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SUBSTITUENT EFFECTS IN ARYL–TIN CLEAVAGE OF ARYLTRIETHYLTIN COMPOUNDS BY MERCURIC ACETATE

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Electrophilic cleavage of aryl–metal bonds has been investigated from various points of view. It has been shown that electrophilic reagents cleave the aryl–Sn bond even more readily than aryl–Si and aryl–Ge bonds in some aryltrialkylmetallics[1]. Eaborn *et al.*[2] measured the rates of cleavage of ring-substituted tricyclohexylphenyltin compounds by aqueous ethanolic perchloric acid and showed that the substituent effects are represented by eqn. (1). On the other hand, iododestannylation of some

$$\log k_X/k_H = -3.8[\sigma+0.4(\sigma^+-\sigma)] \quad (1)$$

$(C_6H_{11})_3SnC_6H_4X$ compounds by iodine in carbon tetrachloride is second order in iodine. The effects on the rate by substituents, X, are complicated and are not in accord with those observed in other electrophilic aromatic substitutions. Some π-complex character in the transition state was suggested[3]. In order to obtain some information about the mechanism of aryl–Sn cleavage, the reaction of some aryltriethyltin compounds with mercuric acetate in tetrahydrofuran (THF) was investigated.

RESULTS AND DISCUSSION

As the result of preliminary experiments on the solubilities of the reagents, THF was selected as a solvent to make the reaction system homogeneous. Only phenylmercuric acetate and triethyltin acetate were isolated and identified from the reaction mixture of triethylphenyltin with mercuric acetate. From the material balance of the above reaction products, the stoichiometric equation of the reaction is expressed by eqn. (2). It may be concluded that other side reactions are negligible.

$$XC_6H_4Sn(C_2H_5)_3+Hg(OCOCH_3)_2 \rightarrow XC_6H_4HgOCOCH_3+(C_2H_5)_3SnOCOCH_3 \quad (2)$$

It was found that the reaction was very fast and that the rates could not be measured by the usual methods. Therefore, the relative rates were obtained by means of the competitive reaction technique, *i.e.*, an excess of substituted and unsubstituted triethylphenyltin compounds was allowed to compete for mercuric acetate, and the arylmercuric acetates produced were converted to the corresponding arylmercuric bromides and then to the corresponding bromobenzenes. The relative amounts of bromobenzenes were determined by gas liquid chromatography (GLC). Relative rates of $XC_6H_4Sn(C_2H_5)_3$ destannylation, where X is *p*-CH_3, *p*-Cl, *p*-CH_3O, H, *m*-CH_3, *m*-CH_3O and *m*-Cl, calculated using the above data, are shown in Table 1.

TABLE 1

RELATIVE RATES FOR ARYL–TIN CLEAVAGE OF $XC_6H_4Sn(C_2H_5)_3$ BY MERCURIC ACETATE IN THF

X	k_X/k_H		
	(20°C)	(40°C)	(60°C)
p-CH_3O	8.30		
p-CH_3	1.76	1.94	2.08
p-Cl	0.25		
H	1.00		
m-CH_3	1.21		
m-CH_3O	0.72		
m-Cl	0.029		

Plots of log k_X/k_H against the Hammett substituent constants (σ) and the Brown substituent constants (σ^+) are shown in Fig. 1. It is obvious that there is a linear relationship between log k_X/k_H and the σ-constants. The value of the reaction constant (ρ) obtained is -3.5. However, a straight line is not obtained for the σ^+-constants. Although the ratio, log $p_f(CH_3)/m_f(CH_3)$* has generally a value of 3.98 ± 0.53^4 for

