THE RELATIVE ELECTRON-RELEASING POWER OF TRIMETHYLSILYL AND *tert*-BUTYL GROUPS

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INTRODUCTION

The relative basicities of the amines $Me_3MCH_2NH_2$ and acidities of the carboxylic acids Me_3MCH_2COOH ($M = C, Si$) indicate that a trimethylsilyl groups releases electrons more strongly than a *tert*-butyl group[1], but the exact significance of the figures is uncertain because of steric effects arising from the proximity of comparatively bulky groups to the reaction centre. To obtain information concerning the relative inductive electron release of trimethylsilyl and *tert*-butyl groups free from such steric effects, we have measured the rates of cleavage of the aryl–silicon bonds in the compounds *m*- and *p*-$(Me_3MCH_2)C_6H_4SiMe_3$, where $M = C$ and Si, a method used previously for comparing the electron-releasing ability of Me_3Si, Me_3Ge and Me_3Sn groups[2,3].

RESULTS AND DISCUSSION

Table 1 lists pseudo first-order rate constants, k_1, derived relative rates, k_{rel}, and the strengths of the (added aqueous) acid used. Data for substituents other than (trimethylsilyl)methyl and neopentyl are included for comparison.

TABLE 1

CLEAVAGE OF $XC_6H_4SiMe_3$ COMPOUNDS BY A MIXTURE OF METHANOL (5 VOL) AND AQUEOUS PERCHLORIC ACID (2 VOL) AT 50.0°

X	*$HClO_4$ (M)*	*10^3k_1 (min^{-1})*	k_{rel}	*X*	*$HClO_4$ (M)*	*10^3k_1 (min^{-1})*	k_{rel}
p-Me	12.4	162	21.5	H	12.4	7.55	1.0
	9.4	36.2	—	*p*-*tert*-$BuCH_2$	9.4	34.8	20.7
	7.6	13.9	—		7.6	13.4	20.7
m-Me	12.4	17.3	2.29	*p*-Me_3SiCH_2	7.6	213	330
m-*tert*-$BuCH_2$	12.4	30.6	4.05	*m*-Me_3SiCH_2			6.2[a]

[a] Ref. 9.

The (trimethylsilyl)methyl substituent accelerates the cleavage much more from the *para*-position than does the neopentyl substituent, as would be expected from the relative electronegativities of carbon and silicon. The reactivity ratios

p-[Me_3SiCH_2/Me_3CCH_2] = 15.9 and p-[Me_3GeCH_2/Me_3SiCH_2] = 1.7 (ref. 2), obtained under similar conditions, are consistent with differences in electronegativity on the Pauling scale[4], *viz*:

$$C(2.5) — Si(1.8) = 0.7$$
$$Si(1.8) — Ge(1.7) = 0.1$$

Attention has been drawn to the possibility of d_π–p_π bonding between vacant silicon d-orbitals and the p_π-orbital on the 1-carbon of the aromatic ring, which would tend to reduce the overall electron-releasing power of an Me_3SiCH_2 substituent[3]. That this substituent releases electrons so much more effectively than the neopentyl group (in which such bonding is impossible) from the *meta*- as well as from the *para*-position indicates that the effect is probably small.

The methyl substituent releases electrons slightly more effectively from the *para*-, but less effectively from the *meta*-position than the neopentyl substituent. A similar order of *para*-activation has been observed in the solvolysis of benzhydryl chlorides in aqueous acetone[5] and in the bromination of alkylbenzenes in aqueous acetic acid[6]. The order of electron release, $Me_3CCH_2 > Me$, applies for both *meta*- and *para*-groups in the ionisation of substituted trityl chlorides in liquid sulphur dioxide[7].

It is of interest to note the value of the ratio [$\log k_{rel}(p\text{-}Me_3SiCH_2)$]/$\log k_{rel}$-($p$-Me)], *viz*., 1.9, is not very different from that of the ratio [$\log k_{rel}(m\text{-}Me_3SiCH_2)$]/[$\log k_{rel}(m\text{-}Me)$], *viz*., 2.2. In other words, replacing one of the hydrogen atoms of the Me group by a Me_3Si group has a similar fractional effect on the substituent constant for *meta*- and *para*-groups [$\sigma(p\text{-}Me_3SiCH_2) = \sigma(p\text{-}Me) + 0.9\ \sigma(p\text{-}Me)$; $\sigma(m\text{-}Me_3SiCH_2) = \sigma(m\text{-}Me) + 1.2\ \sigma(m\text{-}Me)$]. Similar replacement of a hydrogen atom of the Me group by a Me_3C group also has quite a large accelerating effect when the *meta*-position is involved, the value of [$\log k_{rel}(m\text{-}Me_3CCH_2)$]/[$\log k_{rel}(m\text{-}Me)$] being 1.68, and if a similar factor applied to the *para*-substituents a value of *ca*. 170 would be expected for $k_{rel}(p\text{-}Me_3CCH_2)$, which contrasts sharply with the observed value of 20.7. It may be that the inductive influence of the Me_3C group in Me_3CCH_2 in the *para*-position is more than outweighed by the reduction in the hyperconjugative effect arising from replacement of one of the C–H bonds of the p-Me group. The relative activating effects of p-Me and p-*tert*-Bu, on the one hand and m-Me and m-*tert*-Bu on the other, present, of course, a similar unsolved problem[8].

