, since their slopes are near to 60 mV, which is characteristic of reversible electrochemical processes. Since the oxidation of radical $(C_6Cl_5)_3C^{\cdot}$ takes place at the same potential as the reduction of the corresponding cation, and the exchange of anion BF_4^- of the trityl salt with ClO_4^- proceeds in the solution of supporting electrolyte, the triarylmethane derivatives studied can be placed in the following series in order of oxidative activity:

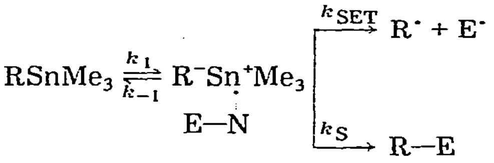
$$\begin{array}{llll} & (C_6Cl_5)_3CClO_4 > & (Ph)_3CClO_4 > & (p\text{-}NO_2C_6H_4)_3CBr \\ E_{1/2}\,(V) & 1.68 & 0.34 & -0.77 \end{array}$$

The electrophilic activities of these salts also show a definite decrease in this series. However, the ratio between the electrophilic and oxidative activities of these salts, as may be judged from the results obtained, changes in a different manner: in the case of $(C_6Cl_5)_3C^+$ the redox reaction is more energetically advantageous, but for Ph_3C^+ electrophilic substitution is more likely (excluding $PhSnMe_3$), and for $(p\text{-}NO_2C_6H_4)_3CBr$ both routes can be realized at the same time.

Thus, only organotin compounds containing a strong electron-withdrawing group R react with $(p\text{-}NO_2C_6H_4)_3CBr$ and the reactivity of $RSnMe_3$ increases with increasing carbanion stability in the order:



Such a dependence has been shown earlier in other electrophilic substitution reactions (for example, in mercury- and iodo-destannylation [17,18]) and has been explained by an S_E2 ion pair mechanism. The reaction of $(p\text{-}NO_2C_6H_4)_3CBr$ with $RSnMe_3$ may be expected to take place with the formation of ion pairs in the pre-equilibrium step as the result of coordination of the metal atom with the nucleophilic part N of an electrophilic agent EN (eq. 9).



$$RSnMe_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{E-N}{R^-Sn^+Me_3} \left\{ \begin{array}{l} \xrightarrow{k_{SET}} R^{\cdot} + E^{\cdot} \\ \xrightarrow{k_S} R-E \end{array} \right. \qquad (9)$$

In this case both processes (oxidation and electrophilic substitution) have a common stage, ionization. The yield of products of oxidation and electrophilic substitution is determined by the ratio between reductive ability of the ion pair (k_{SET}) and its ability to be attacked by the electrophile (k_S). Since the significance of the oxidation process rises with the increase in stability of carbanion

R^- we can suggest that the reductive ability of the ion pair $R^-Sn^+Me_3$ in the series 9-fluorenyl, indenyl, cyclopentadienyl, decreases less than its nucleophilicity.

Experimental

Organotin compounds, triarylmethane derivatives and standards for chromatography were obtained by the usual literature methods: Me_4Sn [28], $CH_2{=}CHCH_2Sn(CH_3)_3$ [29], $PhCH_2Sn(CH_3)_3$ [30], $PhSn(CH_3)_3$ [31], $C_{13}H_9Sn(CH_3)_3$ [32], $C_9H_7Sn(CH_3)_3$ [33], $PhC{\equiv}CSn(CH_3)_3$ [34], c-$C_5H_5Sn(CH_3)_3$ [35], Me_3SnCN [36], Me_3SnBF_4 [37], Ph_3CBF_4 [38], $(C_6Cl_5)_3CSbCl_6$ [7], $(p\text{-}NO_2C_6H_4)_3CBr$ [39], Ph_3CCN [40], $Ph_3CN{=}C$ [41] and $(C_6Cl_5)_3C^{\cdot}$ [42].

Methylene chloride was washed with sulphuric acid, water and a solution of $NaHCO_3$; dried over anhydrous $CaCl_2$ and distilled over CaH_2 into evacuated glass vessels.

General

Reactions of organotin compounds with triarylmethane salts were carried out in evacuated glass vessels. After the required reaction periods the reaction mixture was treated with water, and the aqueous layer was separated and extracte twice with methylene chloride. The combined extracts were dried over anhydrous $MgSO_4$ and analysed.

