Aromatic Reactivity. Part LVII.[1] Detritiation of o- and p-$\mathrm{Me_3Si[CH_2]}_n$-$\mathrm{C_6H_4{\cdot}{}^3H}$ in Trifluoroacetic Acid

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The following rate factors f (the specific rates relative to that for [^{3}H]benzene) have been obtained for detritiation in trifluoroacetic acid at 70° of o- and p-$\mathrm{Me_3Si[CH_2]}_n{\cdot}\mathrm{C_6H_4{\cdot}{}^3H}$ with n = 1—4 : (n =) 1, o- 9300, p- 82,000; 2, o- 450, p- 810; 3, o- 270, p- 580; 4, o- 270, p- 690. Some cleavage of the C–Si bonds also occurs, but it is concluded that this does not significantly influence the detritiation rates. The values of the (log f_o) : (log f_p) ratio all fall within the range 0·865 ± 0·05 previously observed to apply to a wide range of monosubstituted benzenes in electrophilic aromatic substitutions. The rate factors correlate quantitatively with the corresponding factors for cleavage of the compounds o- and p-$\mathrm{Me_3Si[CH_2]}_n{\cdot}\mathrm{C_6H_4{\cdot}SiMe_3}$ by aqueous methanolic perchloric acid except for the o-isomers with n = 1, and it is suggested that an unusual steric effect reduces the rate of the protodesilylation in this case. The significance of the rate factor for p-$\mathrm{Me_3SiCH_2{\cdot}C_6H_4{\cdot}{}^3H}$ for understanding the ease of and cleavage of $\mathrm{ArSiMe_3}$ compounds is discussed, with reference to the importance of hyperconjugative electron-release from $\mathrm{Me_3Si{-}CH_2}$ bonds. It is argued that, contrary to a recent conclusion, such hyperconjugation can be significant in ground states as well as carbonium ions and transition states.

WE have previously discussed the influence of $\mathrm{Me_3Si[CH_2]}_n$ groups on the rates of protodesilylation of o- and p-$\mathrm{Me_3Si[CH_2]}_n{\cdot}\mathrm{C_6H_4{\cdot}SiMe_3}$ (n = 1—4) by aqueous methanolic perchloric acid.[2] We now describe a study of the reactivities of o- and p-$\mathrm{Me_3Si[CH_2]}_n\mathrm{C_6H_4{\cdot}{}^3H}$ in detritiation by trifluoroacetic acid at 70°, a reaction which appears to provide the most satisfactory general guide to the influence of substituents in electrophilic aromatic substitution.[3]

Some special features attach to the influence of $\mathrm{Me_3Si[CH_2]}_n$ groups, as follows. (*a*) The considerable stabilisation of Wheland intermediates (or other carbonium ion species) by suitably placed $\mathrm{Me_3SiCH_2}$ substituents is now firmly associated with hyperconjugative (σ–π conjugative) electron release from the Si–CH$_2$ bond,[4] and such stabilisation was first proposed in order to account for the high reactivity of the compound p-$\mathrm{Me_3SiCH_2{\cdot}C_6H_4{\cdot}SiMe_3}$ in acid cleavage,[5] although an even earlier suggestion for this type of hyperconjugation had been based on spectroscopic effects.[6] (*b*) The influence of the p-$\mathrm{Me_3MCH_2}$ group on the rate of detritiation of p-$\mathrm{Me_3MCH_2{\cdot}C_6H_4{\cdot}{}^3H}$ gives a guide to the influence of the $\mathrm{Me_3M}$ group on the ease of attachment of a proton to the carbon atom bearing the group in $\mathrm{Me_3MPh}$, and thus to the ease of removal of the $\mathrm{Me_3M}$ group by acid.[7-9] (*c*) The high *ortho* : *para* ratio in nitration of benzyltrimethylsilane, $\mathrm{Me_3SiCH_2Ph}$,[10] is not reflected in the rates of desilylation of o- and p-$\mathrm{Me_3SiCH_2{\cdot}C_6H_4{\cdot}SiMe_3}$.[2]

An initial study of detritiation of o- and p-$\mathrm{Me_3Si[CH_2]}_n{\cdot}\mathrm{C_6H_4{\cdot}{}^3H}$ was made on samples prepared by hydrolysis with tritiated water of lithio- or bromomagnesio-derivatives made from o- or p-$\mathrm{Me_3Si[CH_2]}_n{\cdot}\mathrm{Hal}$ (Hal = Cl or Br), but in most cases the kinetics were unsatisfactory, the abnormalities suggesting that tritium might have been incorporated at positions other than those intended.[11] The approximate result obtained in that study for the detritiation of the compound p-$\mathrm{Me_3SiCH_2{\cdot}C_6H_4{\cdot}{}^3H}$ has been used previously,[7] and the work described below shows that it was not very seriously in error.