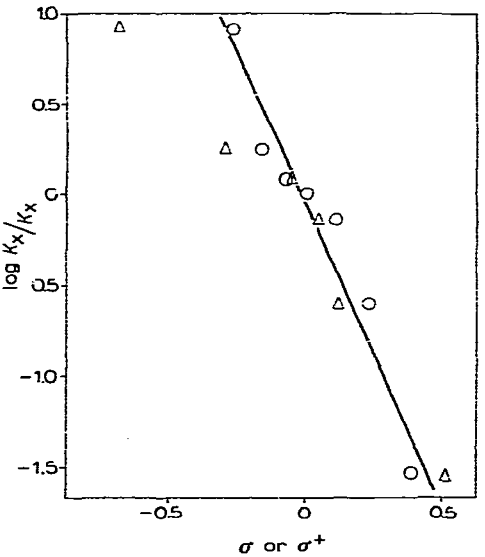

Fig. 1. Relations between relative rates of cleavage of $XC_6H_4Sn(C_2H_5)_3$ and substituent constants. ○ for σ; △ for σ^+.

the usual direct electrophilic substitutions of aromatic rings, in this case the ratio is smaller (2.96). Further, when $1/\sigma$ log k_X/k_H is plotted against σ^+/σ, the points scatter greatly. This shows also that there is no value of r to agree with the Yukawa–Tsuno equation[5], $\log k_X/k_H = \rho[\sigma + r(\sigma^+ - \sigma)]$. These results are in contrast with destannylation[2] and degermylation[6] of $XC_6H_4MR_3$-type compounds or degermylation of

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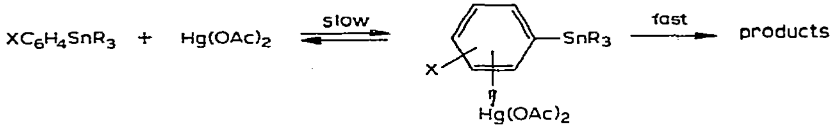
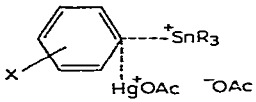
* $p_f(CH_3)$ and $m_f(CH_3)$ are partial rate factor of p- and m-position of toluene respectively.

$XC_6H_4C{\equiv}CGe(C_2H_5)_3$[7] compounds by protonic acids in aqueous ethanol, wherein the substituent effects can be accounted for in terms of σ^+-constants, or better, in terms of a combination of σ-constants with σ^+-constants, *i.e.* the Yukawa–Tsuno equation. The results are rather similar to mercuridesilylation of aryltrimethylsilanes by mercuric acetate in acetic acid, wherein the rates are better correlated by σ-constants than by σ^+-constants[8].

The fact that the substituent effects on the rate of this mercuridestannylation of $XC_6H_4Sn(C_2H_5)_3$ correlate with the Hammett σ-constants reveals that a benzenium ion (σ-complex of Brown) does not participate in the rate-determining step, and thus the contribution of resonance effects of the substituent to the transition state is not as important as in other destannylations. The difference of activation energy of *p*-tolyl- and phenyl- triethyltin was only *ca.* 1 Kcal/mole. It may be then considered that the rate-determining step of the reaction is either the formation of a π-complex type intermediate (eqn. 3) or elimination of the triethyltin group concerted with attack of mercuric acetate or an electrophile derived from it (I).



(3)



(I)

The above mechanistic behavior may be caused, for example, by the specific polarization of aryl–Sn bond in THF, by the specific coordinating ability of the aryltriethyltin compounds to mercuric acetate, by d_π–p_π bonding[2,9] between aromatic ring and tin, or by the specific interaction of mercuric acetate with THF. It is difficult to decide which factor is important until additional data and information are available.

