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SOME ASPECTS OF NEIGHBOURING GROUP PARTICIPATION IN ORGANOTIN CHEMISTRY

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SUMMARY

The kinetics and mechanism of reaction of the iododestannylation and mercuridestannylation of a number of novel trimethyltin derivatives have been studied in a variety of solvents. Both reaction types followed a similar pattern:

$$R_4Sn+EI \rightarrow R_3SnI+RE \qquad (1)$$

$$R_3SnI+EI \overset{\text{rapid}}{\rightleftharpoons} R_3SnI\cdot EI \qquad (2)$$

$$R_4Sn+R_3SnI\cdot EI \rightarrow 2\,R_3SnI+RE \qquad (3)$$

where $E=I$, or HgI. Step (3) was much slower than step (1).

Iododestannylation gave almost exclusive tin–methyl bond cleavage for all the compounds used except the *anti*-7-norbornenyl and 7-norbornadienyl derivatives, for which tin–C7 bond fission occurred. Changes to less polar media resulted in even lower yields of methyl iodide from these two compounds. Possible mechanisms which account for these observations are discussed.

Mercuridestannylation proceeds with almost complete tin–methyl bond fission in all cases except for the 5-substituted norbornenyl derivative. Activation parameters strongly suggest neighbouring group participation by olefinic groups in the transition states for the reactions. The mechanism is discussed in relation to that for iododestannylation.

INTRODUCTION

Current interest in the effect of neighbouring groups on both ground states and transition states of organometallic reactions is expanding rapidly, particularly through the increased use of Mössbauer spectroscopy and double resonance techniques in NMR spectroscopy. Clark and Poller[1] have recently shown that π bonding between neighbouring olefinic double bonds and tin in certain alkenyltin compounds is not significant. Thus, any unusual rate enhancements of these compounds in electrophilic substitution reactions can now be clearly ascribed to a direct interaction in the transition state. Some qualitative evidence for this effect has already been presented[2]. The purpose of this paper is to quantify the effect, using some of the novel bridged trialkylalkenyltin compounds described in a previous paper[3].

DISCUSSION AND RESULTS

The work described here concerns iododestannylation and mercuridestannylation reactions.

Reactions with iodine

Many of the previously reported iododestannylation reactions were too fast to follow using conventional analytical methods. This necessitated using a large excess of added iodide ions to reduce the concentration of "free" iodine in the reaction solution. In cases where iodination was relatively slow, an additional complication arose from the formation of a complex between iodine and the trialkyltin iodide formed by the initial carbon–tin bond fission, resulting in the following reaction scheme:

$$R_4Sn+I_2 \xrightarrow{k_2} RI+R_3SnI \tag{1}$$

$$R_3SnI+I_2 \overset{K_1}{\rightleftarrows} R_3SnI\cdot I_2 \tag{2}$$

$$R_4Sn+R_3SnI\cdot I_2 \xrightarrow{k'_2} RI+2\,R_3SnI \tag{3}$$

This complication can be also avoided by adding excess iodide, which effectively competes with the trialkyltin iodide for iodine. Unfortunately, this introduces another equilibrium constant, that for the formation of triiodide ion, for which thermodynamic data is somewhat scanty. In the present study, no iodide ion was added, and the reaction was followed spectrophotometrically by measuring the increase in absorption due to the formation of the triiodide (λ_{max} 292, 360 nm) in accordance with eqns. (1) and (2). For the reaction of tetramethyltin in methanol, isosbestic points were found at 266 and 422 nm. The absorbance (at 360 nm) of a mixture of tetramethyltin, trimethyltin iodide, iodine and methyl iodide (10^{-4} M in each component), measured immediately on mixing, was found to correspond to within 3 % of the maximum value observed from the reaction of tetramethyltin and iodine (2×10^{-4} M in each component). This is fully in accord with the stoichiometry evident from eqns. (1) and (2). Reaction rates were unaffected on rigorously degassing the solvents used, rendering radical processes unlikely. Rate constants (k_2) were calculated from the data, with the assumption that $K_1 \gg 1$, by analogy with the known values of the equilibrium constants for triiodide formation. The final slow reaction of the trialkyltin iodide/iodine complex with further tetraalkyltin was also followed spectrophotometrically. Confirmation of step (3) came from the observation that values of k'_2 calculated from the reaction of mixtures of tetraalkyltin, trialkyltin iodide, iodine and alkyl iodide coincided with those obtained from tetraalkyltin and iodine at *twice* the concentration. The ratio k_2/k'_2 was found to be greater than 15, and by suitable choice of concentrations the two processes could be determined separately.