For the present study, o- and p-$\mathrm{Me_3SiCH_2{\cdot}C_6H_4{\cdot}{}^3H}$ were made by converting [2- or 4-^{3}H]toluene into [2- or 4-^{3}H]benzyl bromide, and hence into [2- or 4-^{3}H]-benzyltrimethylsilane. The compounds o- and p-$\mathrm{Me_3Si[CH_2]}_n{\cdot}\mathrm{C_6H_4{\cdot}{}^3H}$, n = 2 and 3, were made by cleavage of the corresponding o- and p-$\mathrm{Me_3Si[CH_2]}_n{\cdot}\mathrm{C_6H_4{\cdot}SiMe_3}$ compounds by aqueous methanolic perchloric acid containing tritiated water. The compounds with n = 4 were those prepared previously from the Grignard reagents o- or p-$\mathrm{Me_3Si[CH_2]_4{\cdot}C_6H_4{\cdot}MgHal}$,[11] but refractionated before use. With all these samples good first-order plots were obtained for the loss of tritium, and the observed rate constants are shown in Table 1, along with the values of the rate factor, f, the specific rate

TABLE 1

First-order rate constants, k_{T} for detritiation and k_{D} for decomposition of $\mathrm{XC_6H_4{\cdot}{}^3H}$ in trifluoroacetic acid at 70°, and some derived data

No.	X	10^7k_{T}/ s^{-1}	f [a]	10^7k_{D}/ s^{-1}	log f_o/ log f_p	$-\sigma^+_{\mathrm{Ar}}$
1	o-CH$_3$		220 [b]		0·88	0·27
2	p-CH$_3$	40	450 [b]			0·30
3	o-CH$_2$SiMe$_3$	830	9300		0·81	0·45
4	p-CH$_2$SiMe$_3$	7300	82,000			0·56
5	o-[CH$_2$]$_2$SiMe$_3$	40	450	5·0	0·91	0·30
6	p-[CH$_2$]$_2$SiMe$_3$	72	810			0·33
7	o-[CH$_2$]$_3$SiMe$_3$	24	270	7·0	0·88	0·28
8	p-[CH$_2$]$_3$SiMe$_3$	52	580			0·31
9	o-[CH$_2$]$_4$SiMe$_3$	24	270	10·6	0·86	0·28
10	p-[CH$_2$]$_4$SiMe$_3$	61	690			0·32

[a] Rate relative to that for $\mathrm{C_6H_5{\cdot}{}^3H}$. [b] Ref. 28. Any doubt about the accuracy of these values arising from uncertainty in the rate constant for tritiobenzene, has recently been removed (H. V. Ansell and R. Taylor, *J.C.S. Chem. Comm.*, 1973, 952).

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[1] Part LVI, C. Eaborn, I. D. Jenkins, and D. R. M. Walton, *J.C.S. Perkin II*, 1974, 596.

[2] R. W. Bott, C. Eaborn, and K. Leyshon, *J. Chem. Soc.*, 1964, 1971.

[3] R. Baker, C. Eaborn, and R. Taylor, *J.C.S. Perkin II*, 1972, 97.

[4] C. G. Pitt, *J. Organometallic Chem.*, 1973, **61**, 49.

[5] C. Eaborn, *J. Chem. Soc.*, 1956, 4858.

[6] C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 1954, 939.

[7] R. W. Bott, C. Eaborn, and P. M. Greasley, *J. Chem. Soc.*, 1964, 4804.

[8] H. J. Berwin, *J.C.S. Chem. Comm.*, 1972, 237.

[9] C. Eaborn, *J.C.S. Chem. Comm.*, 1972, 1255.

[10] E. A. Chernyskev, M. E. Dolgaya, and A. D. Petrov, *Bull. Acad. Sci. U.S.S.R.*, 1960, 1323.

[11] K. C. Bancroft, Ph.D. Thesis, University of Leicester, 1963.

