Substituent effects in aromatic substitution of aryltriethyltin compounds by mercuric halides

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(Received August 2nd, 1988)

Abstract

Second-order rate constants are reported for the reaction of some $YC_6H_4SnEt_3$ compounds with mercuric halides in tetrahydrofuran, and show that the reaction is one of low selectivity. The substituent effects can be correlated only in terms of Hammett σ-constants, and the data for the *meta*-methoxy group are anomalous. The results indicate that the rate determining step involves reaction of a π-complex. Activation parameters are reported, and are in accordance with the suggested mechanism.

Introduction

The rate-determining step for the demetallation of arylmetal compounds by an electrophile could involve σ- or π-complexes or both [1–4]. If the rate-determining step involves a transition state close to a σ complex, the effects of substituents in the aryl system would be expected to be much larger than when the transition state resembles a π-complex.

A detailed kinetic study carried out previously on reaction 1 (Y = H and X = Cl, I) in methanol [5], and from the effects of added water, added inert salts, and temperature, the participation of a π-complex intermediate was suggested. In a later study [6], the effects of alcoholic solvents on reaction 1 (Y = H, X = Cl, I) were determined, and the same conclusion drawn about the nature of the transition state.

$$YC_6H_4SnEt_3 + HgX_2 \rightarrow YC_6H_4HgX + XSnEt_3 \qquad (1)$$

A study of the effects of substituents on reaction 1 should provide useful information about the nature of the transition state, and the present report is concerned with such effects for reaction 1 (Y = *p*- and *m*-MeO, Me, Cl, H and

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X = Cl, I) in tetrahydrofuran (THF). This solvent was chosen because (a) the rates in it could be followed conveniently, and, (b) it was of interest to compare the results with those for reaction 1 (X = OAc) in THF [7] obtained by a competition method. The competition method has been the subject of much criticism [8,9].

Results and discussion

Kinetic studies in THF

The rates of reaction 1 (X = Cl, I) in THF were determined as described before [5]. In each run, which was monitored up to at least 40% completion of the reaction, the second-order rate equation was obeyed.

The possibility exists that HgX_3^- be formed from the reaction of Et_3SnX and HgX_2 (X = Cl, I), as was found for reactions in some hydroxylic and aprotic solvents [10–13]. However, in the present work the values of k_2 remained almost constant during each run, indicating that any formation of HgX_3^- is very small and can be ignored. Since THF is a very poor ionizing medium this observation was not unexpected, and it is known that $HgBr_2$ does not form a complex with $BrSnMe_3$ in dioxane or ethyl acetate [14].

Values of k_2 (averaged over 2 to 5 runs) for reaction 1 (X = Cl) at 0 and 25 °C and for reaction 1 (X = I) at 25 °C in THF are given in Table 1. The maximum uncertainty in the rate constants is about ±4%.

Influence of the substrates and reactants

The reaction of Et_4Sn with $HgCl_2$ in THF at 25 °C proved to be very slow (there was little change after four days). It follows that in all the reactions of $YC_6H_4SnEt_3$ with HgX_2, only the YC_6H_4 group is cleaved off; and eq. 1 represents the stochiometry of the reactions.

Table 1

Second-order rate constants for the reaction of $YC_6H_4SnEt_3$ with mercury(II) halides in THF

Y	Initial concentrations		$10^2 k_2 (M^{-1} s^{-1})$		k_{rel}
	$10^4[YC_6H_4SnEt_3]$ (M)	$10^4[HgX_2]$ (M)	at 0 °C	at 25 °C	
A with HgCl$_2$ [a]					
p-Me	20.20	12.00	18.6	63.0	3.3
p-Cl	25.40	14.06	1.0	3.8	0.2
H	19.80	12.80	5.6	19.0	1.0
m-MeO	15.58	8.82	5.6	18.9	1.0
m-Me	26.80	15.80	8.5	21.6	1.1
m-Cl	28.00	14.80	0.6	1.7	0.1
B with HgI$_2$					
p-MeO	15.00	9.50		35.0	5.3
p-Me	22.20	15.58		18.6	2.8
p-Cl	26.40	15.60		2.2	0.3
H	29.00	16.00		6.6	1.0
m-MeO	13.50	7.94		7.4	1.1
m-Me	19.80	13.20		10.4	1.6
m-Cl	25.90	16.60		1.3	0.2

[a] Rate constants are uncorrected for solvent contraction from 25 °C.