EXPERIMENTAL

Materials

The aryltriethyltin compounds used were prepared from triethyltin bromide[10] and appropriate arylmagnesium bromides according to the reported method[1,11]. All were purified by repeated fractional distillation at reduced pressure until GLC showed only one peak. Phenyl-, b.p. 129.5–130.5° (14 mm); *p*-tolyl-, b.p. 127.5–128° (9 mm); *p*-methoxyphenyl-, b.p. 138–138.5° (5 mm); *p*-chlorophenyl-, b.p. 141–141.5° (6.5 mm); *m*-tolyl-, b.p. 133.5–134° (9 mm) (Found: Sn, 39.4. $C_{13}H_{22}Sn$ calcd.: Sn, 39.97%.); *m*-methoxyphenyl-, b.p. 144–145° (7 mm) (Found: Sn, 37.6. $C_{13}H_{22}OSn$ calcd.: Sn, 37.92%); and *m*-chlorophenyl-triethyltin, b.p. 142° (6 mm) (Found: C, 45.34; H, 6.02; Sn, 37.1. $C_{12}H_{19}ClSn$ calcd.: C, 45.41; H, 6.03; Sn, 37.40%.).

Phenylmercuric bromide (m.p. 275.5–276°, lit. 276°) and *p*-tolylmercuric bromide (m.p. 229–230°, lit. 228°) were prepared according to the reported procedure[12] and were recrystallized three times from benzene. THF was dried by refluxing over sodium and distilled immediately before use. Mercuric acetate was of commercial reagent grade.

Competition reactions

(*a*) *Procedure**. Mercuric acetate (*ca.* 3.60 mmoles) was dissolved in 180 ml of THF and the solution was kept constant at 20°. To the magnetically stirred solution was added all at once the solution of triethylphenyltin (*ca.* 3.60 mmoles) and an aryltriethyltin (*ca.* 3.60 mmoles) in 20 ml THF which had been kept at 20°. The mixture was stirred for 1 h at 20°**. Maximum temperature variation during a run was 0.5°. The mixture then was evaporated to dryness on a rotary evaporator at reduced pressure and below 20°. The residue was dissolved in 15 ml THF. The resulting solution was treated with an excess of 3% aq. potassium bromide, stirred and then diluted with sufficient water to give a total volume of 300 ml***. The resulting precipitate was filtered, washed with water and with a small volume of ethanol to remove triethyltin acetate and dried in a vacuum desiccator to give a solid mixture of arylmercuric bromides. The above solid was suspended in 20 ml of chloroform and treated with bromine (*ca.* 4.5 mmoles) in 10 ml chloroform at room temp. for *ca.* 20 h to produce the corresponding bromobenzenes. The chloroform filtrate was washed successively with 3% sodium hydrogen sulfite and 3% potassium bromide and water, and dried over calcium chloride.

It was found in the separate experiments that each arylmercuric bromide (except *m*-chlorophenylmercuric bromide) was converted quantitatively to the corresponding bromobenzene under the conditions described above.

(*b*) *Analysis of relative quantities of products and calculation of relative rates.* The solutions of bromobenzenes in chloroform were analyzed by GLC and the results obtained were corrected by the calibration curve from the authentic samples. Colum temp. 120°, except *p*- and *m*-bromoanisole 130°; carrier gas, hydrogen 80 ml/min; column packing, silicone DC 550).

In the case of the *m*-chlorophenyl derivative, the mixture of *m*-chlorophenyl- and phenylmercuric bromide from (*a*) was analyzed by infrared spectroscopy using key bands of 1095 cm^{-1} for the former and of 730 cm^{-1} for the latter (KBr pellets).

The relative rates, k_X/k_H were calculated from eqns. (4) and (5) using the relative quantities, y_∞/x_∞ determined from the above analyses.

$$c_0 = x_\infty + y_\infty \tag{4}$$

$$\frac{k_X}{k_H} = \frac{\log_{10}[b_0/(b_0 - y_\infty)]}{\log_{10}[a_0/(a_0 - x_\infty)]} \tag{5}$$

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* With another procedure in which mercuric acetate in THF was slowly added to a mixture of two aryltriethyltins in THF, the results obtained were not affected. For example, k_X/k_H of *p*-methoxy derivative was 7.9 in this procedure.