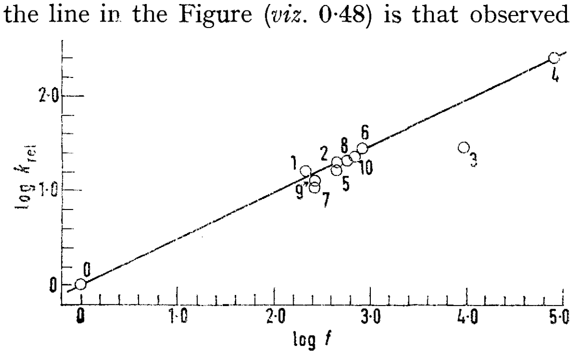
relative to that for the parent [^{3}H]benzene.* Checks by g.l.c., however, showed that in the cases of the compounds with $n = 2$—4, breakdown of $Me_3Si[CH_2]_nPh$ occurred at a significant rate; in the most serious case, that of o-$Me_3Si[CH_2]_4\cdot C_6H_4\cdot {}^3H$, the rate of such loss amounted to 40% of the apparent rate of detritiation, though the corresponding figure for the more important p-isomer was only 17%. For the compound with $n = 1$, the rate of decomposition is insignificant compared with the rate of detritiation, and so was not specifically studied. We thought it likely that the loss of the $Me_3Si[CH_2]_nPh$ compounds involved the cleavage of C–Si bonds (see ref. 12), and this was confirmed in the case of the compound with $n = 4$ by a g.l.c. study of the mixture obtained after three weeks at 70°. Following treatment with water, analysis by g.l.c. and linked g.l.c.–mass spectrometry indicated the presence of the species Me_3SiOH, $(Me_3Si)_2O$, $Ph(CH_2)_4SiMe_2OH$, and $Ph(CH_2)_4H$, as expected for cleavage of both types of C–Si bonds.

The question arises of how and to what extent the observed detritiation rates should be amended to take account of the cleavage. It must first be noted (i) that these side-reactions do not involve loss of tritium, and (ii) that most of the compounds will already have undergone detritiation before cleavage. Furthermore, for the compounds with $n = 3$ and 4, for which the decomposition is most serious, the rates of detritiation of the cleavage products $CF_3CO_2\cdot SiMe_2[CH_2]_n\cdot C_6H_4\cdot {}^3H$ and $H[CH_2]_n\cdot C_6H_4\cdot {}^3H$ will not be very different from those of the original $Me_3Si[CH_2]_n\cdot C_6H_4\cdot {}^3H$ species. (Compare the rates of detritiation of the o- and p-$CH_3\cdot C_6H_4\cdot {}^3H$ with those of the corresponding o- and p-$Me_3Si[CH_2]_n\cdot C_6H_4\cdot {}^3H$ compounds having $n = 3$ and 4.) In the case of the compound with $n = 2$, for which the rate of detritiation of the cleavage product may be only about half of that of the uncleaved material (*cf.* the rates of detritiation of o- and p-$CH_3\cdot C_6H_4\cdot {}^3H$ and of o- and p-$Me_3Si[CH_2]_2\cdot C_6H_4\cdot {}^3H$), the rate of the cleavage is only *ca.* 12% of that of apparent rate of loss of tritium even for the less reactive *ortho*-isomer, o-$Me_3Si[CH_2]_n\cdot C_6H_4\cdot {}^3H$, and in view of point (i) it is unlikely that the observed rate of detritiation of the latter is >3% below the true value. Thus in the subsequent discussion we have assumed that the observed k_{rel} values are a satisfactory measure of the reactivities of the compounds.

The features of the results are as follows. (1) The value of the ratio $(\log f_o)/(\log f_p)$ are ($n =$) 0, 0·88; 1, 0·81; 2, 0·91; 3, 0·88; 4, 0·86. The ratios fall within the range 0·865 ± 0·05 which was shown empirically to apply for a wide range of monosubstituted benzenes,[13] and later shown to be in close agreement with the ratio expected from the charge distribution in the benzenonium ion.[14]

In desilylation of $Me_3Si[CH_2]_n\cdot C_6H_4\cdot SiMe_3$ the corresponding ratios are ($n =$) 0, 0·93; 1, 0·61; 2, 0·85; 3, 0·81; 4, 0·82, indicating that the behaviour of the compound with $n = 1$ in this case is anomalous. (This is discussed below.) The abnormally high $(\log f_o)/(\log f_p)$ ratio, *viz.* 1·24, in nitration of benzyltrimethylsilane is not reflected in either the detritiation or desilylation results, in accordance with the view that there is some specific assistance by the Me_3Si group to *ortho*-nitration.[2,10,15]

(2) In a plot of log k_{rel} for protodesilylation against log f for detritiation, all the points lie close to a straight line through the origin, except for the o-Me_3SiCH_2 substituent, which falls well below the line (see Figure). In view of the analysis in (1), it can be safely concluded that this is due to an anomalously low reactivity of the o-Me_3SiCH_2 compound in protodesilylation; the rate of the reaction would have to be three times that observed to give a point falling on the line. The slope of the line in the Figure (*viz.* 0·48) is that observed for the corresponding plot for a wide range of simple substituted $XC_6H_4\cdot {}^3H$ and $XC_6H_4\cdot SiMe_3$ compounds.[16]



Plot of the logarithms of the relative rates k_{rel} of protodesilylation of $XC_6H_4\cdot SiMe_3$ against logarithms of the relative rates of detritiation (f) of $XC_6H_4\cdot {}^3H$. For numbering denoting X (0 = H) see Table 1.

