Journal of Organometallic Chemistry, 64 (1974) 93 — 100

TRIFLUOROACETOLYSIS OF BENZYLTRIMETHYLSTANNANES

CHRISTOPHER J. MOORE*, MAXWELL L. BULLPITT and WILLIAM KITCHING**
Department of Chemistry, University of Queensland, Brisbane (Australia)
(Received May 1st, 1973)

Summary

The reactions of a series of *m*- and *p*-substituted benzyltrimethylstannanes with excess trifluoroacetic acid in benzene solvent have been studied. While the rate of disappearance of stannane is strictly first-order, both benzyl—tin and methyl—tin cleavages were occurring for the parent compound, as well as for substituted compounds, *m*- and *p*-Cl, *m*- and *p*-CF_3, *p*-CH_3 and *p*-OCH_3. From product analyses, the appropriate *k*-values could be factored from the overall pseudo first-order rate constant. For *m*-CH_3 and *m*-OCH_3, the rates were abnormally fast (for *m*-OCH_3 essentially instantaneous) and CH_3—Sn cleavage was not detected, indicating a change in mechanism. Evidence is presented that in these two cases, the strong concerted activating effects of —OCH_3 (and CH_3) and —$CH_2Sn(CH_3)_3$, when *m*-disposed, promotes attack at the ring. For the other substituents, relative rates are correlated satisfactorily with σ_n parameters, and there seems to be little resonance interaction with the ring, in the transition state.

Introduction

Recently we have reported features of the sulfur dioxide insertion reaction of organotin compounds [1], and noted that this reaction of benzylstannanes was poorly responsive to substituent effects [2]. Because the evidence generally indicated the SO_2 insertion into C—Sn bonds was an electrophilic substitution at carbon, it was desirable to know the effects substituents exert in an authentic electrophilic cleavage of benzylstannanes. Although Eaborn and Parker [3] and others [4] have examined the cleavage of benzyl—Si and benzyl—Sn systems, these employed basic conditions where attack at the metal to generate a carbanionic benzyl—C was likely. Essentially no data for

---

* Current address: London School of Pharmacy, Brunswick Sq., London, WC1.

** Address correspondence to this author at Department of Chemistry, Ohio State University, Columbus, Ohio 43210, (U.S.A.).

vigorous electrophiles such as strong acids or metal salts are available. To provide information of this type, we have examined kinetically the cleavage of benzyltrimethylstannanes by trifluoroacetic acid in benzene solvent.

Results and discussion

Preliminary investigations with I_2 and $HgCl_2$ as electrophiles indicated that an ^1H NMR kinetic method was not conveniently applicable, although it was clear that I_2 showed a strong preference for benzyl cleavage while $HgCl_2$ was not particularly discriminating. The same substrate (benzyltrimethylstannane) was cleaved by acetic acid far too slowly for convenience, but did react at a satisfactory rate in dichloroacetic acid (neat). The $(CH_3)_3Sn$ resonance diminished in a first-order fashion having $t_{1/2} \approx 60$ min at ambient probe temperature (ca. 33°). Both benzyl and methyl cleavage occurred as shown below where $X = -OCOCHCl_2$.

$$(CH_3)_3SnBz + HX(\text{excess}) \left\{ \begin{array}{l} \xrightarrow{k_1} (CH_3)_3SnX + C_6H_5CH_3 \\ \xrightarrow{k_2} (CH_3)_2(Bz)SnX + CH_4 \end{array} \right.$$

If the two pathways followed pseudo first-order kinetics the products from one pathway should remain in constant molar ratio to those from the other. However, the molar ratios of the dichloroacetates formed, changed during the reaction, and it was clear that a redistribution reaction was occurring*.

$$(CH_3)_3SnBz + (CH_3)_3SnOCOCHCl_2 \rightarrow (CH_3)_2(Bz)SnOCOCHCl_2 + (CH_3)_4Sn$$

(This was verified by addition of authentic samples for NMR examination.) Because this reaction interfered considerably this system was not pursued further, although we surmised that a less polar medium than dichloroacetic acid would suppress any redistribution phenomena.

