KINETICS AND MECHANISM OF IODODESTANNYLATION OF STANNATRANES

M.D. RAVENSCROFT and R.M.G. ROBERTS

Department of Chemistry, University of Essex, Wivenhoe Park, Colchester, Essex C04 3SQ (Great Britain)

(Received April 4th, 1986)

Summary

A detailed kinetic study of iododestannylation of phenylstannatranes is reported. Reaction rates were compared with reference systems $PhSnBu_3$, $PhSn(OMe)_3$. No evidence was found for iodide catalysis. The reaction is interpreted as involving rate determining Sn–C bond fission. Rates for the stannatranes are some seven times greater than those for $PhSn(OMe)_3$ indicative of increased Sn–N coordination in the transition state. Salt effects were significantly smaller for the stannatranes commeasurate with decreased charge on the electrofugal tin. For $PhSn(OMe)_3$, the reaction was followed in the absence of iodide ion, enabling the evaluation of the association constant for the species $[(MeO)_3Sn]^+ I_3^-$ formed during the reaction.

Introduction

Destannylation reactions have been the subject of intensive mechanistic studies during the past three decades. Iododestannylation has been reviewed fairly comprehensively [1–3]. We have recently [4] undertaken a kinetic study of mercuridestannylation of stannatranes with a view to elucidating the effect of pentacoordination at tin in controlling reaction rates. As an adjunct to this work, we also examined the corresponding iododestannylation reactions in solvent methanol, the results of which form the basis of this report.

Results and discussion

As with the mercuridestannylation reactions, we studied the reactivity of two phenylstannatranes $PhSn(OCH_2CH_2)_3N$ and $PhSn(OC_6H_4)_3N$ relative to reference systems $PhSnBu_3$ and $PhSn(OMe)_3$. Prior to embarking on this work, the stannatranes were examined for iodide-catalysed ring opening cf. acid-catalysed solvolyses [5].

$$\text{(1)}$$
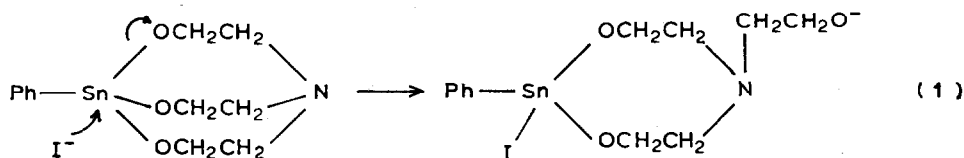
Such a process was shown not to occur under the conditions employed in this study. The reactions were heterolytic in nature, rigorous degassing having no effect on the observed rates. Like mercuridestannylation, the iodinations are complicated by complexation of I_2 with the product R_3SnI (step 3). Step (4) is usually much slower than (2).

$$PhSnR_3 + I_2 \overset{k_2}{\rightarrow} PhI + R_3SnI \tag{2}$$

$$I_2 + R_3SnI \overset{K_{ass}}{\rightleftharpoons} [R_3Sn^+] + [I_3^-] \tag{3}$$

$$[R_3Sn^+] + [I_3^-] + PhSnR_3 \overset{k_2'}{\rightarrow} PhI + 2R_3SnI \tag{4}$$

In the present study, both stannatranes and $PhSnBu_3$ reacted too rapidly with I_2 for convenient measurement, and reactions were therefore conducted in the presence of excess iodide ion, to reduce the free iodine concentration. This has the advantage that step (3) is inhibited and the kinetic treatment becomes much simpler. For $PhSn(OMe)_3$, however, rates were sufficiently slow to render the addition of iodide unnecessary. UV scans of reaction mixtures showed the formation of I_3^- at 360 nm which reached a maximum at 50% conversion in accordance with the above scheme, assuming K_{ass} is large. There followed a slow decay of the I_3^- peak. Steps (2) and (4) could therefore be treated separately and k_2 was shown to be about seven times larger than k_2'. Gielen and Nasielski [6] have considered three contributing reactions to the overall iodination represented by the equation

$$\text{rate} = k_1[R_4Sn][I_3^-] + k_2[R_4Sn][I_2] + k_3[R_4Sn][I_2][I^-] \tag{5}$$

The first term gives the contribution of attack by I_3^-, the second the simple bimolecular attack by iodine and the third term results from iodide ion catalysis. Such an expression gives

$$k_2^{obs} = k_2/\{K_I[I^-]\} + k_1 + k_3/K_I \tag{6}$$

where K_I is the formation constant of the triodide ion $[I_2 + I^- = I_3^-]$.

