RELATIVE ELECTRON-RELEASING EFFECTS OF TRIMETHYL-SILYL, -GERMYL, AND -STANNYL GROUPS

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INTRODUCTION

Because of the uncertainty about the relative electronegativities of the Group IVB elements[1], the rates of cleavage by aqueous-methanolic perchloric acid of the aryl-silicon bonds were measured for p-$Me_3M-CH_2-C_6H_4-SiMe_3$ compounds in which $M = Si$ and Ge, and it was found that the compound containing germanium was more reactive than that containing silicon, indicating that the trimethylgermyl group releases electrons more strongly than the trimethylsilyl group[2]. (Aspects of the infrared spectra of $Me_3M-O-CO-Me$ compounds indicate the same order[3].) Information could not be obtained about the trimethylstannyl group because with the compound p-$Me_3Sn-CH_2-C_6H_4-SiMe_3$ the benzyl-tin bond was cleaved more rapidly than the aryl-silicon bond. To remedy this omission, we have measured the rates of cleavage of the aryl-tin bonds of the compounds p-$Me_3M-CH_2-C_6H_4-SnMe_3$ in which $M = Si$, Ge, and Sn; the benzyl-tin bond is stable at the low acid concentrations involved.

RESULTS AND DISCUSSION

The results are shown in the table as pseudo first-order rate constants, k_1, and as relative rates; the strength of the acid shown is that of the aqueous acid before mixing.

TABLE

CLEAVAGE OF $Me_3M-CH_2-C_6H_4-SnMe_3$ COMPOUNDS BY A MIXTURE OF METHANOL (5 VOL.) AND AQUEOUS PERCHLORIC ACID (2 VOL.) AT 30.25°

M	$10^2[HClO_4]$ *(M)*	10^2k_1 *(min^{-1})*	*Rel. Rate*	*M*	$10^2[HClO_4]$ *(M)*	10^2k_1 *(min^{-1})*	*Rel. Rate*
Si	2.10	56	1.00	Si	1.07	34	1.00
Ge	2.10	76	1.36	Ge	1.07	46	1.35
Sn	2.10	180	3.21	Sn	1.07	109	3.21

The order of reactivity is (M =) Sn > Ge > Si, and so the order of electron release to the reaction centre is $Me_3Sn > Me_3Ge > Me_3Si$. The difference between the effects of the trimethyl-germyl and -silyl groups is smaller than in cleavage of

$Me_3M{-}CH_2{-}C_6H_4{-}SiMe_3$ compounds[2], in keeping with the generally smaller spread of rates in protodestannylation than in protodesilylation (*e.g.*, $f_p^{Me} = 5.4$, in the former[4], and 21 in the latter[5] reaction).

It was previously assumed that the magnitude of the electron release to the aromatic ring by a $Me_3M{-}CH_2$ group was a measure of the inductive release of electrons by the Me_3M group to a saturated carbon atom[2]. It is not, however, unambiguously so, since there is a possibility of some interaction between the p_π electrons of the ring and the *d*-orbitals of the metal atom, the overall electron release towards the ring representing the difference between inductive supply of electrons and return of them by the $p_\pi{-}d_\pi$ bonding. Such bonding would be analogous to the $d_\pi{-}p_\pi$ bonding suggested to occur between silicon and a halogen or oxygen atom on a carbon atom adjacent to the silicon[6]. If there is interaction between the metal atom and the p_π-orbital of the 1-carbon atom of the ring it must, of course, be small, since the $Me_3M{-}CH_2$ groups are strongly electron releasing groups (markedly more so than the methyl group itself), and in our opinion its variation from metal to metal is unlikely to reverse the trend set by the inductive release of electrons, which we thus believe to increase in the order $Me_3Si < Me_3Ge < Me_3Sn$*.