We found that the reaction of CF_3COOH in benzene with the benzylstannanes (*ca.* 15-fold excess of acid was used) could be studied conveniently by the ^1H NMR technique. Although some slight changes in relative peak heights occurred [i.e. of $(CH_3)_3SnOCOCF_3$ and $(CH_3)_2(Bz)SnOCOCF_3$] no $(CH_3)_4Sn$ was detected, and nor did the consumption of $(CH_3)_3SnBz$ deviate from first-order kinetics. One reaction mixture was quenched as early as possible to allow measurement of product ratios.

For the scheme drawn above (where now $X = OCOCF_3$) the rate constant for consumption of stannane is $(k_1 + k_2)$ and the ratio $[(CH_3)_3SnOCOCF_3]/[(CH_3)_2(Bz)SnOCOCF_3] = k_1/k_2$. (The probability factor of 3 is included since methyl cleavage is three times as probable as benzyl cleavage.)

Results of the study are presented in Table 1.

---

[*] A small peak ascribable to $(CH_3)_2SnBz_2$ was also detected, presumably due to: $(CH_3)_3SnBz + (CH_3)_2(Bz)SnOCOCHCl_2 \rightarrow (CH_3)_3SnOCOCHCl_2 + (CH_3)_2SnBz_2$

TABLE 1

KINETICS OF CF_3COOH CLEAVAGE OF SUBSTITUTED BENZYLTRIMETHYLTINS

Substituent	Organotin conc.[a]	k_1[b]	k_2[c]	$k_{1(rel)}$
H	0.095	0.0073	0.0019	1
m-Cl	0.092	0.0019	0.0005	0.26
p-Cl	0.096	0.0022	0.0013	0.30
m-CF_3	0.096	0.0009	0.0013	0.123
p-CF_3	0.098	0.0007	0.0005	0.096
m-CH_3	0.094	0.1066		14.60
p-CH_3	0.099	0.0131	0.003	1.79
m-OMe	0.099	Instantaneous		
p-OMe	0.098	0.0077	0.0005	1.05

[a] Mole·litre^{-1}. [b] Refers to benzyl—tin cleavage. [c] Refers to methyl—tin cleavage. The first-order rate constants are in units of min^{-1} and are the average of two determinations which in each case were reproducible to within 5%. The probability factor of 3 has been applied to k_1 and k_2.

Regarding benzyl—tin cleavage (see k_1 and $k_{1(rel)}$ in Table 1) it is clear there is something superficially odd about the results for *m*-CH_3 and *m*-OCH_3 when considered alongside the results for *p*-CH_3 and *p*-OCH_3. This is made quite clear when $\log k_{(rel)}$ is plotted against σ_n (Fig. 1), where *m*-CH_3 deviates wildly from an otherwise orderly plot, while *m*-OCH_3 reacts so fast that no rate constant was obtainable and also would be well removed from the correlation line. For both these cases, cleavage of the benzyl group is exclusive. The reasons for this behaviour are discussed later in the paper.

From Fig. 1 it is seen that an acceptable linear free energy relation holds for *m*- and *p*-Cl, *m*- and *p*-CF_3, *p*-CH_3 and *p*-OCH_3, and substituents with larger (more positive) σ_n values are associated with a decreasing rate of

