Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

ELECTROPHILIC AROMATIC SUBSTITUTION
IX*. THE ACETOLYSIS OF PHENYLTRIALKYLTINS AND THE BEHAVIOUR OF LITHIUM CHLORIDE IN ACETIC ACID

J. NASIELSKI, O. BUCHMAN, M. GROSJEAN AND M. JAUQUET

Université Libre de Bruxelles, Service de Chimie Organique, Faculté des Sciences, 50 Avenue F. D. Roosevelt, Bruxelles 5 (Belgium)

(Received June 8th, 1969)

SUMMARY

The rates of the acetolysis of substituted phenyltrimethyltins follow a $\rho\sigma^+$ correlation with $\rho = -2.24$. Lithium chloride strongly accelerates the destannylation, but this catalysis is depressed if lithium acetate is also present. The rate enhancement caused by lithium chloride can be attributed to the formation of small amounts of hydrogen chloride, which is a much stronger electrophile than acetic acid itself. The equilibrium constant for this process is $[HCl][AcOLi]/[LiCl] = 2.5 \times 10^{-6}$ mole/l.

The acetolysis shows a solvent isotope effect k(AcOH)/k(AcOD) of 10. The experimental facts are in agreement with a transition state which is rather different from a localised intermediate, and it is suggested that the σ-complex is a very poor approximation to the true transition state in electrophilic aromatic destannylations.

INTRODUCTION

The kinetics of the electrophilic demetallation of substituted phenyltrialkyltins have been examined under a variety of conditions: iodine in CCl_4[2], perchloric acid in aqueous ethanol[2], iodine[3] or HCl[4] in methanol, $Hg(OAc)_2$ in THF[5], or bromine in methanol[6]. The general conclusion is that these reactions obey, more or less accurately, the laws governing classical electrophilic aromatic substitutions and show a weak sensitivity to substituent effects. We now report on the acetolysis of some phenyltrimethyltins and on the influence of salts on rate and mechanism.

RESULTS AND DISCUSSION

1. *Structure–reactivity relationship*

The reaction $ArSn(CH_3)_3 + AcOH \rightarrow ArH + AcOSn(CH_3)_3$ is cleanly first order in substrate; it is easily followed by spectrophotometry since the UV spectrum of the starting material is shifted a few nm to the red compared with the product, and it is possible to find for every compound a wavelength where absorptions differ at least by a factor of two. A plot of $\log_{10}(D_t - D_\infty)$ versus t, where D_t is the absorption at

---

* For Part VIII see ref. 1.

time t (in seconds) and D_∞ is the absorbance reached after at least 20 half-lives yields a straight line with a slope equal to 2.303 k. The results are summarised in Table 1; the initial concentration of the organometallic substrate is approximately 10^{-3} M.

TABLE 1

ELECTROPHILIC DEMETALLATIONS OF PHENYLTRIMETHYLTINS, $Y\text{–}C_6H_4\text{–}Sn(CH_3)_3$, AT 25°

Y	10^5 k (25°; AcOH)	k (25°; I_2/CH_3OH)[3]	10^2 k (25°; HCl/CH_3OH)[4]
p-Br	1.26	121	1.70
H	4.28	507	3.24
m-CH_3	6.01	759	5.62
o-CH_3	17.6		
p-CH_3	22.1	2510	18.6
p-OCH_3	304	32400	158

According to Table 1 the acetolysis shows similar effects to those observed for the destannylations in methanol, and is to be considered as a classical electrophilic aromatic substitution proceeding in two steps. Once again, the sensitivity to substituents, is very low ($\rho = -2.24$), and is close to that found under other reaction conditions[2-6]. An explanation for this low sensitivity would relate selectivity to reactivity[7], with the transition state lying farther from the σ-complex and closer to the initial state than in other electrophilic substitutions, and thus involving less electron demand from the substituent[8].

Two factors may be important in increasing the reactivity of aryltins: the weakness of the carbon–tin bond, and the polarisability of the tin atom. Since many aromatic electrophilic destannylations occur in two steps, the *first* of which is rate-determining, it is not clear why changes in the energy of the bond *not broken* in the rate-determining step[9] should lead to such a large difference in rate between deprotonations and destannylations. Polarisability effects on the other hand may be the reason for these differences, as was shown by Bunnett[10] in the case of S_NA^* reactions and as is indicated by the fact that perchloric acid is more effective than iodine in cleaving arylsilicons, whereas the reverse is true for aryltins. Eaborn[11] has suggested that electron release from the Me_3Sn group leads to an acceleration by stabilizing the incipient Wheland intermediate; in our opinion, this polar effect should be of less importance than the polarizability of the leaving group.

It has been argued that small ρ values indicate a concerted mechanism, involving a concomitant breaking of the carbon–tin bond[5]. It is clear that such a hypothesis is not demanded by the results, especially for reactions in polar solvents.