Reaction with mercuric iodide

A very similar reaction scheme has been described by Abraham[4] in mercuridestannylation reactions, *viz.*:

$$R_4Sn+HgX_2 \xrightarrow{k_2} RHgX+R_3SnX \tag{4}$$

$$R_3SnX + HgX_2 \overset{K_2}{\rightleftarrows} R_3SnX \cdot HgX_2 \tag{5}$$

$$R_4Sn + R_3SnX \cdot HgX_2 \xrightarrow{k_2'} RHgX + 2\,R_3SnX \tag{6}$$

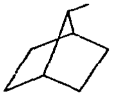
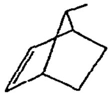
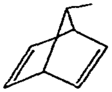
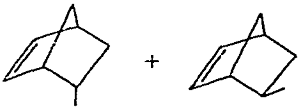
In the present study isosbestic points were observed in solvents methanol (270, 285.5 nm), acetonitrile (272, 285.5 nm) and dimethyl sulphoxide (271, 297 nm) for all the tin compounds used. The k_2/k_2' ratio for mercuridestannylation was higher than that for iododestannylation by a factor of about four.

Products and rates of iododestannylation reactions

Reactions of iodine with trimethylalkyltin compounds gave almost quantitative yields of methyl iodide in all solvents used, with the important exception of the norbornenyl and norbornadienyl derivatives (Table 1). 7-*anti*-(Trimethylstannyl)-2-norbornene (I) gave quantitative yields of MeI in the more polar solvents methanol and DMSO but only 39% in acetonitrile. Even more striking are the results for 7-(trimethylstannyl)-2,5-norbornadiene (II) where less than 5% methyl iodide was formed. Added iodide ion increased the yield to 33%. The olefinic double bonds in the bridged compounds clearly have particular significance in facilitation C7–Sn bond fission, since the acyclic alkenyl derivatives behave normally. That this effect

TABLE 1

PERCENTAGE METHYL IODIDE FORMED FROM THE CLEAVAGE OF TRIMETHYLALKYLTIN COMPOUNDS (Me_3SnR) IN MeCN, MeOH, DMSO AT ROOM TEMPERATURE

R	MeCN	MeOH	DMSO
$-Me$	92	95	90
$-(CH_2)_3Me$	80	93	90
$-(CH_2)_4Me$	82		
$-(CH_2)_4Ph$	96		
$-(CH_2)_2CH{=}CH_2$	86		
$-(CH_2)_3CH{=}CH_2$	90		
$-(CH_2)_2CO_2Me$	100	95	92
	77		90
	39	100	88
	< 5 (33)[a]	39 (53)	
	17 (18)	52	

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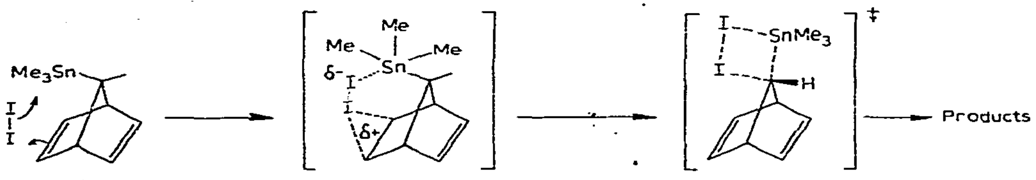
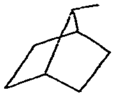
[a] Figures in parentheses refer to reactions carried out using excess NaI.

occurs in the more weakly polar solvents suggests that it results from destabilisation of the developing carbanionic charge on C7 by a direct field effect from the π electron system. Polar solvents are better able to stabilise this charge and may well intervene between the olefinic moiety and C7 to diminish the destabilising influence and thus restore the normal order of bond fission. The fact that the norbornadienyl derivatives are much less stable than their norbornenyl analogues would seem to support this[3]. An alternative explanation is that iodine forms a π complex which has particularly suitable stereochemistry for the eventual formation of the transition state, involving only a small subsequent molecular movement. More polar solvents would solvate the central tin atom making complexation more difficult.



