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THE ELECTRON-RELEASING EFFECTS OF MONO-, BIS-, AND TRIS-(TRIMETHYLSILYL)METHYL GROUPS. THE IMPORTANCE OF HYPERCONJUGATION IN THE ELECTRONIC EFFECTS OF α-METALLOALKYL GROUPS

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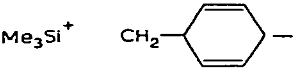
SUMMARY

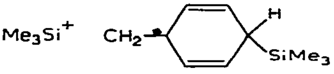
The rates of cleavage of the aryl–Si bonds in $(Me_3Si)_xCH_{3-x}C_6H_4SiMe_3$ compounds by aqueous methanolic perchloric acid, and thus the electron release by the $(Me_3Si)_xCH_{3-x}$ groups, increase in the order $x=0<3<1<2$ for both the *m*- and *p*-compounds. The ^{19}F chemical shifts in the *p*-$(Me_3Si)_3CH_{3-x}C_6H_4F$ compounds indicate the same order of electron release. This order is not consistent with attribution of effects of the $(Me_3Si)_xCH_{3-x}$ groups entirely or even primarily to inductive release of electrons by the Me_3Si groups, but is consistent with hyperconjugative release of electrons from the Me_3Si–C bond.

INTRODUCTION

In 1956 one of us drew attention to the large electron releasing ability of the Me_3SiCH_2 group in comparison with that of the CH_3 group, as revealed by the ease of acid cleavage of appropriate $XC_6H_4SiMe_3$ compounds, an electrophilic aromatic substitution which is markedly facilitated by electron release from X. It was suggested that in addition to any inductive release of electrons to carbon by the Me_3Si group, there was also hyperconjugative release of electrons from the Me_3Si–CH_2 bond, represented by structures such as (I) for a ground state and by structures such as (II)



(I)



(II)

for a Wheland intermediate. More recently, even greater electron-releasing effects have been observed for other metallomethyl groups in electrophilic aromatic substitutions and related reactions[2], and have been attributed mainly to hyperconjugation by the M–CH_2 bonds such as we previously postulated*. Powerful electron release by Me_3SiCH_2 and related groups has also been revealed by spectroscopic studies of appropriately substituted ethylenes and benzenes (see below)[4–6].

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* Hyperconjugation involving C–M bonds seems first to have been suggested for β-mercuriketones[3].

In an attempt to throw more light on the nature of the electron release from the $Me_3Si{-}C$ bond we have studied the effect of Me_3SiCH_2, $(Me_3Si)_2CH$, and $(Me_3Si)_3C$ groups on the ease of electrophilic attack at the *meta*- and *para*-positions of the aromatic ring (involving spectrophotometric measurement of the rates of acid cleavage of appropriate $XC_6H_4SiMe_3$ compounds) and on the ^{19}F chemical shift in $p\text{-}XC_6H_4\text{-}^{19}F$ compounds. In the cleavage, effects on a transition state are largely involved[7], while the chemical shifts reflect ground state polarization[8,9].

RESULTS AND DISCUSSION

The results of the cleavage study are presented in Table 1, which for each $XC_6H_4SiMe_3$ compound lists the wave-length used, the acid concentration, the observed first-order rate constant, k, and the rate, k_{rel}, relative to that of the parent phenyltrimethylsilane. The values, $\delta(p\text{-}^{19}F)$, of the chemical shifts (measured in carbon tetrachloride) of the $p\text{-}XC_6H_4{}^{19}F$ compound relative to that in fluorobenzene are shown in Table 2.

The results of the cleavage studies indicate an electron-releasing order of $(Me_3Si)_2CH > Me_3SiCH_2 > (Me_3Si)_3C > H_3C$ for both *m*- and *p*-groups, and the ^{19}F studies indicate the same order for the *p*-groups. Such an order is not consistent with attribution of the effect of replacing H–C by $Me_3Si{-}C$ bonds primarily or