A plot of k_{obs} vs. $[I^-]^{-1}$ should therefore be linear and from known values of K_I [7], k_2 can be calculated. k_3 and k_1 cannot of course be separated. In the present work, the intercepts for all the substrates used in the I_2/I^- system were statistically zero (i.e. the standard deviations were greater than the actual value). There is, therefore, no evidence for iodide catalysed processes in solvent methanol, which supports previous findings [6,8]. The results appear in Tables 1–6. k_2 values were calculated from

$$k_2 = k_2^{obs}K_I[I^-] \tag{7}$$

The order of reactivity of the primary cleavage step (2) is $PhSnBu_3 >$ $PhSn(OCH_2CH_2)_3N = PhSn(OC_6H_4)_3N > PhSn(OMe)_3$. The stannatranes have almost identical reactivity and are considerably more reactive than $PhSn(OMe)_3$. Reaction 2 can be formulated as an electrophilic substitution in the usual way, with

TABLE 1

VALUES OF PSEUDO-FIRST ORDER RATE CONSTANTS k_ψ (s^{-1}), k_2^{obs} AND k_2 (both in M^{-1} s^{-1}) FOR THE REACTION OF $PhSnR_3$ WITH I_2 IN 0.01 M NaI IN MeOH

R_3	T (°C)	$10^4[PhSnR_3]$ (M)	$10^4 k_\psi$	k_2^{obs}	k_2
Bu_3	34.8	3.0	5.2	1.72	157
		4.0	6.8	1.71	156
		6.0	10.7	1.79	163
		8.0	13.8	1.73	157
		10.0	17.0	1.70	155
					$\overline{158 \pm 3}$
$(OCH_2CH_2)_3N$	34.8	3.0	1.32	0.44	40.1
		4.0	1.80	0.45	41.0
		5.0	2.35	0.47	42.8
		6.0	2.52	0.42	38.3
		8.0	3.52	0.44	40.1
		10.0	4.20	0.42	38.3
					$\overline{40.1 \pm 1.7}$
$(OC_6H_4)_3N$	30.0	3.0	1.03	0.34	38.1
		4.0	1.22	0.31	34.7
		6.0	1.80	0.30	33.6
		8.0	2.33	0.29	32.5
		10.0	3.07	0.31	34.7
					$\overline{34.7 \pm 2.1}$

TABLE 2

VALUES OF k_2 (M^{-1} s^{-1}) FOR THE REACTION OF $PhSn(OMe)_3$ WITH I_2 IN METHANOL AT 25.0°C

$10^5[PhSn(OMe)_3]$ (M)	$10^5[I_2]$ (M)	k_2
2.0	2.0	2.62
3.0	3.0	2.72
4.0	4.0	2.73
6.0	6.0	2.75
6.0	3.0	2.81
2.0	6.0	2.69

TABLE 3

PSEUDO-FIRST ORDER RATE CONSTANTS k_ψ (s^{-1}) AND SECOND-ORDER RATE CONSTANTS k_2' (M^{-1} s^{-1}) FOR THE REACTION OF $PhSn(OMe)_3$ WITH $(MeO)_3Sn^+I_3^-$ IN METHANOL AT 25.0°C

$10^5[PhSn(OMe)_3]$ (M)	$10^6 k_\psi$	k_2'
3.0	11.1	0.37
2.5	8.5	0.34
2.0	7.2	0.36
1.5	5.1	0.34