Iododestannylation of (II) was too rapid to be accurately measured, $k_2(II)/k_2(I)$ having a value of at least 10^3. Free radical processes[5] cannot be entirely excluded particularly in view of the increased Sn–Me cleavage when iodide ion, apparently a radical inhibitor[6], is employed. However, it seems unlikely, since the reactivity of (I) which has 61% Sn–C7 bond fission is unaffected by degassing solutions. The high value of the rate ratio is either steric in origin, (I) having an unsuitable stereochemistry for the conversion of the π complex to the product forming transition state or polar in origin, (I) possessing only one olefinic double bond to labilise the Sn–C7 bond.

The following relative rates ($Me_4Sn = 1.00$) were obtained in acetonitrile at 25° for the trimethylstannyl series (Me_3SnR).

$R = -(CH_2)_2CO_2Me > -(CH_2)_2CH{=}CH_2 \sim$ 

(24.8) (1.09) (1.03)

The enhanced rate of the methyl propionate derivative indicates possible neighbouring group participation by oxygen but the activation parameters listed in Table 2 show that the rate increase is almost wholly due to an entropy effect acting in the opposite sense to that anticipated for participation by oxygen in the transition state. The origins of this effect remain obscure. Iododestannylation of the trimethyl-

TABLE 2

ACTIVATION PARAMETERS FOR THE CLEAVAGE OF SOME TRIMETHYLALKYLTIN COMPOUNDS (Me_3SnR) BY IODINE IN ACETONITRILE

R	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger a}$ (e.u.)
–Me	5.8±0.1	–33.4±0.3
$-(CH_2)_2CO_2Me$	6.4±0.3	–25.8±1.1

[a] Calculated at 25°.

alkyltins is faster in acetonitrile than in methanol by a factor of about five. Abraham[7] has shown that change from methanol to acetonitrile leads to an increase in enthalpy of reactants in mercuridestannylation reactions. The values of the solvent activity coefficient log $^{w}\gamma^{s}_{I_2}$ (w = water as reference solvent) for methanol and acetonitrile are -2.3 and -2.5 respectively[8]. It seems likely therefore that the increase in rate can be attributed mainly to reduced solvation of the organotin compounds in acetonitrile relative to methanol.

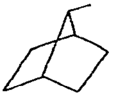
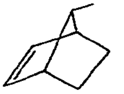
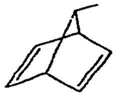
Products and rates of mercuridestannylation reactions

With the exception of 6-(trimethylstannyl)-2-norbornene, all substrates used gave methylmercury iodide on reaction with mercuric iodide. A direct comparison of the reactivity of the tin–methyl bond was now possible in the series of compounds already discussed. The mercuridestannylation reactions proceeded about twenty times more slowly than the analagous iododestannylation processes.

Table 3 lists the activation parameters obtained for this series of compounds. Relatively small differences in rate were observed for reactions in solvents acetonitrile, methanol and DMSO. As in the iododestannylation reactions, methyl 3-(trimethylstannyl)propionate reacted faster than tetramethyltin in acetonitrile by virtue of a more favourable $\Delta S^{\ddagger}$. The reactions of the 1-butene and 1-pentene derivatives in acetonitrile are characterised by a more favourable enthalpy and less favourable