Reaction of $RSnMe_3$ with Ph_3CBF_4

The reaction products were isolated by means of chromatography on alumina II (benzene/hexane 1/1). The following compounds were isolated: allyltriphenylmethane, m.p. 69.5—70.5°C [43]; phenylethynyltriphenylmethane, m.p. 136.5°C [44]; 1-triphenylmethylindene, m.p. 216°C [45]; 9-triphenylmethylfluorene, m.p. 248—251°C [46]. The reaction of $PhSnMe_3$ with Ph_3CBF_4 was stopped by the addition of excess I_2, and volatile reaction products were distilled into a vessel cooled by liquid nitrogen. The nonvolatile residue was dissolved in CH_2Cl_2, washed with a solution of $Na_2S_2O_3$, then water and dried over $MgSO_4$. Chloroform (m/e 119.5), tetramethyltin (m/e 164 (—Me)), benzene (m/e 78), and iodobenzene were detected in the volatile reaction products by GLC and mass spectrometry. Triphenylcarbinol was detected in the nonvolatile reaction products. The PMR spectrum of the reaction mixture in the region of Me_3Sn proton signals was consistent with the presence of tetramethyltin (δ 0.06), phenyltrimethyltin (0.28), trimethyltin tetrafluoroborate (0.7 ppm); apparently the signal at 0.51 ppm is due to the methyl protons of $PhMe_2SnBF_4$. The same signal was determined in the PMR spectrum of phenyltrimethyltin after treatment with BF_3, $Et_2O{\cdot}BF_3$ or Me_3SnBF_4 in methylene chloride.

Reaction of $Ph_3CN{=}C$ with Ph_3CBF_4

An investigation of this reaction was carried out by IR spectroscopy. It was found that in the presence of Ph_3CBF_4 (2×10^{-3} M) $Ph_3CN{=}C$ (ν 2136 cm^{-1}, 2×10^{-1} M) isomerised quickly in PhCCN (ν 2241 cm^{-1}).

Reaction of $RSnMe_3$ with $(p\text{-}NO_2C_6H_4)_3CBr$

Products of the reaction were isolated by chromatography on SiO_2 (hexane/ benzene 4/1, chloroform). The quantity of $(p\text{-}NO_2C_6H_4)_3C^{\cdot}$ formed was determined by gravimetric methods. The following compounds were isolated: 9-tris-(*p*-nitrophenyl)methylfluorene, m.p. 212°C (chloroform). Anal.: found: C, 69.36; H, 4.00; N, 7.52%. $C_{32}H_{21}N_3O_6$ calcd.: C, 70.70; H, 3.87; N, 7.74; O, 17.70%; tris(*p*-nitrophenyl)methylindene, m.p. 221°C (chloroform). Anal.: found: C, 68.51; H, 3.94; N, 8.39%. $C_{28}H_{19}N_3O_6$ calcd.: C, 68.15; H, 3.85; N, 8.52; O, 19.48%. In the reaction of $(p\text{-}NO_2C_6H_4)_3CBr$ with $C_{13}H_9SnMe_3$ the formation of bis(9-fluorenyl) was detected by TLC on 'Silufole" (hexane/ benzene 4/1).

The reaction of $RSnMe_3$ with $(C_6Cl_5)_3CSbCl_6$ was studied by UV spectroscopy in quartz cuvettes 0.1 and 1.0 cm. For determination of the concentrations of $(C_6Cl_5)_3C^{\cdot}$ and $(C_6Cl_5)_3CSbCl_6$ optical density was measured for λ 562 (ϵ 1200) and 691 nm (ϵ 30000).

GLC analyses

These were performed on a column of length 1 m and diameter 3 mm, Chromosorb W, silanized by Me_2SiCl_2, 5% E-301, nitrogen flow rate 10—30 ml/min, 20—200°C. Instrumental errors did not exceed ±5%. Ph_3CCN was used as internal standard.

Electrochemical studies

The electrochemical reduction of triarylmethyl compounds was investigated by polarography on a platinum disk electrode of area 0.5 cm^2. The measurements were performed in a cell of volume 15 ml at 25 ± 0.1°C. Polarograms were obtained on polarograph LP-60 and potentiostat P-5848 instruments. Measurements errors did not exceed 5 mV.

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