TABLE 4

VARIATION OF k_2^{obs} (M^{-1} s^{-1}) WITH NaI CONCENTRATION FOR THE CLEAVAGE OF PhSnR$_3$ BY I$_2$ IN MeOH AT CONSTANT IONIC STRENGTH ^{a} ($\mu = 0.01$) TOGETHER WITH CALCULATED VALUES OF k_2 (M^{-1} s^{-1})

R$_3$	T (°C)	10^3[I$^-$] (M)	1/[I$^-$]	k_2^{obs}	k_2
Bu$_3$	34.8	1.0	1000	17.2	157
		1.5	667	11.9	162
		2.0	500	8.7	159
		4.0	250	4.5	165
		6.0	167	2.87	157
		8.0	125	2.11	154
		10.0	100	1.75	160
					$\overline{159 \pm 4}$
(OCH$_2$CH$_2$)$_3$N	34.8	4.0	250	1.17	42.7
		5.0	200	0.93	42.4
		6.0	167	0.77	42.1
		7.0	143	0.72	45.9
		8.0	125	0.62	45.2
		10.0	100	0.44	40.1
					$\overline{43.0 \pm 2.1}$
(OC$_6$H$_4$)$_3$N	30.0	2.5	400	1.19	33.4
		5.0	200	0.63	35.2
		6.0	167	0.47	31.6
		8.0	125	0.42	37.6
		10.0	100	0.30	33.6
					$\overline{34.3 \pm 2.2}$

^{a} Using NaClO$_4$ to make up $\mu = 0.01$.

$$(8)$$

$$(9)$$
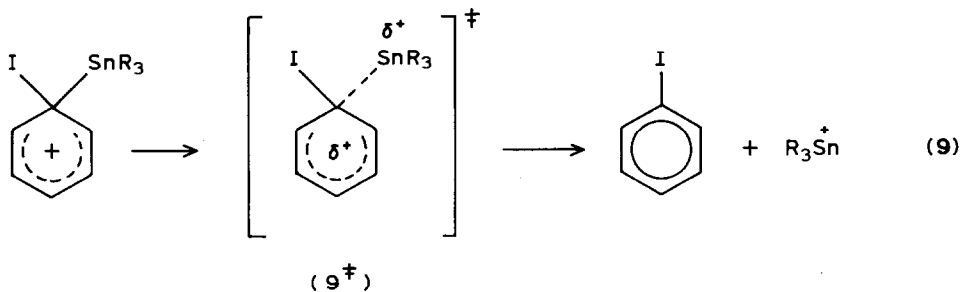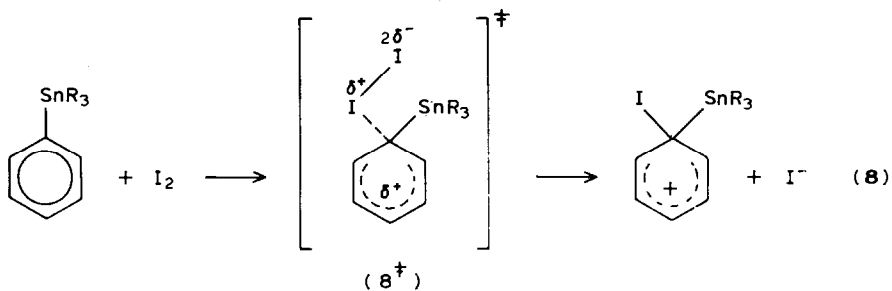
TABLE 5

EFFECT OF IONIC STRENGTH ^{a} μ (M) ON k_2 $(M^{-1} s^{-1})$ FOR THE REACTION OF PhSnR$_3$ WITH I$_2$ IN MeOH

R$_3$	T (°C)	[I$^-$] (M)	k_2	μ
Bu$_3$	34.8	0.01	158	0.01
		0.01	190	0.10
		0.10	185	0.10
		0.01	209	0.20
		0.05	267	0.50
(OC$_6$H$_4$)$_3$N	30.0	0.01	34.7	0.01
		0.01	36.7	0.05
		0.01	37.6	0.10
		0.02	38.1	0.10
		0.01	39.9	0.15
		0.01	41.2	0.20