2. *Salt effects*

The addition of lithium chloride causes a large increase in rate, but this accelerating effect is depressed by adding lithium acetate. The results for 0.01 M LiCl solutions in acetic acid are given in Table 2; the retardation due to AcOLi is shown in Table 3.

The results show that the rate depends on the ratio [LiCl]/[LiOAc], *i.e.* $k = k_0 + B \cdot [\text{LiCl}]/[\text{LiOAc}]$, where k_0 is the rate for the uncatalyzed reaction.

TABLE 2

INFLUENCE OF LITHIUM CHLORIDE ON THE ACETOLYSIS OF SUBSTITUTED PHENYLTRIMETHYLTINS $Y{-}C_6H_4{-}Sn(CH_3)_3$, IN THE PRESENCE OF 0.01 *M* LiOAc AT 25°

The rate constants have been multiplied by 10^5 (in sec^{-1}). α is the slope of the line $k=k_0+\alpha\cdot[LiCl]$, in $l\cdot mole^{-1}\cdot sec^{-1}$.

Y	[LiCl] (mole/l)									$10^3\alpha$
	0.00	0.01	0.02	0.03	0.05	0.08	0.10	0.15	0.50	
p–OCH_3	304	357	421	555	621	950				77
p–CH_3	22.1	32			70	107	135	181		10.7
H	4.3	5.95	7.6	9.4	12.6		21.7	29.4		1.68
p–Br	1.26	1.80			3.50		5.84		28.6	0.5

TABLE 3

RETARDING EFFECT OF LITHIUM ACETATE ON THE LITHIUM CHLORIDE-CATALYZED ACETOLYSIS OF PHENYLTRIMETHYLTIN AT 21° FOR A CONSTANT CONCENTRATION OF LITHIUM CHLORIDE (0.568 mole/l)

[LiOAc] (mole/l)	10^5 *k* (sec^{-1})
0	261
0.00552	152
0.0164	65
0.023	47
0.12	19

TABLE 4

INFLUENCE OF SALTS ON THE ACETOLYSIS OF PHENYLTRIMETHYLTIN

Concentration of lithium salts (mole/l)			10^5 *k* (25°)
[LiOAc]	[$LiClO_4$]	[LiCl]	
0	0	0	4.28
0.01	0	0	4·30
1.00	0	0	7.0
0	1.00	0	126
0.01	0	1.00	172

TABLE 5

SOLVENT ISOTOPE EFFECT ON THE ACETOLYSIS OF (*p*-METHOXYPHENYL)TRIMETHYLTIN AT 25°

AcOD (%)	k_{obs}	k_H/k_D
0	3.0×10^{-3}	(1.0)
30	1.0×10^{-3}	3.0
50	6.0×10^{-4}	5.0

Lithium perchlorate leads to a large increase in rate, although less so than lithium chloride, as shown in Table 4. Lithium acetate alone causes no retardation but rather a slight accelerating effect; this shows that the reaction does not involve the acetoxylium ion as the only reagent.

Further insight into the mechanism was gained from a study of the solvent isotope effect. The data of Table 5, when extrapolated to 100% deuterium acetate, gives a ratio k_H/k_D of 10.

The most consistent interpretation for the salt and isotope effects is to assume the following reaction scheme:

$$\begin{array}{ll} CH_3COOH + LiCl \rightleftarrows CH_3COOLi + HCl & K \\ ArSnMe_3 + CH_3COOH \rightarrow ArH + CH_3COOSnMe_3 & k_1 \\ ArSnMe_3 + HCl \rightarrow ArH + Me_3SnCl & k_2 \end{array}$$

The observed rate constant is then given by:

$$k_{obs} = k_1 + k_2 \cdot [HCl] = k_1 + k_2 \cdot K \cdot [LiCl]/[LiOAc] \qquad (1)$$

where the concentration of acetic acid is included in K and k_1; this rate expression is identical with the experimental equation.

The proposed mechanism implies the formation of HCl in acetic solutions of LiCl. This has been checked by using α-naphtholbenzein as an indicator in acetic acid; increasing amounts of LiCl transform the dye into its acid form, and comparison with AcOH/HCl solutions yields a K value of 2×10^{-6} mole/l.

A second implication of this mechanism is that HCl must be a more active reagent than acetic acid. This was found to be so by reacting (*p*-bromophenyl)trimethyltin with HCl in acetic acid (the other aryltins proved much too reactive). The reaction is first order in organotin and first order in HCl; the rate constant is 2.0 ± 0.1 $l \cdot mole^{-1} \cdot sec^{-1}$ at 25°. From eqn. (1) and the known values for k_1 and k_2 it is possible to deduce the value 2.5×10^{-6} mole/l for K. This compares quite well with the value found by the indicator method.