EXPERIMENTAL

m- and p-Bromopropiophenones

The *meta*-isomer was prepared by brominating propiophenone in the presence of aluminium chloride[12] and the *para*-isomer by Friedel-Crafts acylation of bromobenzene in carbon disulphide.

Successive side-chain methylations of the bromopropiophenones by treatment with freshly prepared sodamide in toluene followed by methyl iodide according to Tsatsas[10] afforded bromophenyl isopropyl ketones: *meta*-isomer*, b.p. 91°/0.8 mm,

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* New compound.

n_D^{25} 1.5519 (Found: C, 53.05; H, 4.9. $C_{10}H_{11}BrO$ calcd.: C, 52.9; H, 4.9%); *para*-isomer, b.p. 96–98°/1.2–1.5 mm, n_D^{25} 1.5592; and bromopivalophenones: *meta*-isomer*, b.p. 98°/1.6 mm, n_D^{25} 1.5438 (Found: C, 54.7; H, 5.35. $C_{11}H_{13}BrO$ calcd.: C, 54.8; H, 5.4%); *para*-isomer, b.p. 98–100°/1.0 mm, n_D^{25} 1.5430 (lit.[7] b.p. 108–111°/3 mm, n_D^{24} 1.5440). Yields of 60–70% were obtained at each methylation stage.

m- and p-Bromoneopentylbenzene

Wolff-Kishner reduction of the bromopivalophenones by the Huang-Minlon modification[11] afforded *ca.* 60% yields of bromoneopentylbenzenes: *meta*-isomer, b.p. 71°/1.2 mm, n_D^{25} 1.5210 (lit.[7] b.p. 80–81°/2 mm, n_D^{25} 1.5232); *para*-isomer, b.p. 70–71°/0.9 mm, n_D^{25} 1.5238 (lit.[7] b.p. 96–98°/3 mm, n_D^{25} 1.5240).

*Trimethyl(m-neopentylphenyl)silane**

m-Neopentylphenyllithium, prepared by briefly refluxing *m*-bromoneopentylbenzene (9.1 g, 0.04 mole) in ether (20 ml) with *n*-butyllithium (0.044 mole, Lithium Corporation, 1.67 *M* solution in hexane) was treated with chlorotrimethylsilane (5.5 g, 0.05 mole) in ether (20 ml). After 20 min refluxing, the reaction mixture was cooled and hydrolysed with saturated aqueous ammonium chloride. The organic layer was separated, dried and fractionated to give trimethyl(*m*-neopentylphenyl)silane (6.2 g, 70%), b.p. 80°/2.0 mm, n_D^{25} 1.4852. (Found: C, 76.3; H, 11.1. $C_{14}H_{24}Si$ calcd.: C, 76.3; H, 11.0%.)

*Trimethyl(p-neopentylphenyl)silane**

The product (4.3 g) prepared by an identical cross-metallation of *p*-bromoneopentylbenzene (5.0 g, 0.022 mole) with *n*-butyllithium (0.024 mole) followed by treatment with chlorotrimethylsilane (0.03 mole) contained traces of impurity, probably unreacted bromoneopentylbenzene. This was removed by boiling with lithium (2 g, Lithium Corporation 50% dispersion in hexane) in ether (30 ml) for 20 min. Excess lithium was filtered off, the reaction mixture was hydrolysed and worked up as above to give trimethyl(*p*-neopentylphenyl)silane (3.9 g, 80%) b.p. 70°/1.2 mm, n_D^{25} 1.4876. (Found: C, 76.2; H, 10.9%.)

Rate studies

The cleavage of arylsilicon bonds in the compounds $XC_6H_4SiMe_3$ was followed spectrophotometrically at 50.0° and at suitable wavelengths listed in Table 2, by the method described previously[9]. Rate measurements were made in a mixture of a methanolic solution (5 vol) of the organosilicon compound of concentration given in Table 2, and aqueous perchloric acid (2 vol) of strength specified in Table 1. In the case of the unsubstituted compound, sealed tubes (reaction samples) were used for *infinity* readings (10 half-lives).

Cleavage products

A mixture of trimethyl(*m*-neopentylphenyl)silane (6.0 g) methanol (100 ml) and 12.4 *M* aqueous perchloric acid (40 ml) was refluxed for 4 h. The reaction mixture was cooled, hydrolysed and neutralised with sodium bicarbonate. The organic material

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* New compound.

TABLE 2

CONCENTRATION OF SILANE IN METHANOL AND WAVELENGTH USED IN RATE STUDIES

X	*10^3 Concn.* (*M*)	λ (*mμ*)
p-Me	7.2	273
p-tert-$BuCH_2$	2.4	272
m-tert-$BuCH_2$	0.3	274.5
p-Me_3SiCH_2	1.2	248
m-Me	10	270
H	4.3	264

was extracted with ether, and the ether extracts dried and distilled to give neopentylbenzene (2.9 g, 77 %) b.p. 183–184°, n_D^{25} 1.4855.

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SUMMARY

The compounds *m*- and *p*-$(Me_3CCH_2)C_6H_4SiMe_3$ have been synthesized, and the rates of their cleavage by aqueous-methanolic perchloric acid have been measured and compared with those of the corresponding *m*- and *p*-$(Me_3SiCH_2)C_6H_4SiMe_3$ compounds. The results show that the inductive release of electrons to a saturated carbon atom is markedly greater for the Me_3Si than for the Me_3C group.

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