The presence of an excess of I^- (in the form of n-Bu$_4$NI) for the reaction with HgI$_2$ in THF prevented the reaction; this is because the halide ion converts the HgI$_2$ into the less reactive HgI$_3^-$. From Table 1, the order of increasing electrophilic activity towards ArSnEt$_3$ is: HgCl$_2$ > HgI$_2$ $\gg$ HgI$_3^-$.

Substituent effects

Observed second-order rate constants, k_2, along with the rate, k_{rel}, for the compound YC$_6$H$_4$SnEt$_3$ relative to that of the unsubstituted compound C$_6$H$_5$SnEt$_3$, are listed in Table 1. The data reveal that although electron-releasing substituents facilitate and electron-withdrawing substituents hinder the reaction, as usually expected for an electrophilic aromatic substitution, there are clear anomalies. The most striking of these are the small overall spread of rates and the fact that a m-OMe group activates the HgI$_2$ reaction.
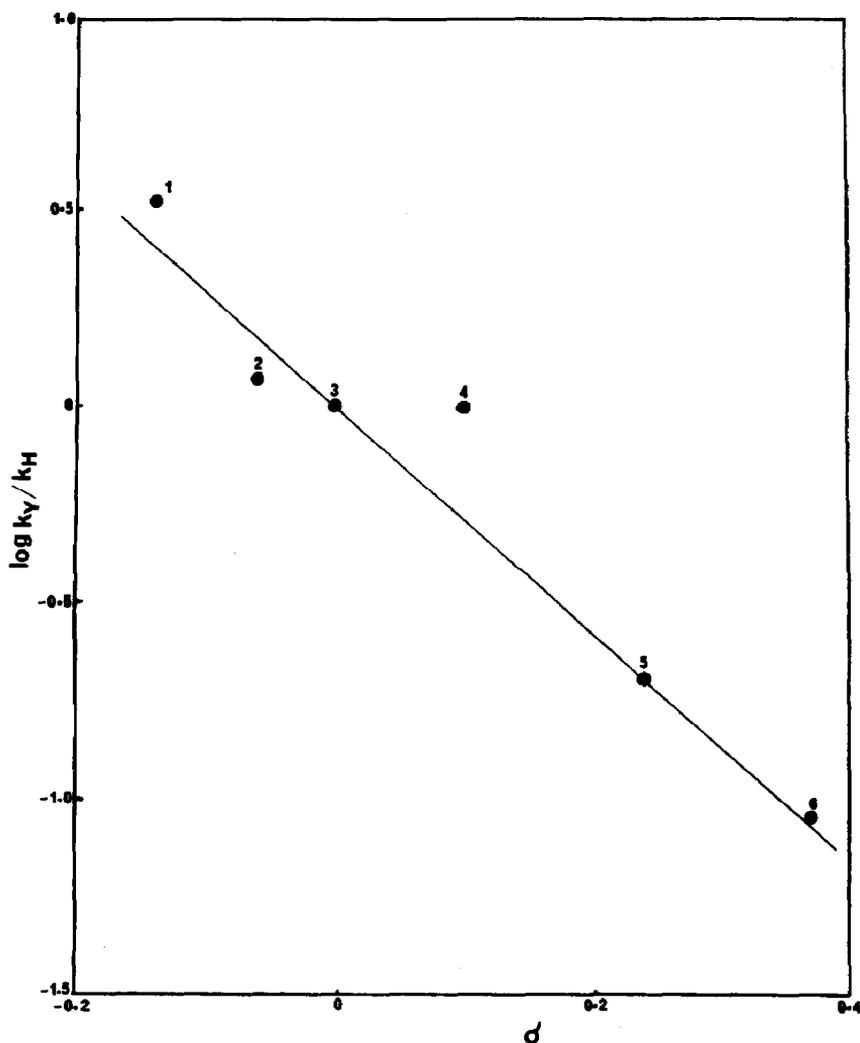

Fig. 1. Plot of log k_Y/k_H against σ for cleavage of YC$_6$H$_4$SnEt$_3$ by HgCl$_2$ in THF at 25°C. The numbers of the points refer to the substituents Y, as follows: 1, p-Me; 2, m-Me; 3, H; 4, m-MeO; 5, p-Cl; 6, m-Cl.

We first consider the implication of the small overall spread of rates. In electrophilic aromatic substitution reaction in which the electron demand at the transition state is high, the overall spread of rates is large. For example a p-Me group activates 2420 times in aromatic bromination in acetic acid [15]. In contrast, in reaction 1 (X = Cl), a p-Me group activates only 3.3 times (for X = I the figure is 2.8). Further, the spread of rates on going from m-Cl to p-Me for the $HgCl_2$ reaction is only 38, and for HgI_2 reaction 14. This implies that the electron demand in the reaction is not high, or in other words little charge is developed in the transition state. This situation is very similar to that in the cleavage of aryl–tin bonds by iodine in carbon tetrachloride [16] and by mercuric acetate in THF [7], reactions in which π-complexes are believed to be involved in the rate-determining steps.