TABLE 1

CLEAVAGE OF $X{-}C_6H_4{-}SiMe_3$ COMPOUNDS IN AQUEOUS-METHANOLIC PERCHLORIC ACID AT 50.0°

X	$[HClO_4]^a$ (M)	λ^b (mμ)	10^3k (min^{-1})	k_{rel}
H	12.1	231	8.05	1.0
m-Me	12.1	277	19.5	2.4
m-CH_2SiMe_3	12.1	283	52	6.5
m-$CH(SiMe_3)_2$	12.1	284	67.5	8.4
m-$C(SiMe_3)_3$	12.1	283.3	27.5	3.4
p-Me	12.1	273	170	21
	4.7	273	3.10	
p-CH_2SiMe_3	4.7	280	41.5	280
	7.5	280	250	
p-$CH(SiMe_3)_2$	4.7	281	98.5	670
p-$C(SiMe_3)_3$	7.5	252	175	200

[a] Concn. of aqueous perchloric acid, 2 vol. of which was mixed with 5 vol. of a methanolic solution of the organosilane. [b] Wavelength at which the rate was measured.

TABLE 2

^{19}F CHEMICAL SHIFTS IN $p\text{-}XC_6H_4F$ COMPOUNDS

X	$\delta(p\text{-}^{19}F)$	X	$\delta(p\text{-}^{19}F)$
H	0.00	$CH(SiMe_3)_2$	7.47
CH_3	5.34	$C(SiMe_3)_3$	6.93
CH_2SiMe_3	7.06		

entirely to an electron-releasing inductive influence of the Me_3Si group, since successive replacements would be expected to bring about progressive increase in the overall electron-release of the $(Me_3Si)_xH_{3-x}C$ group, although the effects of additional Me_3Si groups might be less than expected for simple additivity. The relatively low rate of cleavage of the $(Me_3Si)_3CC_6H_4SiMe_3$ compound could, in isolation, be plausibly attributed to steric hindrance to solvation by the bulky $(Me_3Si)_3C$ group, but this must be rejected as the explanation because it cannot be applied to the parallel results of the NMR studies.

The value of k_{rel} for the p-$Me_3SiCH_2C_6H_4SiMe_3$ compound is in agreement with that, *viz.* 270, reported in one earlier study[10], and somewhat smaller than that, *viz.* 315, reported in the first study[1]. The last value has been used to derive a value of -0.62 for σ^+-constant of the p-Me_3SiCH_2 group[11], and the quite large magnitude of the difference $(\sigma^+ - \sigma)$, *viz.* -0.41, is a good indication of a substantial electron-releasing resonance effect. The corresponding difference for the p-OMe group, which has a large resonance effect, is little greater, *viz.* -0.51, while that for the p-Me group, which is normally regarded as having a substantial electron-releasing hyperconjugative ability, is markedly smaller, *viz.* -0.14. For the Me_3SiCH_2 group this resonance component is most simply associated with hyperconjugation from the Me_3Si–CH_2 bond[1]. If the effect of replacing a H–C by a Me_3Si–C bond lay wholly in the change in hyperconjugative ability, the large effect of the first such replacement, to give the Me_3SiCH_2 group, would be followed by a markedly smaller effect of the second such replacement, since only one of the Me_3Si–C bonds can be in a position for maximum overlap with the p_π-orbitals of the ring[12]; the configuration for maximum combined effectiveness of the two Me_3Si–C bonds places them at angles of 45° above and below the plane of the ring, and this is probably close to or coincident with the sterically preferred configuration since it involves the least interaction between the Me_3Si groups and the *ortho*-hydrogen atoms, and places only a side-chain hydrogen atom in opposition to an *ortho*-hydrogen atom. The third replacement, to give $(Me_3Si)_3C$, should not, to a first approximation, have any further effect, since the extent of hyperconjugation is unchanged by rotation of the group about the C_α–C_{aryl} bond (*cf.* the discussion of hyperconjugation by the CH_3 group[12]), and in one configuration two of the Me_3Si–C bonds would have the orientation described above for the $(Me_3Si)_2CH$ group, and the third such bond would be in the plane of the ring and unable to hyperconjugate. [The preferred configuration for the $(Me_3Si)_3C$ group is probably that in which one Si–C bond is at right angles to the plane of the ring, since this will involve the smallest steric interaction between the Me_3Si groups and the *ortho*-hydrogen atoms, so that all three Me_3Si–C bonds contribute to the hyperconjugation, but together have only the same effect as the two such bonds of the $(Me_3Si)_2CH$ group in the configuration which leads to maximum hyperconjugation.]