It seems thus well established that the catalytic activity of lithium chloride is due to its ability to release HCl when dissolved in acetic acid. It is interesting to note in this connection that Winstein[12] has shown that lithium perchlorate gives kinetically significant amounts of $HClO_4$ in the same solvent, explaining thus the accelerating effect of this salt in the destannylation reaction. Similarly, Eaborn, Jackson and Taylor[13] have given compelling evidence that LiCl in trifluoroacetic acid yields HCl in very large amounts.

Our results are incompatible with a mechanism in which LiCl catalyzes the departure of tin from a preformed Wheland intermediate. The high value for the solvent isotope effect shows that the proton transfer is rate determining, and is compatible with a transition state where the proton is nearly half-way between both reactants. This high value is difficult to reconcile with a mechanism involving substantial cleavage of the C–Sn bond, and once again, the σ-complex seems to be a poor approximation to the true transition state in these reactions. Chloride ion is a strong base towards tin[14] and can thus accelerate the departure of the tin-leaving group; such a nucleophilic catalysis has been found in other cleavages involving tin[15–18]. In our case however such an assistance plays no part in the rate enhancement induced by LiCl.

EXPERIMENTAL

The substituted phenyltrimethyltins were available from previous studies[3,4,19]. Glacial acetic acid from UCB was recrystallized until it melted at 16.5°. UCB lithium chloride, Fluka lithium perchlorate and Fischer lithium acetate were used as such. Deuterium acetate was made from acetic anhydride and deuterium oxide; the deuterium content was determined by NMR with a Varian A60 spectrometer. The kinetics were followed in 4 cm cells with a Zeiss spectrophotometer; the cell compartment was thermostatted with the help of a Haake circulating thermostat.

ACKNOWLEDGEMENT

We thank Professor R. H. Martin for his interest. We also appreciate stimulating discussions with Professors C. Eaborn, S. Winstein and E. A. Halevi. We express our gratitude to the Institut pour l'encouragement de la Recherche Scientifique dans l'Industrie et l'Argriculture for a fellowship (M.J.) and the Fonds de la Recherche Fondamentale Collective for financial support to the Laboratory.

REFERENCES

1 J. Nasielski, O. Buchman, M. Grosjean, J.-J. Schurter and G. Vandendunghen, *Bull. Soc. Chim. Belg.*, 77 (1968) 349.
2 R. W. Bott, C. Eaborn and J. A. Waters, *J. Chem. Soc.*, (1962) 681; C. Eaborn and K. C. Pande, *J. Chem. Soc.*, (1960) 1566; C. Eaborn and J. Waters, *J. Chem. Soc.*, (1961) 542.
3 O. Buchman, M. Grosjean and J. Nasielski, *Helv. Chim. Acta*, 47 (1964) 1679.
4 O. Buchman, M. Grosjean and J. Nasielski, *Helv. Chem. Acta*, 47 (1964) 1695.
5 H. Hashimoto and Y. Morimoto, *J. Organometal. Chem.*, 8 (1967) 271.
6 P. Alcais and J. Nasielski, *J. Chim. Phys.*, 66 (1969) 95.
7 H. C. Brown and L. M. Stock, in V. Gold (Ed.), *Advances in Physical Organic Chemistry*, Vol 1, Academic Press, London, 1963, p. 35.
8 G. S. Hammond, *J. Amer. Chem. Soc.*, 77 (1955) 334.
9 J. Nasielski, O. Buchman, M. Grosjean and E. Hannecart, *Bull. Soc. Chim. Belg.*, 77 (1968) 15.
10 J. F. Bunnett, *J. Amer. Chem. Soc.*, 79 (1957) 5969.
11 R. W. Bott, C. Eaborn and P. M. Greasley, *J. Chem. Soc.*, (1964) 4804.
12 S. Winstein, private communication.
13 C. Eaborn, P. M. Jackson and R. Taylor, *J. Chem. Soc.*, *B*, (1966) 613.
14 M. Gielen and N. Sprecher, *Organometal. Chem. Rev.*, 1 (1966) 455.
15 R. E. Dessy and F. Paulik, *J. Amer. Chem. Soc.*, 85 (1963) 1812.
16 T. Chivers and B. David, *J. Organometal. Chem.*, 13 (1968) 177.
17 R. D. Chambers, J. A. Cunningham and D. A. Pyke, *Tetrahedron*, 24 (1968) 2783.
18 C. Eaborn, H. L. Hornfeld and D. R. M. Walton, *J. Chem. Soc.*, *B*, (1967) 1036.
19 O. Buchman, M. Grosjean and J. Nasielski, *Bull. Soc. Chim. Belg.*, 71 (1962) 467.