^{a} Using added NaClO$_4$.

the usual problem of deciding which step 8, or 9 is rate-determining. In the case of mercuridestannylation we concluded from a number of considerations that rate determining C–Sn bond fission occurred. For the iododestannylations the situation appears less clear cut since the C–Sn and C–I bond strengths are similar. Leaving aside, for the moment, the question of solvation of transition states $8^{\neq}$ and $9^{\neq}$, their relative stability should be governed by the relative electron donating abilities of iodine and SnR$_3$. The former withdraws electron density via a fairly strong inductive effect ($\sigma_I \sim 0.40$) and has a relatively weak $+M$ effect ($\sigma_R \sim -0.15$) [9].

Trialkyltin groups on the other hand appear to be weak overall donors [9]. This suggests that $9^{\neq}$ is less stable than $8^{\neq}$. Reinforcing this is steric hindrance to solvation at tin encountered in the former. Recently attention has been drawn to the exact correlations which occur between relative reactivities of aromatic compounds with halogens and mercuric salts and charge transfer transition energies measured in inert solvents [10]. This has led to the postulate that transition states in electrophilic aromatic substitutions should be regarded as having ion pair character, ArH$^+ \cdot$E$^-$.

Electron transfer to iodine will be much more favourable than to R$_3$SnI. From these arguments it is likely that step 9 is rate-limiting. Supporting this is the excellent correlation between the $\Delta G^{\neq}$ values for iodo- and mercuridestannylation ($r = 0.999$, gradient 0.95 4 points, see Table 7).

TABLE 6

VALUES OF k_2 AND k_2' (both $M^{-1} s^{-1}$) FOR THE REACTION OF PhSnR$_3$ WITH I$_2$ IN METHANOL AT VARIOUS TEMPERATURES

| R$_3$		T (°C) = 15.0	20.0	25.0	30.0	34.8	40.0	45.0
Bu$_3$	(k_2)	79	90	122	143	158	190	–
(OCH$_2$CH$_2$)$_3$N	(k_2)	18.4	20.5	26.6	36.3	40.1	48.5	62.6
(OC$_6$H$_4$)$_3$N	(k_2)	14.2	19.1	24.8	34.7	42.1	43.0	62.0
(OMe)$_3$	(k_2)	–	2.21	2.71	4.0	5.0	–	9.1
(OMe)$_3$	(k_2')	–	0.23	0.36	0.39	0.68	–	1.05

TABLE 7

ARRHENIUS PARAMETERS FOR IODODESTANNYLATION REACTIONS (ΔH^{*}, ΔG^{*} in kcal mol^{-1} ΔS^{*} in cal K^{-1} mol^{-1})

Compound	ΔH^{*}	ΔS^{*}	ΔG^{*}	ΔG^{*} ^{a} (HgI$_2$)
PhSnBu$_3$	5.8 ± 0.4	-29.5 ± 1.3	14.6 ± 0.5	13.9
PhSn(OcH$_2$)CH$_2$)$_3$N	7.0 ± 0.4	-28.6 ± 1.3	15.5 ± 0.5	14.8
PhSn(OC$_6$H$_4$)$_3$N	8.0 ± 0.6	-25.4 ± 1.9	15.6 ± 0.5	14.9
PhSn(OMe)$_3$	10.0 ± 0.5	-22.9 ± 1.6	16.8 ± 0.5	16.2
PhSn(OMe)$_3$ ^{b}	10.6 ± 0.5	-25.0 ± 1.5	18.1 ± 0.5	

^{a} Corresponding ΔG^{*} values for mercuridestannylation. ^{b} Data refers to slow step 4 governed by k_2'.