Once again steric hindrance to solvation must be rejected as an explanation of the observed decrease in electron release which accompanies introduction of the third Me_3Si group, but other steric effects may be operating, namely steric hindrance to the shortening of the C_α–C_{aryl} bond which would be associated with the partial double bond character of the bond resulting from hyperconjugation. Such hindrance would be most serious for the $(Me_3Si)_3C$ group, and in this case the Me_3Si groups lie uncomfortably close to the *ortho*-hydrogens even in the ground-state configurations involving least strain.

It is now revealing to consider results of other spectroscopic studies, which indicate an order of electron-release of $(Me_3Si)_3C > (Me_3Si)_2CH > Me_3SiCH_2 > CH_3$, though with a relatively small difference between the first two members of the series[4-6]. The predominant effects in all these cases are almost certainly on spectroscopically excited states (in which markedly enhanced hyperconjugative effects could operate), and the steric hindrance to bond shortening postulated above for the $(Me_3Si)_3C$ group would not be relevant, since the atomic positions cannot change in the time of a spectroscopic transition. Thus the difference between the order of electron release in the ground state or transition state and that revealed by spectroscopic studies is understandable. (The same kind of explanation has been applied to the difference between the relative effects of *p*-Me and *p*-tert-Bu groups as revealed by reaction rate measurements on the one hand and spectroscopic studies on the other[13].) Of course, if the electron release from Me_3Si–C bonds arose wholly from hyperconjugative effects the $(Me_3Si)_3C$ would not have a significantly larger influence than the $(Me_3Si)_2$-CH group, except in so far as the sterically-preferred ground state configuration with the latter might not permit maximum overlap. There may also, however, be some inductive release from the Me_3Si groups, which would raise the overall effect of the $(Me_3Si)_3C$ above that of the $(Me_3Si)_2CH$ group if the hyperconjugative effects were equal.

In one spectroscopic study, that of the positions of the charge transfer maxima for the tetracyanoethylene complexes of $PhCH_2SiMe_3$, *p*-$(Me_3SiCH_2)_2C_6H_4$ and reference compounds, the additivity of the strong electron releasing effects of the two Me_3SiCH_2 group in the case of the compound *p*-$(Me_3SiCH_2)_2C_6H_4$ has been interpreted as indicating an exclusively inductive influence of the Me_3SiCH_2 substituents[5], but in our view such additivity is also consistent with the existence of hyperconjugative contributions to the electron release*. Indeed the change transfer spectra of the tetracyanoethylene complexes of monosubstituted benzenes, XC_6H_5 (in which the frequencies can be correlated with σ^+-constants), have been interpreted as clear evidence for hyperconjugative electron release from M–CH_2 bonds[14].

We conclude that in the present state of knowledge the large electron release from Me_3Si–C bonds attached to π-systems is best interpreted as involving substantial contributions from hyperconjugation, as originally proposed[1]. Our analysis has the drawback of implying that hyperconjugation is significant even in ground states, whereas current thinking is against the existence of significant effects of hyperconjugation in such states, at least as far as H–C bonds are concerned, but this is less serious than the difficulties which result from attempting to attribute electron release from the Me_3Si–C bonds entirely or even primarily to inductive effects.

A note on the solvolysis of $R_3SiCH_2CH_2Cl$ compounds, and on addition of hydrogen halides to $R_3SiCH{=}CH_2$ compounds

The above discussion is relevant to explanations of the great ease of unimolecular solvolysis of $R_3SiCH_2CH_2Cl$ and related compounds[15,16]. Recent studies indicate that rate-determining ionization of the $Me_3SiCH_2CH_2$–Cl bond is involved,

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* Dr. H. Bock, in a personal communication (see also ref. 6), has confirmed that in describing the electron release as an inductive effect he did not wish to imply exclusion of hyperconjugation, but only of electron-withdrawing conjugative effects such as are involved when an Me_3Si group is attached directly to a olefinic or aromatic carbon atom.