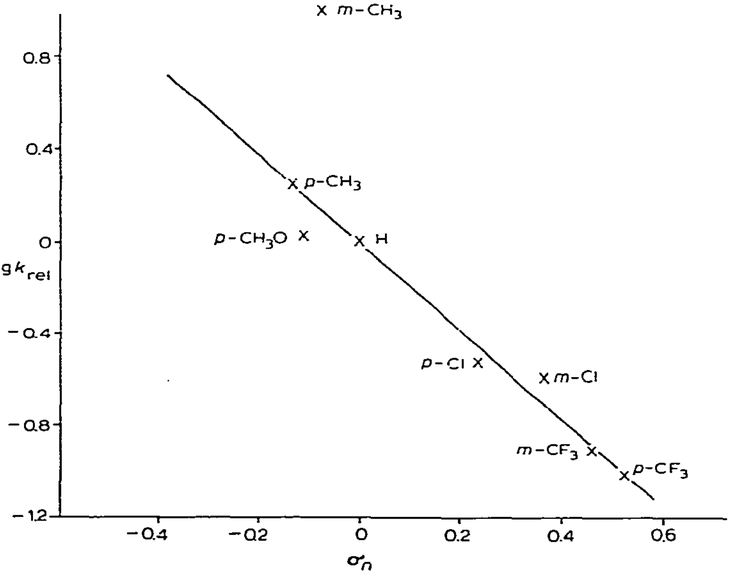
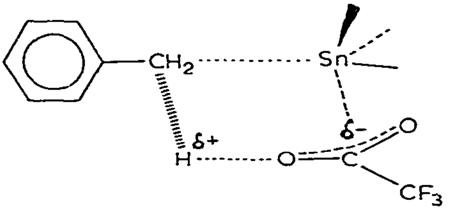


Fig. 1. Substituent effects: trifluoroacetolysis of *m*- and *p*-substituted benzyltrimethylstannanes. Log $k_{(rel)}$ vs. σ_n. Note the marked deviation for *m*-CH_3 and the point for *m*-OCH_3 is not accommodated by the scale due to its enhanced reactivity. (σ_n values from the compilation in ref. [11]).

benzyl—tin cleavage*. The ineffectiveness of *p*-OCH_3 to influence the cleavage indicates that direct resonance interaction between the benzyl carbon and the ring is unimportant. However the retarding effect of *m*- and *p*-CF_3 and Cl and the slight acceleration due to *p*-CH_3 is consistent with less negative character at the benzylic carbon in the transition state compared with the ground state. This would be in line with C—H bond formation being well advanced in the transition state. The poor ion-solvating ability of benzene probably means that molecular acid is involved with oxygen coordination to tin being rather important.



It is quite clear that not only is trifluoroacetolysis more sensitive to substituents than is SO_2 insertion, but that the natures of the transition states are in general dissimilar, exhibiting in the main the opposite type of dependence on substituent. This can be ascribed to the comparative weakness of SO_2 as an electrophile (compared with CF_3COOH) so that C—S bond formation is not pronounced in the transition state whereas C—H bond formation is. A consequence of this is that C—Sn rupture, without appreciable C—S bond formation, results in increased negative charge on the benzylic—C in the transition state, so that *p*-CF_3, for example, leads to a rate enhancement.

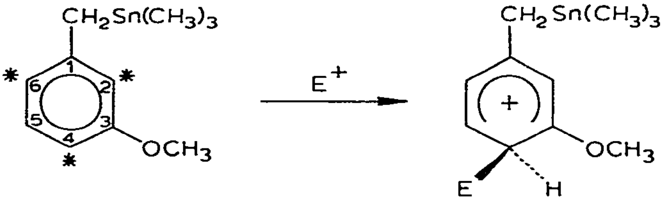
It was anticipated that as the electronegativity of the benzyl group altered, the rate of CH_3—Sn cleavage should also vary. This seems to be borne out by the data (k_2) in Table 1, with k_2 for *p*-CH_3 being greater, and k_2 for *p*-CF_3 being less than k_2 for the parent. The rate spread is not large, and it is unclear how well the Sn atom should transmit the effects of remote substituents. The very low k_2 value for the *p*-OCH_3 case is puzzling. In all cases, however, the rate of cleavage of the Sn—CH_3 bond (k_2) was much less than k_2 for cleavage of $(CH_3)_4Sn$ under the same conditions. This is presumably due to greater polarisation of the benzyl—tin bond, with relatively less negative charge on the CH_3—Sn carbon.