The slow step (9) can be formulated in two ways, one with the so-called "open" transition state, the other involving assistance by iodine ion, viz.
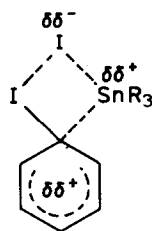
The latter involves little charge separation and is not usually found for reactions in such a nucleophilic solvent as methanol. The observed positive salt effects confirm this (Table 5). We are thus in a position to account for the observed rates in terms of a mechanism involving rate-limiting C–Sn bond fission in an "open" transition state. Both stannatranes show enhanced rates relative to the model PhSn(OMe)$_3$. Differences in steric effects are likely to be quite small between the two systems. The activation data show that the chief differences occur in the enthalpy terms ΔH^{*}, the values for the stannatranes being 2–3 kcal lower than that of PhSn(OMe)$_3$. In addition the ΔS^{*} are somewhat more negative for the stannatranes. Although such small ΔS^{*} differences are difficult to account for exactly, nevertheless they would fit the case where increased Sn–N interaction is occurring in 9^{*}. Such interaction would lower the charge on the tin atom which should result in a lower sensitivity to ionic strength effects, Plots of log k_2 against $\mu^{1/2}$ using the data in Table 5 give reasonably good straight lines. For PhSnBu$_3$ the slope is 0.37 whereas that for PhSn(OC$_6$H$_4$)$_3$N is 0.21, results which offer support for the above postulate. For PhSn(OMe)$_3$ in the absence of iodide, the two rate constants k_2 and k_2' could be evaluated. As for mercuridestannylation, the slow step (4) comprises two reactions

$$[R_3Sn^{+}] + [I_3^{-}] \overset{K_{\text{diss}}}{\rightleftharpoons} R_3SnI + I_2 \tag{10}$$

$$I_2 + PhSnR_3 \overset{k_2}{\rightarrow} PhI + R_3SnI \tag{11}$$

Since k_2 is known from the initial phase of the reaction K_{diss} may be calculated

$$k_2' = K_{\text{diss}} k_2 = 1/K_{\text{ass}} \cdot k_2 \tag{12}$$

where K_{ass} is the association constant for the complex. In free energy terms

$$\Delta G^{\neq\prime} = -\Delta G_{ass} + \Delta G^{\neq}$$

or $\Delta G_{ass} = \Delta G^{\neq} - \Delta G^{\neq\prime}$ \hfill (13)

From the data in Table 7, ΔG_{ass}, is calculated as -1.3 kcal mol^{-1}, from which a value of K_{ass} (25°C) of about 10 is found. This is, of course, a very approximate value due to the uncertainties in activation parameters, and compares with a value of ~ 25 for the corresponding HgI$_2$ complex.

Experimental

Methanol was rigorously dried as previously described [4]. Iodine was BDH AnalaR grade. The commercial material was sublimed from a mixture with potassium iodide, then resublimed in vacuo. The sample was dried over CaCl$_2$ in vaccuo. Purified iodine was manipulated with a Teflon spatula to prevent contamination with transition metal ions.

The stannatranes and PhSn(OMe)$_3$ were prepared as described previously [4].

Product analysis

Reaction solutions were examined qualitatively by thin layer chromatography. R_f values observed are given in Table 8. Only four spots were observed for each reaction mixture, and these were identified by comparison of R_f values with those of authentic samples which were chromatographed on the same plate.

Quantitative product analyses were carried out using GLC to determine the amount of iodobenzene formed during the course of the reaction. This was identified by comparison with an authentic sample under identical conditions. The quantity of iodobenzene formed was estimated from calibration curves. Data are presented in Table 9.

For some reactions a 100% excess of iodine was used, the unreacted iodine being determined by titration with standardised sodium thiosulphate solution, with starch as an indicator. The results appear in Table 9. As can be seen, there is good agreement between the amount of iodine consumed in the reaction and the quantity of iodobenzene produced.