with breaking of the Me_3Si–CH_2 bond occurring in a subsequent fast step[17]. This implies a very considerable stabilization of the forming carbonium ion Me_3SiCH_2-CH_2^+, which would be difficult to explain in terms of the inductive effect of the Me_3Si group [particularly since alkyl halides RR'$(Me_3Si)CCl$ with R and R' = aryl, alkyl, or H, bearing an α-silicon atom, in which the inductive effects would be expected to be much larger, ionize markedly *less* readily than the parent RR'HCCl compounds[18]]. Such stabilization would be consistent with the assumption that the Me_3Si–C bond is capable of considerable hyperconjugative electron release. (See also ref. 14.) The ρ factor for solvolysis of $XC_6H_4Me_2SiCH_2CH_2Cl$ compounds indicates that a considerable degree of positive charge lies on the silicon atom in the transition state[15], which is again consistent with the hyperconjugative explanation, but there may also be some neighbouring group participation, involving interaction of the β-Me_3Si group with the forming positive charge at the α-carbon atom[17].

The direction of polar addition of hydrogen halides to the olefins R_3SiCH_2=CH_2 (*e.g.* $Me_3SiCH_2{=}CH_2 + HBr \rightarrow Me_3SiCH_2CH_2Br$) is usually explained in terms of a ground state polarization which, because of $(p \rightarrow d)_\pi$ bonding to silicon, makes the β- more positive than the α-carbon of the olefin (*cf.* the structure $\overset{-}{Me_3Si}{=}\underset{\alpha}{C}H$–$\overset{+}{\underset{\beta}{C}}H_2$)[19]. It is more likely that the dominant effect is that of the R_3Si group on the carbonium ions formed by proton attachment at the α- or β-carbon[20]. (For example, hydrogen bromides add to the olefin p-$NO_2C_6H_4\underset{\alpha}{C}H{=}\underset{\beta}{C}H_2$ to give the halide p-$NO_2C_6H_4CHBrCH_3$[21]. The ground state polarization almost certainly places a greater positive charge at the β- than at the α-carbon, so that the proton might be expected to attach to the α-carbon, but the carbonium ion p-$NO_2C_6H_4CH_2\overset{+}{C}H_2$ will be less stable than p-$NO_2C_6H_4\overset{+}{C}HCH_3$ because of conjugation of the positive centre with the aromatic ring in the latter case.) Thus the ion $Me_3SiCHCH_2^+$ seems to be more stable than the ion $Me_3Si\overset{+}{C}HCH_3$, in spite of the fact that the latter bears an electron-releasing α-Me as well as an α-Me_3Si group. Again this would be inconsistent with attribution of the effect of electron releasing effects of Me_3Si groups wholly or even predominantly to induction, but is in accord with the postulate of considerable electron releasing hyperconjugation from the Me_3Si–C bond.

EXPERIMENTAL

Phenyltris(trimethylsilyl)methane

This was made by Merker and Scott's method[22] from benzotrichloride, chlorotrimethylsilane, magnesium turnings, and tetrahydrofuran, but after removal of the solvent and hexamethyldisiloxane the residue was distilled under reduced pressure, and the distillate fractions were cooled in ice. The solid which separated was recrystallised from methanol to give phenyltris(trimethylsilyl)methane (20%), m.p. 206–208°*. (Found: C, 62.1; H, 10.3. $C_{16}H_{32}Si_3$ calcd.: C, 62.3; H, 10.5%.) GLC revealed < 1% of impurity, and the proton NMR spectrum had the expected integration pattern and chemical shifts.

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[*] Bock, Seidl and Fochler reported[4] a m.p. of 160°, but Dr. Bock informs us that a sample purified by sublimation is identical with ours.

(p-Bromophenyl)tris(trimethylsilyl)methane

Bromine (8.9 g, 0.075 mole) in glacial acetic acid (10 ml) was added dropwise during 2 h to a stirred suspension of tris(trimethylsilyl)phenylmethane (16.8 g, 0.054 mole) and iron filings (2 g) in the same solvent (30 ml). The mixture was subsequently refluxed for 2 h and then neutralized with saturated aqueous sodium bicarbonate. Organic products were extracted with ether, the ethereal extract was dried (Na_2SO_4), and the ether was removed under reduced pressure to leave an oil, which crystallised on standing. Recrystallisation from methanol gave (*p*-bromophenyl)tris(trimethylsilyl)methane, (13.8 g, 83%), m.p. 37–38° (Found: C, 49.8; H, 8.3. $C_{16}H_{31}BrSi_3$ calcd.: C, 49.6; H, 8.1%.)