TABLE 3

ACTIVATION PARAMETERS FOR THE CLEAVAGE OF VARIOUS TRIMETHYLALKYLTIN COMPOUNDS (Me_3SnR) BY MERCURIC IODIDE

R	Solvent	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger a}$ (e.u.)
–Me	MeCN	9.6 ± 0.1	-27.8 ± 0.5
	MeOH	10.8 ± 0.5	-26.9 ± 1.7
		9.2^{b}	-28.4
	DMSO	10.0 ± 0.5	-23.9 ± 1.7
$-(CH_2)_2CO_2Me$	MeCN	9.3 ± 0.4	-22.3 ± 1.5
	MeOH	10.0 ± 0.5	-29.0 ± 1.8
	DMSO	10.0 ± 0.6	-23.8 ± 1.9
$-(CH_2)_3Me$	MeCN	10.0 ± 0.2	-25.5 ± 0.6
$-(CH_2)_2CH{=}CH_2$	MeCN	7.8 ± 0.2	-33.4 ± 0.5
$-(CH_2)_3CH{=}CH_2$	MeCN	7.5 ± 0.1	-34.0 ± 0.3
$-(CH_2)_4Ph$	MeCN	8.4 ± 0.3	-31.4 ± 1.4
	MeCN	11.1 ± 0.4	-22.2 ± 1.4
	MeCN	10.5 ± 0.6	-24.4 ± 2.1
	MeCN	6.3 ± 0.5	-36.1 ± 1.8

[a] Calculated at 25°. [b] Data using 96% MeOH 4% H_2O (ref. 4).

entropy of activation compared with the n-butyl analogue. These observations are compatible with neighbouring group participation by the olefinic π electrons in the transition state. The same trends are evident in the phenyl butyl compound, implying participation by the aromatic π electrons. The effect appears to be even more marked in the bicyclic series. The activation enthalpy for the norbornadienyl derivative is some 5 kcal/mole lower, and the activation entropy 14 e.u. more negative than those of either the fully saturated or the 7-*anti*-norbornenyl analogue. This suggests that donor–acceptor interactions are important in the transition state.

The reason for the difference in the nature of the cleavage by iodine and mercuric iodide is perhaps a combination of inherent instability of the C7–Hg bond and the general increase in steric hindrance in changing to the more bulky electrophile HgI_2. It is significant that all attempts to synthesise 7-(halomercuri)-2,5-norbornadienes via the Grignard method always resulted in the precipitation of elemental mercury from the reaction solutions.

EXPERIMENTAL

Purification of materials

Mercuric iodide (B.D.H. laboratory grade) was recrystallised, twice from methanol and dried at 75° (5 mm) for 3 h prior to use. Resublimed Analar iodine was used. Solvents methanol, acetonitrile and dimethylsulphoxide were purified by standard procedures appearing in a previous paper[2].

Kinetic methods

(*i*). *Iododestannylation reactions.* The reactions were followed using an SP 500 spectrophotometer by observing the increase in absorption at 363 nm due to the formation of the triiodide intermediate shown in eqn. (2). Concentrations of the organotin compounds and iodine were in the range 5×10^{-5} to $2 \times 10^{-4}\,M$. Isosbestic points were obtained from repeated scans using an SP 800 instrument.

Calculations of second order rate constants (k_2) were based on the assumption that $K_1 > 1$, using data from the first 15–20% reaction. The kinetic equation used was:

$$V = k_2 \cdot (a-x) \cdot (b-2x) \tag{7}$$

where a and b are the initial concentrations of organotin compound and iodine respectively. The integrated rate equation for equimolar concentrations may be formulated as

$$k_2 = \frac{2.303}{a \cdot t} \cdot \log\left[0.5 \cdot \left(1 + \frac{D_\infty - D_0}{D_\infty - D_t}\right)\right] \tag{8}$$

in terms of the measured absorptions (D) at $t=0$, t and ∞. The values of k_2 thus calculated showed standard deviations of not more than 6.5% (Table 4). The fact that eqn. (8) gave linear plots for upwards of 35% overall reaction supports the assumptions made in its derivation. Where tin–methyl bond fission was dominant, the appropriate statistical correction was applied. Activation parameters, together with standard deviations were obtained by computer using the Arrhenius equation and a least squares programme.