The failure of *m*-OCH_3 and *m*-CH_3 to conform to an otherwise satisfactory σ_n plot (because of their faster rates) seemed inexplicable by any modification of the mechanism appropriate for the other substrates, where CH_3—Sn and benzyl—Sn cleavage were competitive. (Benzyl—tin cleavage was exclusive for *m*-OCH_3 and *m*-CH_3). There was no reasonable precedent for supposing that the *m*-OCH_3 and *m*-CH_3 compounds should react much faster than their *para*-relatives, by essentially the same mechanism. It now seemed that initial electrophilic attack was occurring at a nuclear carbon, and not the C—Sn bond. Considering the strong electron-releasing effect of the — $CH_2Sn(CH_3)_3$ group, which would act in concert with other electron-releasing groups disposed *meta*

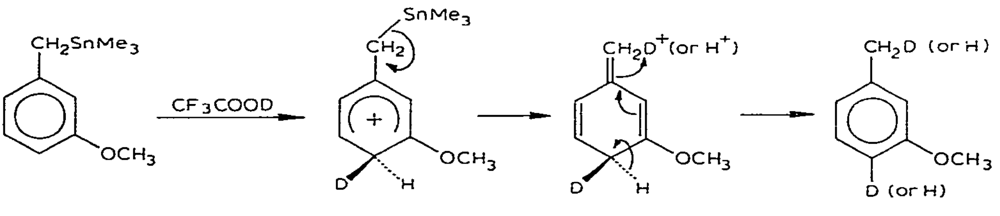
---

*Least squares treatment yields ρ = —1.70 and r = 0.984.

to it, it was clear that certain nuclear positions in (*m*-methoxybenzyl)trimethyltin, for example, should be highly prone to electrophilic attack. The positions marked (*) are in this category, since the intermediates or transition states at these positions are highly stabilised*, e.g.:



Experiments involving CF_3COOD in (C_6D_6) were then conducted to determine if nuclear attack was the initial step. Reaction of (*m*-methoxybenzyl)trimethyltin with *ca.* one molar equivalent of CF_3COOD (in C_6D_6 in a sealed NMR tube) was complete in about fifty minutes at ambient probe temperature, and the resonance positions of the product agreed with those for authentic *m*-methoxytoluene. [$(CH_3)_3SnOCOCF_3$ was also produced.] Careful integration of the spectrum established that the product contained 70% of $-CH_2D$ and 30% of $-CH_3$ groups (using the $-OCH_3$ signal as standard for 3H). If direct CH_2—Sn cleavage were occurring then 98 - 100% of CH_2D should be produced. This result indicated release of protium during the reaction and which subsequently was incorporated into the CH_3 group. The only conceivable source of such protium is nuclear, arising via aromatic H—D exchange. Mass spectrometric examination indicated the *m*-methoxytoluene to consist of 30% d_0, 50% d_1 and 20% d_2 species. Although the location of the deuterium in the d_1 species is not determined i.e. in CH_3 or ring, the mass and NMR spectral data are consistent only with significant deuterium incorporation in the ring**. These findings are consistent with a mechanism of the type shown in scheme 1.



SCHEME 1

These results for trifluoroacetolysis suggested that other electrophiles might prefer initial nuclear attack, and we have examined the brominolysis of (*m*-methoxybenzyl)trimethyltin in methanol to explore this possibility. Accor-

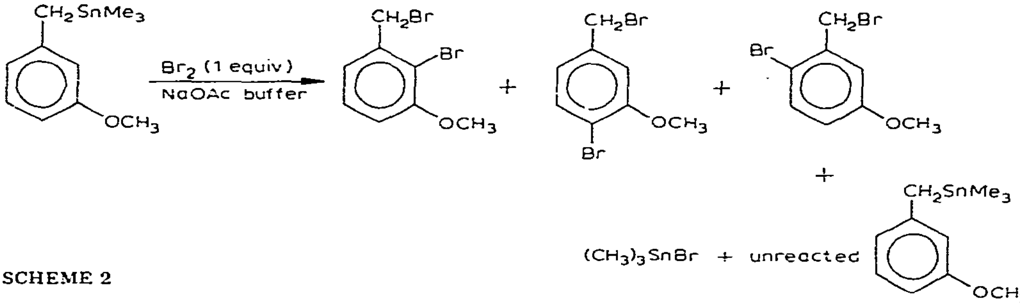
---

*Our ^{13}C NMR studies of *meta*-substituted benzyltrimethylstannanes indicate pronounced (ground-state) nuclear shielding for positions C_4 and C_6 (and to a lesser extent, C_2) with electron donating substituents [10]