The log k_{rel} values give a good linear plot (Fig. 1) against σ [17 *] except for the points for the m-OMe compound (see for example a plot of log k_{rel} vs σ for chloride reaction at 25 °C); the values of the slopes ρ are -2.91 and -2.18 for the $HgCl_2$ and HgI_2 reactions respectively. (A value of ρ -2.95 can be calculated for the $HgCl_2$ reactions at 0 °C). The correlations (plots not shown) are very poor with Brown σ^+ constants. Furthermore, with the values of k_{rel} listed for reaction 1 (X = Cl, I) in Table 1, no value of r leads to correlation in terms of the Yukawa–Tsuno equation log $k_{rel} = p[\sigma + r(\sigma^+ - \sigma)]$, where r is a measure of the demand on electron polarisability effects of substituents. Thus the transition state does not seem to be as far along the reaction coordinate towards the σ-complex as in most electrophilic aromatic substituents.

These results are similar to those for the reaction 1 (X = OAc) in THF [7], the reaction of $ArSiMe_3$ with $Hg(OAc)_2$ in acetic acid [18], and the iododestannylation of R_3SnAr in CCl_4 [16]. However, the data contrast with those for protodemetallation of $ArMR_3$ compounds (M = Ge, Sn) in aqueous methanol [19] and aqueous ethanol [20]. It can be suggested that the transition state for reaction 1 (X = Cl, I) in THF lies well away from a σ-complex and is nearer to a π-complex. From the work of Hashimoto and Morimoto [7], the value of ρ for reaction 1 (X = OAc) in THF is -3.5. Clearly the values of ρ decrease from $Hg(OAc)_2$ to $HgCl_2$ and to HgI_2, in accord with the order of electrophilicity of the mercury(II) salts.

A significant feature of our results is that the effects of the m-OMe group are anomalous. This substituent normally deactivates in electrophilic aromatic substitution, but does not do so in the reaction with $HgCl_2$, it mildly activates in the reaction with HgI_2. Bott et al. [16] have suggested that in a transition state which has considerable π character, a $meta$-substituent will appear to have some $para$-character and vice versa. Our results for reaction 1 are also consistent with this picture of a transition state, in which a π-complex is in the process of conversion into a σ-complex but is well removed from the latter along the reaction coordinate.

Activation parameters

The values for the activation parameters calculated from data in Table 1, for $HgCl_2$ reactions are listed in Table 2. The low sensitivity of the reactions to substituent effects is reflected by the narrow range of $\Delta H^{\ddagger}$ values. These values are

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* Reference numbers with asterisks indicate notes in the list of references.

Table 2

Activation parameters for the reaction of $YC_6H_4SnEt_3$ by $HgCl_2$ at 25°C [a]

Y	$\Delta G^{\ddagger}$ [b]	$\Delta H^{\ddagger}$	$-\Delta S^{\ddagger}$
p-Me	16.24	7.3	30.1
p-Cl	17.90	7.9	33.5
H	17.01	6.9	33.8
m-MeO	16.96	7.2	32.7
m-Me	16.88	5.4	38.4
m-Cl	18.39	6.6	39.6

[a] $\Delta G^{\ddagger}$ (+/−0.02), $\Delta H^{\ddagger}$ (+/−0.4) in kcal/mole, and $\Delta S^{\ddagger}$ (+/−1.2) in kcal/mole on the mole fraction scale. Quoted errors are standard deviations for a 4% error in the rate constants. [b] The values of $\Delta G^{\ddagger}$ were calculated after conversion of k_2 from the molar scale to the mole fraction scale.

generally low, and we associate them with the process of complex formation. Thus, from the work of Reutov et al. [13] on some reactions of $RSnMe_3$ (R = Ph, C_6F_5, $CH_2 = CH$, and Me) with $HgCl_2$ in methanol, the values of $\Delta H^{\ddagger}$ for π-complexing organic groups are much lower than for compounds of the type Me_4Sn, for which such complexation is not possible. Indeed, charge transfer complexes have been described between mercury(II) salts and aromatic hydrocarbons [21].