(*p*-Trimethylstannylbenzyl)trimethylstannane was made from the Grignard reagent obtained in tetrahydrofuran from (*p*-bromobenzyl)trimethylstannane (which was itself made from trimethylstannyllithium[8] and *p*-bromobenzyl bromide in the same solvent). Attempts to make it from (*p*-chlorobenzyl)trimethylstannane were unsuccessful, and some of them confirmed the ease with which the benzyl–tin bond is cleaved by organolithium reagents (*cf.* ref. 9) or lithium. For example, the chloride reacted readily with lithium in tetrahydrofuran, and when the resulting mixture was hydrolysed, *p*-chlorotoluene was obtained in good yield, but when bromotrimethylstannane was added before the hydrolysis, hexamethyldistannane was obtained in good yield and most of the (*p*-chlorobenzyl)trimethylstannane was recovered. The reactions involved appear to be those in equations (1)–(4).

$$p\text{-}Cl{-}C_6H_4{-}CH_2{-}SnMe_3 + 2Li \longrightarrow p\text{-}Cl{-}C_6H_4{-}CH_2{-}Li + Me_3SnLi \qquad (1)$$

$$p\text{-}Cl{-}C_6H_4{-}CH_2{-}Li + Me_3SnBr \longrightarrow p\text{-}Cl{-}C_6H_4{-}CH_2{-}SnMe_3 + LiBr \qquad (2)$$

$$Me_3SnLi + Me_3SnBr \longrightarrow Me_3Sn{-}SnMe_3 + LiBr \qquad (3)$$

$$p\text{-}Cl{-}C_6H_4{-}CH_2{-}Li + H_2O \longrightarrow p\text{-}Cl{-}C_6H_4{-}CH_3 + LiOH \qquad (4)$$

Again, when (*p*-chlorobenzyl)trimethylstannane was treated with *n*-butyllithium in ether and the mixture hydrolysed, *p*-chlorotoluene and *n*-butyltrimethylstannane were obtained in approximately equimolar proportions.

Such cleavages account for the failures[2] to prepare (*p*-carboxybenzyl)trimethylstannane from the *p*-chloro-compound via the *p*-lithio-compound.

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* It is not known with certainty how the ease of $d\pi{-}p\pi$ bonding varies for tetrahedrally-bonded silicon, germanium, and tin, but there is evidence that it falls from silicon to germanium in the anions derived from $Me_3M{-}Ph$ compounds[7].

EXPERIMENTAL

Trimethyl(p-trimethylstannylbenzyl)germane

Bromotrimethylstannane (5.4 g, 0.022 mole) was refluxed for 2 h, with the organolithium reagent from (*p*-chlorobenzyl)trimethylgermane[10] (5.4 g, 0.022 mole) and lithium (0.70 g, 0.10 g-atom) in ether (200 ml). Treatment with saturated aqueous ammonium chloride, followed by separation, drying, and fractionation of the ethereal layer gave trimethyl(*p*-trimethylstannylbenzyl)germane (1.2 g, 15 %), b.p. 114–115°/2.4 mm, n_D^{25} 1.5278. (Found: C, 41.9; H, 6.7. $C_{13}H_{24}GeSn$ calcd.: C, 42.0; H, 6.5%.) and unchanged (*p*-chlorobenzyl)trimethylgermane (2.8 g, 52 %).

(p-Bromobenzyl)trimethylstannane

A little (*ca.* 2 ml) of a solution of bromotrimethylstannane (30 g, 0.123 mole) in tetrahydrofuran (50 ml) was added to lithium shot (2.1 g, 0.30 g-atom) in the same solvent (80 ml), the mixture becoming warm and dark red. The remaining bromotrimethylstannane solution was added with stirring during 30 min, the temperature of the mixture being kept at about —10°. After a further 10 min stirring, the solution was filtered under nitrogen through glass wool. The yield of trimethylstannyllithium was 73 % (by titration).

p-Bromobenzyl bromide (5.0 g, 0.020 mole) in tetrahydrofuran (80 ml) was added during 10 min to a solution of trimethylstannyllithium (0.022 mole) in the same solvent (40 ml). The mixture was warmed on a water bath for 10 min then treated with aqueous ammonium chloride. Ether extraction, followed by washing, drying (Na_2SO_4), and fractionation of the ethereal layer gave (*p*-bromobenzyl)trimethylstannane (6.0 g, 89 %), b.p. 99°/1.5 mm (lit.[2] b.p. 126°/6 mm), n_D^{25} 1.5770.