[p-(Trimethylsilyl)phenyl]tris(trimethylsilyl)methane

(*p*-Bromophenyl)tris(trimethylsilyl)methane (15 g, 0.050 mole) was added to n-butyllithium (100 ml of 1.3 *M* solution in ether). The mixture was refluxed for 1 h, then treated with chlorotrimethylsilane (8.1 g, 0.075 mole) and refluxed for a further 4 h. Ice-cold water was then added, the ethereal layer was separated, dried (Na_2SO_4), and evaporated to leave an oil (12 g). This was crystallized from methanol, and recrystallized from the same solvent to give [*p*-(trimethylsilyl)phenyl]tris(trimethylsilyl)methane (5 g, 33%), m.p. 93–94°. (Found: C, 59.9; H, 10.6. $C_{19}H_{40}Si_4$ calcd.: C, 59.9; H, 10.65%.)

(p-Bromophenyl)bis(trimethylsilyl)methane

Bromine (28 g, 0.2 mole) was added dropwise during 3 h to a suspension of iron filings (2 g) in phenylbis(trimethylsilyl)methane (44 g, 0.2 mole) at −10°. The mixture was subsequently stirred for 3 h at −10°, then allowed to attain room temperature and treated with saturated aqueous sodium bicarbonate solution. The organic layer was separated, the aqueous layer was extracted with ether (3 × 50 ml), and the combined organic phases were dried (Na_2SO_4) and distilled to give (*p*-bromophenyl)bis(trimethylsilyl)methane (42 g, 63%), b.p. 118°/2.5 mm, n_D^{25} 1.5296. (Found: C, 49.9; H, 7.3. $C_{13}H_{23}BrSi_2$ calcd.: C, 49.5; H, 7.4%.)

[p-(Trimethylsilyl)phenyl]bis(trimethylsilyl)methane

(*p*-Bromophenyl)bis(trimethylsilyl)methane (20.0 g., 0.06 mole) and magnesium (2.0 g, 0.08 g-atom) and ether (90 ml) were refluxed together for 12 h. Chlorotrimethylsilane (10.8 g, 0.1 mole) was then added, and the mixture was refluxed for a further 2 days, then treated with ice-water. Organic products were extracted with ether, the ethereal layer was dried (Na_2SO_4) and fractionally distilled to give phenylbis(trimethylsilyl)methane (32%), followed by [*p*-(trimethylsilyl)phenyl]bis(trimethylsilyl)methane (9 g, 45%), b.p. 114°/2.1 mm, m.p. 19°, n_D^{25}1.4991 (lit.[23], n_D^{23} 1.4984). (Found: C, 61.9; H, 9.8. $C_{16}H_{32}Si_3$ calcd.: C, 62.3; H, 10.0%.)

Bromo[m-(trimethylsilyl)phenyl](trimethylsilyl)methane

A mixture of *N*-bromosuccinimide (17.8 g, 0.1 mole), [*m*-(trimethylsilyl)benzyl]trimethylsilane (23.6 g, 0.1 mole) and carbon tetrachloride (300 ml) was refluxed with stirring for 12 h, then allowed to stand at room temperature for 2 days. Succinimide was filtered off, the solvent was removed under reduced pressure, and the residue fractionated to give bromo[*m*-(trimethylsilyl)phenyl](trimethylsilyl)-

methane (14.4 g, 46%), b.p. 81°/0.25 mm, n_D^{25} 1.5193. (Found: C, 49.3; H, 7.1. $C_{13}H_{23}BrSi$ calcd.: C, 49.5; H, 7.4%.)