** For example, even if the entire d_1 population had the deuterium in the CH_3 group, i.e. CH_2D, only one of the deuteriums in the d_2 species could be located in the CH_3 group to balance the NMR integrations of 30% CH_3 and 70% CH_2D. Hence at *least* 20% of the product has a ring—D. It seems unlikely that *none* of the d_1 species is ring-deuterated, since the fractionation would almost certainly favor such incorporation. There appears to be no plausible mechanism leading to incorporation of two deuteriums in the CH_3 group. Suitable checks (by mass spectrometry) for subsequent H—D exchange in *m*-methoxytoluene were conducted and found not to be a problem.

ding to the above scheme, two moles of bromine should be consumed per mole of tin substrate, with HBr, $(CH_3)_3SnBr$ and either 2-, 4-, or 6-bromo-3-methoxybenzyl bromide being the products. (This assumes no cleavage role for HBr.) Addition of one molar equivalent of bromine in methanol-d_4 to the tin compound in the same solvent (NMR tube) resulted in instantaneous disappearance of bromine and an immediate spectral scan showed some tin compound unreacted but this gradually disappeared. [The (residual) — OH resonance of the methanol-d_4 also sharpened and increased in intensity indicating production of an exchangeable acidic proton.] This second slower reaction was considered to be HBr cleavage of the unreacted tin substrate and separate experiments showed HBr did react at an appropriate rate to produce *m*-methoxytoluene. Under $NaOCOCH_3$-buffered conditions, only half of the original tin compound was consumed [using 1/1 molar ratio of (Sn)/(Br_2)], indicating consumption of two moles of bromine per mole of tin substrate*.

In the NMR spectrum three similarly shaped signals appeared in the δ 4.43 - 4.68 ppm region (the normal location for Aryl — CH_2—Br) indicating formation of different bromo-substituted 3-methoxybenzyl bromides**. Integration also indicated the loss of one aromatic proton and the complex, smeared appearance (≈1 ppm) of the aryl—H region could be rationalised only by the presence of a number of compounds. This region for the starting tin compound and authentic *m*-methoxybenzyl halides is quite characteristic (Scheme 2).



SCHEME 2

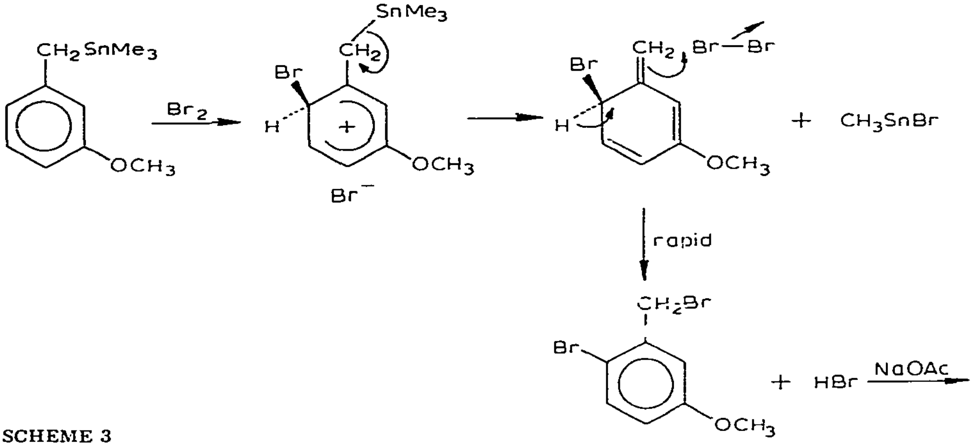
We account for these observations in Scheme 3, illustrating with one of the (three) possible nuclear positions.