Experimental

The aryltriethyltin compounds were prepared from triethyltin bromide [22] and the appropriate arylmagnesium bromide by the reported procedure [23]. They were distilled under reduced pressure, with boiling points as follows: phenyl- as before [6]; p-methoxyphenyl-, b.p. 138–140°C at 6 mmHg (Lit. [7], 138–138.5°C at 5 mmHg); m = methoxyphenyl-, b.p. 145–147°C at 7 mmHg (Lit. [7], 144–145°C at 7 mmHg); p-tolyl-, b.p. 127–129°C at 8 mmHg (Lit. [7], 127.5–128 at 9 mmHg); m-tolyl-, b.p. 135°C at 12 mmHg (Lit. [7] 133.5–134, 9 mm); p-chlorophenyl, b.p. 120–121°C at 2.5 mm (Lit [7], 141–141.5, 6.5 mmHg); and m-chlorophenyl-triethyl-tin, b.p. 119–121°C at 3 mmHg (Lit. [7], 142°C at 6 mmHg). For each of the above compounds the NMR spectrum was as expected.

Mercury(II) salts treated as before [5]. THF was dried by refluxing over sodium and then distilled shortly before use.

Kinetics. Rate were determined spectrophotometrically as described previously [5,6]. Calibration was carried out by taking aliquots of $HgCl_2$ solution (10 points with appropriate concentrations) in THF and quenching with a methanolic solution of KI [5] (the dilution of the aliquots was 10-fold, as in the kinetic run). Calibration values are: $D = 10823.9$ (HgX_2) + 0.007 where D is the observed absorbance of the solution at 315 nm with 1 cm cells.

Acknowledgments

References

1 C. Eaborn, J. Organomet. Chem., 100 (1975) 43.
2 R. Taylor in C.H. Bamford and C.F.H. Tipper (Eds.), Comprehensive Chemical Kinetics, Amsterdam, Vol. 13, 1972.
3 M.H. Abraham and P.L. Grellier in F.R. Hartley and S. Patai (Eds.), The Chemistry of the Metalcarbon bond, John Wiley and Sons LTD, New York, Vol. 2, 1985.
4 I.P. Beletskaya, K.P. Butin, V.N. Shishkin, I.F. Gun Kin, and O.A. Reutov, J. Org. Chem. (USSR), 11 (1975) 2549.
5 M.H. Abraham, and M.R. Sedaghat-Herati, J. Chem. Soc., Perkin Trans. II, (1978) 729.
6 M.R. Sedaghat-Herati, and P. Nahid, J. Organomet. Chem., 239 (1982) 307.
7 H. Hashimoto, and Y. Morimoto, J. Organomet. Chem., 8 (1967) 271.
8 S.Y. Caille and R.J.P. Corriu, Chem. Comm., (1967) 1251.
9 G.A. Olah, S.J. Kuhn, and S.H. Flood, J. Am. Chem. Soc., 83 (1961) 4571.
10 M.H. Abraham, and T.R. Spalding, J. Chem. Soc. A, (1968) 2530.
11 M.H. Abraham, and F. Behbahany, J. Chem. Soc. A, (1971) 1469.
12 M.H. Abraham, and M.J. Hogarth, J. Chem. Soc. A, (1971) 1474.
13 A.N. Kashin, I.P. Beletskaya, A.Ts. Malkhasyan, and O.A. Reutov, J. Org. Chem. (USSR), 9 (1973) 1119.
14 J.K. Chipperfield, A.C. Hater, and D.E. Webster, J. Chem. Soc., Dalton, (1977) 485.
15 H.C. Brown, and L.M. Stock, J. Am. Chem. Soc., 79 (1957) 1421.
16 R.W. Bott, C. Eaborn, and J.A. Waters, J. Chem. Soc., (1963) 681.
17 σ^+ and σ values were taken from J. March, Advanced Organic Chemistry, 3rd edit., John Wiley and Sons Inc. 1985, p. 244.
18 A. Benkeser, T.V. Liston, and G.M. Stanton, Tetrahedron Lett., 1, 15, 1.
19 R.W. Bott, C. Eaborn, and D.R.M. Walton, J. Organomet. Chem., 1 (1964) 420; C. Eaborn, and K.C. Pande, J. Chem. Soc., (1961) 297.
20 C. Eaborn, and J.A. Waters, J. Chem. Soc., (1961) 542.
21 S. Fukuzumi, and J.K. Kochi, J. Phys. Chem., 85 (1981) 648.
22 H. Gilman, and C.E. Arntzen, J. Org. Chem., 15 (1950) 994.
23 C. Eaborn, and K.C. Pande, J. Chem. Soc., (1960) 1566.