** It had been found in preliminary experiments that the reaction is almost completed in the order of minutes.

*** In other experiments, each arylmercuric acetate produced in the reactions was converted almost quantitatively to the corresponding arylmercuric bromide under the same conditions. *m*-Tolyl-, *m*-chlorophenyl- and *m*-methoxyphenyl-mercuric bromide formed had m.p. of 183–183.5°, 224.5–225° and 151–152°, respectively.

Where a_0, b_0 and c_0 are initial concentrations of triethylphenyltin, substituted triethylphenyltin and mercuric acetate, respectively; x_∞ and y_∞ are the concentrations of unsubstituted and substituted triethylphenyltin reacted.

Reaction products of triethylphenyltin

Triethylphenyltin (8.83 g, 31.2 mmole) and mercuric acetate (9.95 g, 31.2 mmole) were allowed to react in 600 ml of THF and worked up in the manner similar to that in (*a*), except that the mixture was concentrated to 50 ml volume and treated with saturated aqueous sodium chloride instead of 3% potassium chloride. The resulting precipitate was filtered and washed with water and then with ether to give 11.54 g of solid. The filtrate was extracted with ether. The extracts and the ether washings were combined and concentrated to dryness to give 5.46 g of pure triethyltin acetate, m.p. 117–118.5° (identified by comparison with the authentic sample). The above solid was heated with *ca.* 200 ml of ether and filtered to give 7.69 g of pure phenylmercuric chloride, m.p. 250–251.5°. The solid (2.95 g, m.p. 117–125°) obtained by concentration of the filtrate was fractionally recrystallized from ether to give 0.81 g of additional phenylmercuric chloride and 1.90 g of triethyltin acetate. Total yields of phenylmercuric chloride and triethyltin acetate were *ca.* 87% and 89%, respectively. (Considering the losses involved in this procedure, their actual yields will be more than 90%.)

SUMMARY

Aryltriethyltin compounds, $XC_6H_4SnEt_3$, reacted with mercuric acetate in tetrahydrofuran to give arylmercuric acetates and triethyltin acetate. Relative rates of aryl–tin cleavage in these compounds, obtained by competition reactions at 20°, are as follows: p-CH_3O, 8.30; p-CH_3, 1.76; p-Cl, 0.25; H, 1.00; m-CH_3, 1.21; m-CH_3O, 0.72; m-Cl, 0.029. Substituent effects are fairly related to the Hammett equation, $\log k_X/k_H = -3.5\,\sigma$. The results indicate that the reaction is an electrophilic replacement in which a benzenium ion-type intermediate does not participate in the rate-determining step.

REFERENCES

1 C. Eaborn and K. C. Pande, *J. Chem. Soc.*, (1960) 1566.
2 C. Eaborn and J. A. Waters, *J. Chem. Soc.*, (1961) 542.
3 R. W. Bott, C. Eaborn and J. A. Waters, *J. Chem. Soc.*, (1963) 681.
4 L. M. Stock and H. C. Brown, in V. Gold, *Advances in Physical Organic Chemistry*, Vol. 1, Academic Press Inc., London, 1963, p. 54.
5 Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc., Japan*, 32 (1959) 971.
6 C. Eaborn and K. C. Pande, *J. Chem. Soc.*, (1961) 297.
7 R. W. Bott, C. Eaborn and D. R. M. Walton, *J. Organometal. Chem.*, 1 (1964) 420.
8 R. A. Benkeser, T. V. Liston and C. M. Stanton, *Tetrahedron Letters*, (1960) (15) 1.
9 H. H. Huang and K. M. Hui, *J. Organometal. Chem.*, 2 (1964) 288.
10 H. Gilman and C. E. Arntzen, *J. Org. Chem.*, 15 (1950) 994.
11 J. Chatt and A. A. Williams, *J. Chem. Soc.*, (1954) 4403.
12 F. C. Whitmore, *Organic Compounds of Mercury*, Chemical Catalog Company, New York, 1921, p. 173 and p. 183.