TABLE 4

VALUES OF k_2 ($l \cdot mole^{-1} \cdot sec^{-1}$) FOR THE CLEAVAGE OF Me_4Sn BY I_2 (4×10^{-5} M in each) IN ACETONITRILE AT 35.2°

t (sec)	D_{363}	$D_\infty - D_t$	$\frac{D_\infty - D_0}{D_\infty - D_t}$	$\log\left[0.5 \cdot \left(1 + \frac{D_\infty - D_0}{D_\infty - D_t}\right)\right]$	k_2
0	0.048	0.189	1.00	0.000	
15	0.069	0.168	1.12	0.025	96
30	0.082	0.155	1.22	0.045	86
45	0.093	0.144	1.31	0.063	81
60	0.102	0.135	1.40	0.079	76
75	0.118	0.119	1.59	0.112	86
90	0.122	0.115	1.64	0.121	78
120	0.142	0.095	1.99	0.174	84
150	0.158	0.079	2.40	0.230	88
180	0.170	0.067	2.82	0.281	90
210	0.179	0.058	3.26	0.327	90
240	0.189	0.048	3.94	0.393	96
∞	0.237				av. 86±6

(*ii*). *Mercuridestannylation reactions.* A similar analytical procedure was adopted, absorption measurement being made at 301.5 nm with reagent concentrations in the range 5×10^{-4} to 2×10^{-3} M using 0.2 cm silica cells. The method of calculating k_2 was similar to that used by Abraham[4] from the first 15–20% reaction.

Values of k_2 showed a standard deviation of not more than 3%. In general, the data obtained from mercuridestannylation were more reproducible than those from iododestannylation. Statistical corrections were made as and where appropriate. Some kinetic runs were made using degassed solutions[9] for both reaction types. No appreciable variation in rates was observed.

Product analyses

Yields of MeI produced in the iododestannylation reactions were estimated using a Perkin–Elmer F11 GLC instrument. 3 μl of 0.1 M reaction solution was injected directly and the products analysed using a non-polar column (Silicone oil MS 555 + Bentone 34 on Chromosorb W) and a column temperature of 90°. Under these conditions, methyl iodide has a retention time of 110 sec. The yield of methyl iodide was calculated by reference to standard solutions. Standard deviations observed were not greater than 5%.

Methylmercury iodide was characterised by its R_F value from TLC experiments using Silica gel "S" (Hopkins and Williams) as the adsorbent. The chromatograms were developed using cyclohexane/chloroform mixtures (3/1). The plates were sprayed with 1% dithizone in acetone. Tetramethyltin/mercuric iodide reaction mixtures (5×10^{-3} M) were spotted at regular intervals across the plate so that a correction could be made for uneven layer thicknesses. Under these conditions, methylmercuric iodide and trimethyltin iodide produced during the reaction had average R_F values of 0.71 ±0.05 (yellow spot) and 0.00 (pink spot) respectively. On making the appropriate correction from the calibration curve, all the organomercury iodides were found to have identical R_F values within experimental error with those of methylmercury iodide, with the exception of the products from 6-(trimethylstannyl)-2-

norbornene which showed, in addition, a component (R_F 0.85) which gave a pink spot. This compound remains unidentified.

Preparations

The preparative details for most of the organotin compounds used in this study appears in a previous paper[3].

Trimethyltin iodide was obtained by refluxing tetramethyltin with iodine in benzene for 1 h followed by fractional distillation[10,11].

Attempted synthesis of 7-(chloromercuri)-2,5-norbornadiene

7-Chloro-2,5-norbornadiene (1.26 g, 0.01 mole) was added to a suspension of magnesium (0.24 g, 0.01 mole) in dry THF (50 ml) under dry nitrogen. The mixture was refluxed for 6 h after which most of the magnesium had disappeared and the reaction solution had become cloudy. A solution of mercuric chloride (2.71 g, 0.01 mole) in dry THF (20 ml) was added whereupon a grey precipitate settled out. The mixture was stirred overnight, filtered and the grey residue (1.8 g) was shown to comprise mainly elemental mercury.

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