[m-(Trimethylsilyl)phenyl]bis(trimethylsilyl)methane

A solution of bromo[*m*-(trimethylsilyl)phenyl]trimethylsilylmethane (14.4 g, 0.46 mole) in tetrahydrofuran (50 ml) was added dropwise to a mixture of magnesium turnings (3.1 g, 0.13 g-atom) and chlorotrimethylsilane (10.8 g, 0.10 mole) in tetrahydrofuran (20 ml). Reaction set in when the mixture was warmed. A further 50 ml of solvent was added to facilitate stirring, and the mixture was refluxed for 6 h. Residual magnesium was filtered off and the filtrate was treated with ice-water and worked up in the usual way. Fractional distillation gave [*m*-(trimethylsilyl)phenyl]bis(trimethylsilyl)methane (8.4 g, 64%), b.p. 80.5°/0.4 mm, n_D^{25} 1.4912. (Found: C, 62.6; H, 10.3. $C_{16}H_{32}Si_3$ calcd.: C, 62.3; H, 10.6%.)

Dibromo[m-(trimethylsilyl)phenyl](trimethylsilyl)methane

A mixture of *N*-bromosuccinimide (78 g, 0.48 mole), [*m*-(trimethylsilyl)-benzyl]trimethylsilane (52.5 g, 0.22 mole) and carbon tetrachloride (400 ml) was refluxed for 6 h. Succinimide was filtered off and the filtrate was fractionally distilled to give dibromo[*m*-(trimethylsilyl)phenyl](trimethylsilyl)methane (58 g, 67%) b.p. 114°/0.3 mm, n_D^{25} 1.5480 (Found: C, 39.4; H, 5.5. $C_{13}H_{22}Br_2Si_2$ calcd.: C, 39.6; H, 5.6%.)

[m-(Trimethylsilyl)phenyl]tris(trimethylsilyl)methane

Dibromo[*m*-(trimethylsilyl)phenyl](trimethylsilyl)methane (19 g, 0.05 mole) in tetrahydrofuran (20 ml) was added during 1 h to a mixture of magnesium turnings (40 g, 0.17 g-atom) and chlorotrimethylsilane (12.0 g, 0.11 mole) in tetrahydrofuran (50 ml). Reaction set in immediately. After the addition the mixture was refluxed for 6 h, then treated with ice-water. The usual work-up, culminating in fractional distillation, gave [*m*-(trimethylsilyl)phenyl]bis(trimethylsilyl)methane (7.7 g, 50%) followed by [*m*-(trimethylsilyl)phenyl]tris(trimethylsilyl)methane (0.8 g, 4.3%), b.p. 114°/0.12 mm, n_D^{25} 1.5220. (Found: C, 60.6; H, 10.8. $C_{19}H_{40}Si_4$ calcd.: C, 59.9; H, 10.65%.)

(p-Fluorophenyl)tris- and -bis(trimethylsilyl)methane

A mixture of chlorotrimethylsilane (97 g, 0.9 mole), magnesium turnings (20 g, 0.83 g-atom), and tetrahydrofuran (200 ml) was heated to 60° and a solution of *p*-fluorobenzotrichloride (53 g, 0.23 mole) in tetrahydrofuran (70 ml) was added at such a rate so as to maintain gentle reflux. After the addition, the reaction mixture was refluxed for 1 h, then cooled and poured on to crushed ice. The organic layer was separated, washed with water, dried (Na_2SO_4), and fractionally distilled to give (*p*-fluorophenyl)tris(trimethylsilyl)methane (57 g, 76%), b.p. 94°/0.1 mm, m.p. 135–136°. (Found: C, 58.7; H, 9.2. $C_{16}H_{31}FSi_3$ calcd.: C, 58.95; H, 9.5%.)

p-Fluorobenzal chloride (60 g, 0.33 mole), similarly gave (*p*-fluorophenyl)bis-(trimethylsilyl)methane (58 g, 68%), b.p. 80°/2.0 mm, n_D^{25} 1.4893. (Found: C, 61.4; H, 9.0. $C_{13}H_{23}FSi_2$ calcd.: C, 61.3; H, 9.1%.)

(p-Fluorobenzyl)trimethylsilane

A redistilled sample had b.p. 73°/10 mm, n_D^{25} 1.4742 (lit.[24], b.p. 194°, n_D^{20} 1.4765).

Rate measurements

The rates of cleavage were determined spectrophotometrically by the general method previously described[1]. The spectra of the reaction mixtures at "infinite" time (ten half-lives) agreed exactly with those of corresponding solutions of the cleavage products, XC_6H_5.