Trimethyl(p-trimethylstannylbenzyl)stannane

(*p*-Bromobenzyl)trimethylstannane (16.7 g, 0.05 mole) was brought into reaction with magnesium turnings (1.94 g, 0.08 g-atom) in tetrahydrofuran (40 ml) containing ethyl bromide (*ca.* 0.5 ml). Bromotrimethylstannane (14.6 g, 0.060 mole) in tetrahydrofuran (20 ml) was added, and the mixture was refluxed for 15 min, then cooled and worked up in the usual way to give trimethyl(*p*-trimethylstannylbenzyl)stannane (6.7 g, 64 %), b.p. 98–100°/0.04 mm, n_D^{25} 1.5550. (Found: C, 37.7; H, 5.8. $C_{13}H_{24}Sn_2$ calcd.: C, 37.4; H, 5.8 %.)

Attempted preparation of trimethyl(p-trimethylstannylbenzyl)stannane from (p-chlorobenzyl)trimethylstannane

(*i*) Most of the *p*-chlorobenzyl chloride was recovered from attempts to couple it with bromotrimethylstannane via a Wurtz-Fittig reaction with sodium in boiling light petroleum (b.p. 60–80°) or toluene, or via a Grignard reagent in tetrahydrofuran.

(*ii*) An exothermic reaction occurred when (*p*-chlorobenzyl)trimethylstannane (72 g, 0.25 mole) was added to lithium shot (4.1 g, 0.60 g-atom) in tetrahydrofuran (150 ml) at 0°. The mixture was halved; one half was treated with aqueous ammonium chloride, and the usual working-up (involving ether extraction) gave *p*-chlorotoluene (12.7 g, 0.11 mole, 88 %). The other half was boiled for 10 min with bromotrimethylstannane before the hydrolysis, and the usual working-up gave hexamethyldistannane (33 g, 0.10 mole, 80%), and (*p*-chlorobenzyl)trimethylstannane (34.6 g, 0.12 mole, 96%).

(*iii*) A mixture of *n*-butyllithium (0.10 mole) and (*p*-chlorobenzyl)trimethylstannane (28.8 g, 0.10 mole) in ether (130 ml) was stirred for 2 h at room temperature. The usual working-up gave unchanged (*p*-chlorobenzyl)trimethylstannane (8.2 g, 28 %) and material (16 g) of b.p. 150–164°, which was shown by vapour-phase chromatography to be an approximately equimolar mixture of *p*-chlorotoluene and *n*-butyltrimethylstannane.

Rate studies

A methanolic solution (5 ml) of the p-Me_3M–CH_2–C_6H_4–$SnMe_3$ compound [10^4 × concn.: (M =) Si, 13; Ge, 12; Sn, 7 *M*] was mixed with 2 ml of aqueous perchloric acid of the strength specified in the Table. Rate measurements were determined spectrophotometrically at 30.25° ± 0.02° by the method previously described[4,5], "infinity" values being measured on the reaction mixture after 10 half-lives. The wave-lengths employed were (M =) Si, 278.5; Ge, 256; Sn, 272 mμ.

Products

With trimethyl(*p*-trimethylstannylbenzyl)stannane there was a slight possibility that cleavage of the benzyl–Sn might accompany cleavage of the aryl–Sn bond, but the ultra-violet spectrum of the reaction mixture after 10 half-lives was identical with that of a solution of benzyltrimethylstannane. A small-scale preparative cleavage was carried out with stronger acid than used for rate studies. A solution of trimethyl(*p*-trimethylstannylbenzyl)stannane (5.0 g) in methanol (80 ml) was mixed with 1.0 *M* aqueous perchloric acid (20 ml); the mixture was warmed on a water bath for 12 min, and then added to an excess of saturated aqueous ammonium chloride. Ether extraction, followed by washing, drying (Na_2SO_4) and fractionation of the extract gave benzyltrimethylstannane (3.4 g, 71 %), b.p. 96°/1.1 mm, n_D^{25} 1.5420. No toluene or trimethyl-*p*-tolylstannane was detected.

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SUMMARY

The rates of cleavage of the aryl–tin bond of p-Me_3M–CH_2–C_6H_4–$SnMe_3$ compounds by aqueous methanolic perchloric acid increases in the order (M =) Si < Ge < Sn, which means that electron release by the Me_3M groups also increases in this order.

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