Mechanisms closely related to the above have been proposed for certain reactions of other benzylmetallics by Reutov [5], Traylor [6] and Johnson [7]. While detailed experiments with (*m*-methylbenzyl)trimethyltin were not conducted, it appears completely reasonable that similar mechanisms account for the otherwise unreasonably fast trifluoroacetolysis of this compound. With strong electron-withdrawing groups e.g. CF_3 disposed *meta* to $-CH_2SnMe_3$ the overall carbonium ion stabilising ability of the ring system is sufficiently reduced that direct cleavage of the CH_2Sn bond occurs. In some respects, these

---

*Note that this stoichiometry is inconsistent with a predominantly direct Br_2 cleavage of the CH_2—Sn bond.

**Another uncharacteristically broad signal (of lower intensity) was also observed but its shape was not consistent with a Ar—CH_2—Br resonance.



SCHEME 3

results are a further manifestation of the strong hyperconjugative electron-releasing ability of the CH_2Sn group [8] *.

Experimental

Organotin compounds

The substituted benzyltrimethylstannanes have been described previously [1].

Kinetics

1 ml of a 1.504 *M* stock solution of CF_3COOH in benzene, pre-equilibrated at 32°, was injected into an NMR tube containing a known weight of the organotin compound (approximately 0.0001 mole), the tube sealed with a serum cap, the contents well mixed and the tube inserted into the probe of the JEOL MH-100 NMR spectrometer. (Probe temperature 32 ± 1°.) The solution so prepared was *ca.* 0.1 *M* in tin substrate and contained a 15-fold excess of acid.

The reaction mixtures containing organotins with $t_{1/2} > 100$ min (*m*- and *p*-CF_3, *m*- and *p*-Cl) were placed in a constant temperature bath and transferred to the spectrometer probe periodically. The other runs were conducted with the tube in the probe for the duration of the run.

Peak height measurements were taken at regular intervals, depending on the rate of the reaction. Three or four height measurements of the $(CH_3)_3Sn$ resonance were made at each observation, and the average height calculated. To minimise the effects of changes in the state of tuning of the instrument during a run, the peak height of an external TMS standard or internal cyclohexane was monitored and to which the $(CH_3)_3Sn$ resonance was referred.

Plots of $\log_{10}$ (peak height) vs. time were then obtained and first order rate constants calculated.

---

[*] For related observations in this general area see ref. [9]

Reaction products

The NMR spectra of the substituted toluenes agreed with spectra of authentic samples.

Trimethyltin trifluoroacetate was prepared by reaction of Me_3SnCl and $AgOCOCF_3$ in ethanol. The product was sublimed. (Found: C, 21.35; H, 3.27. Calcd.: C, 21.66; H, 3.25%.) M.p. 121 - 123°; ν(C—O) 1620 cm^{-1}.

Acknowledgements

The authors are grateful to the Australian Research Grants Committee for financing part of this work. Helpful discussions with Dr. M. McCamish are acknowledged.

References

1 C.J. Moore and W. Kitching, J. Organometal. Chem., 59 (1973) 225.
2 W. Kitching and C.W. Fong, Organometal. Chem. Rev., 5 (1970) 281.
3 C. Eaborn and S.H. Parker, J. Chem. Soc., (1955) 126.
4 R. Alexander, C. Eaborn and T.G. Traylor, J. Organometal. Chem., 21 (1970) 65.
5 Yu.G. Bundel, N.D. Antonova and O.A. Reutov, Dokl. Akad. Nauk SSSR, 166 (1966) 1103.
6 W. Hanstein and T.G. Traylor, Tetrahedron Lett., 45 (1967) 4451.
7 S.N. Anderson, D.H. Ballard and M.D. Johnson, J. Chem. Soc. D, (1971) 779.
8 See, for example, W. Hanstein, H.J. Berwin and T.G. Traylor, J. Amer. Chem. Soc., 92 (1970) 7476.
9 C. Eaborn and G.J. Wright, J. Chem. Soc. B, (1971) 2262.
10 D. Doddrell, M. Bullpitt, C.J. Moore, W. Kitching, W. Adcock and B.D. Gupta, Tetrahedron Lett., (1973) 665.
11 P.R. Wells, Linear Free Energy Relationships, Academic Press, 1968, p. 14 - 15.