^{19}*Fluorine NMR spectra*

Fluorine spectra were recorded on a Varian 100 megacycle Spectrometer using 10% solutions of the appropriate organosilicon compound in carbon tetrachloride containing fluorotrichloromethane as internal standard.

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REFERENCES

1 C. Eaborn, *J. Chem. Soc.*, (1956) 4858.

2 W. Hanstein and T. G. Traylor, *Tetrahedron Lett.*, (1967) 4451, 4457, and references therein; T. G. Traylor and J. C. Ware, *J. Amer. Chem. Soc.*, 89 (1967) 2304.

3 A. N. Nesmeyanov and I. F. Lutsenko, *Dokl. Akad. Nauk SSSR*, 59 (1948) 707.

4 H. Bock and H. Alt, *Angew. Chem. Int. Ed. Engl.*, 6 (1967) 941, 1085; H. Bock, H. Seidl and M. Fochler, *Chem. Ber.*, 101 (1968) 2815; H. Bock, H. Alt and H. Seidl, *J. Chem. Soc.*, *B*, (1968) 1158; *J. Amer. Chem. Soc.*, 90 (1968) 5694; 91 (1969) 355.

5 H. Bock and H. Alt, *Angew. Chem. Int. Ed. Engl.*, 6 (1967) 942.

6 H. Bock, H. Alt and H. Seidl, *J. Amer. Chem. Soc.*, 91 (1969), in the press.

7 C. Eaborn and R. W. Bott, in A. G. MacDiarmid (Ed.), *Organometallic Compounds of the Group IV Elements*, Vol. 1, Part 1, 1968, pp. 407–417.

8 R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson and G. T. Davis, *J. Amer. Chem. Soc.*, 85 (1963) 709, 3146, and references therein.

9 M. J. S. Dewar and A. P. Marchand, *J. Amer. Chem. Soc.*, 88 (1963) 3318; W. Adcock and M. J. S. Dewar, *J. Amer. Chem. Soc.*, 89 (1967) 379.

10 R. W. Bott, C. Eaborn and K. Leyshon, *J. Chem. Soc.*, (1964) 1971.

11 R. O. C. Norman and R. Taylor, *Electrophilic Substitution in Benzenoid Compounds*, Elsevier, Amsterdam, 1965, p. 287.

12 J. N. Murrell, S. F. A. Kettle and J. M. Tedder, *Valence Theory*, Wiley, 1965, pp. 311–313.

13 C. Eaborn and R. Taylor, *J. Chem. Soc.*, (1961) 247.

14 W. Hanstein, H. J. Berwin and T. G. Traylor, *J. Amer. Chem. Soc.*, in the press.

15 L. H. Sommer and G. A. Baughman, *J. Amer. Chem. Soc.*, 83 (1961) 3346.

16 R. W. Bott, C. Eaborn and B. M. Rushton, *J. Organometal. Chem.*, 3 (1965) 455; C. Eaborn and R. W. Bott, ref. 7, p. 385.

17 A. W. P. Jarvie, A. Holt and J. Thompson, *2nd International Symposium on the Chemistry of Organosilicon Compounds, Abstracts of Communications*, 1968, p. 101; *J. Chem. Soc.*, B, (1969) 852.

18 M. A. Cook, C. Eaborn and D. R. M. Walton, unpublished work.

19 M. Kumada, M. Ishikawa, S. Maeda and K. Ikura, *J. Organometal. Chem.*, 2 (1964) 146.

20 Ref. 7, p. 446.

21 P. B. de la Mare and R. Bolton, *Electrophilic Addition to Unsaturated Systems*, Elsevier, Amsterdam, 1966, p. 63.

22 R. L. Merker and M. J. Scott, *J. Amer. Chem. Soc.*, 85 (1963) 2243.

23 R. West and P. C. Jones, *J. Amer. Chem. Soc.*, 90 (1968) 2656.

24 H. R. Allcock and C. Eaborn, quoted by V. Bažant, V. Chvalovský and J. Rathouský, *Organosilicon Compounds*, Vol. 2 (1), Czechoslovak Academy of Sciences, Prague, 1965, p. 378.