TABLE 8

R_f VALUES FOR REACTANTS AND PRODUCTS OF IODODESTANNYLATION

	Compound			
	PhSnBu$_3$	PhSn(OCH$_2$CH$_2$)$_3$N	PhSn(OC$_6$H$_4$)$_3$N	PhSn(OMe)$_3$
R_F (acetone)	0.70 [a]	0.00	0.00	0.37
R_F (9/1, CHCl$_3$/HOAc)	0.78 [b]	0.83	0.43	0.52
	Compound				
	Bu$_3$SnI	ISn(OCH$_2$OH$_1$)$_3$N	ISn(OC$_6$H$_4$)$_3$N	ISn(OMe)$_3$	PhI
R_F (acetone)	0.34 [a]	0.44	0.05	0.31	0.75
R_F (9/1, CHCl$_3$/HOAc)	0.67 [b]	0.66	0.52	0.45	0.78

[a] Eluant CHCl$_3$. [b] Eluant CHCl$_3$/MeOH = 9/1.

TABLE 9

QUANTITATIVE PRODUCT ANALYSES FOR IODODESTANNYLATION REACTIONS

Compound	Found [a] (%)	
	I_2 [b]	PhI [c]
PhSnBu$_3^n$	8	92
PhSn(OCH$_2$CH$_2$)$_3$N	9	93
PhSn(OC$_6$H$_4$)$_3$N	13	87
PhSn(OMe)$_3$	10	90

[a] Average of 4 determinations. [b] By titration with Na$_2$S$_2$O$_3$. [c] By GLC.

Attempted ring opening of stannatranes by iodide

A solution of PhSn(OCH$_2$CH$_2$)$_3$N or PhSn(OC$_6$H$_4$)$_3$N (ca. 5×10^{-3} M) in a solution of sodium iodide (0.01 M) in methanol was left to stand for several days in a closed flask at 30.0°C. During this period samples were withdrawn and examined by TLC. No reaction was observed during this period, and the only spots found on the plates (using (i) iodine vapour (ii) UV light, and (iii) dithizone spray, for detection) were those corresponding to PhSn(OCH$_2$CH$_2$)$_3$N or PhSn(OC$_6$H$_4$)$_3$N and sodium iodide.

Kinetic methods

The reactions with added I^- were monitored by measuring the decrease in $[I_3^-]$ spectrophotometrically at 365 nm.

All of the iododestannylations were carried out for convenience using an excess of organotin compound over iodine, and the resulting pseudo-first-order rate constants were converted to k_2 values in the usual way. Standard deviations in the second-order rate constant k_2 thus determined were found to be less than 5%. Mean rate constants were reproducible to within ±4%. Rates were unaffected by degassing of samples, and no induction periods were ever detected.

For the reaction of PhSnBu$_3$ at 25°C (μ 0.01 M) a value of k_2 of 122 M^{-1} s^{-1} was obtained which is in reasonably good agreement with the previously reported value (107 M^{-1}, s^{-1}, Ref. 7).

For the reactions of PhSn(OMe)$_3$, procedures identical to those for the corresponding mercuridestannylation were adopted [4].

References

1 M.H. Abraham in C.H. Bamford and C.F.H. Tipper (Eds.), Electrophilic Substitution at a Saturated Carbon Atom, Elsevier, Amsterdam, 1973.
2 M. Gielen, Acc. Chem. Res., 6, (1973) 198.
3 D.S. Matteson, Organometallic Reaction Mechanisms, Academic Press, New York, 1974.
4 M.D. Ravenscroft and R.M.G. Roberts, J. Organomet. Chem., 312 (1986) 33.
5 A. Daneshrad, C. Eaborn, R. Eidenschink and D.R.M. Walton, J. Organomet. Chem., 90 (1975) 139.
6 M. Gielen and J. Nasielski, Bull. Soc. Chim. Belges, 71 (1962) 32.
7 O. Buchman, M. Grosjean and J. Nasielski, Helv. Chim. Acta, 47 (1964) 1679, 1688.
8 R.M.G. Roberts, J. Organomet. Chem., 24 (1970) 675.
9 O. Exner in N.B. Chapman and J. Shorter (Eds.), Correlation Analysis in Chemistry, Plenum Press, New York, 1978, Ch. 10.
10 S. Fukuzumi and J.K. Kochi, J. Am. Chem. Soc., 103, (1981) 7246.