The low reactivity of the o-$Me_3SiCH_2\cdot C_6H_4\cdot SiMe_3$ compound in protodesilylation is most simply associated with some steric hindrance to *ortho*-substitution in this reaction. The nature of such hindrance is not immediately obvious, however, since such steric effects of *ortho*-substituents as operate in protodesilylation (and they are usually very small for compounds bearing only one *ortho*-substituent, but significant when two such substituents are present) tend to accelerate rather than retard the reaction.[17] This is because with simple o-$XC_6H_4\cdot SiMe_3$ compounds, there can be interference between the X and $SiMe_3$ groups, associated with the coplanarity of the aryl–X and aryl–Si bonds, which is relieved as the Me_3Si group moves in the rate-determining

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* Discussion is always better concentrated on k_{rel} values than on absolute values of the rate constants, since the acidity of the trifluoroacetic acid, and thus the observed rates, vary somewhat with the origin of the acid, but the k_{rel} values are reproducible from worker to worker.

[12] C. Eaborn and R. W. Bott, in ' Organometallic Compounds of the Group IV Elements,' ed. A. G. MacDiarmid, Dekker, New York, 1968, vol. 1, part 1, pp. 360—367, 406.

[13] F. P. Bailey and R. Taylor, *J. Chem. Soc.* (*B*), 1971, 1446.

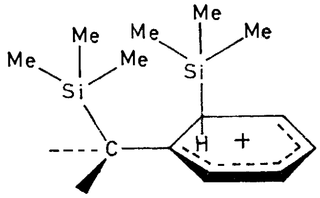
[14] H. V. Ansell, J. Le Guen, and R. Taylor, *Tetrahedron Letters*, 1973, 13.

[15] R. O. C. Norman and R. Taylor, ' Electrophilic Substitution in Benzenoid Compounds,' Elsevier, Amsterdam, 1965, pp. 77—79.

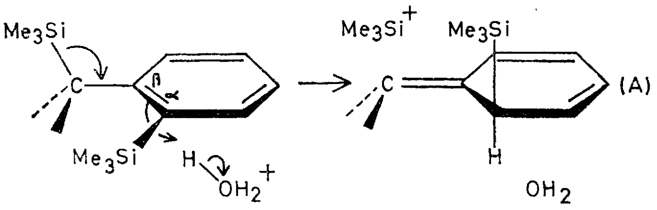
[16] C. Eaborn, Z. Lasocki, and J. A. Sperry, *J. Organometallic Chem.*, 1972, **35**, 245.

[17] Ref. 12, p. 412.

step towards the (roughly) tetrahedral disposition which will exist around the carbon atom to which the proton is attached in the Wheland intermediate. However, a special constraint applies to the Me_3SiCH_2 substituent, *viz.*, the hyperconjugative (σ–π conjugative) release of electrons from the $Me_3Si–CH_2$ bond, which constitutes the major electronic influence of the group, is at a maximum only when the $Me_3Si–CH_2$ bond is in a plane at right angles to that of the aromatic ring.[18,19] It is easy to see that there can be substantial interference between the two Me_3Si groups in the Wheland intermediate if they both lie on the same side of the plane of the ring, as in (I), but there is no reason why they should do so, and it is more likely that they will lie on opposite sides to relieve strain. But in the transition state on the way to the Wheland intermediate it is reasonable to expect that the two Me_3Si groups will, indeed, lie on the same side of the plane of the ring, because the interaction of the electrons of the $Me_3Si–CH_2$ bond with the orbitals of the β-carbon atom will take place preferentially on the side of that atom opposite to that from which the π-electrons are being supplied to the incoming proton. The process, which is represented in an exaggerated form for simplicity in process (A), is closely analogous to the reverse of an *E*2-type elimination process (B) and the factors which favour the *trans*-disposition of the incoming and leaving groups in (B) are essentially the same as those which favour such a position for the incoming group and σ-electron-releasing bond in (II).



(I)



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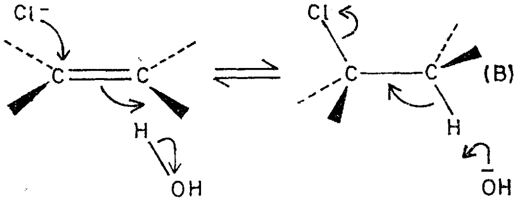
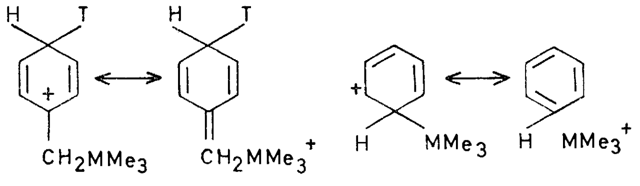


If the $Me_3Si–CH_2$ bond lay on the same side as the attacking oxonium ion there could still be some interference in the transition state, but this should not be significantly greater than that in detritiation. It is possible that even in the detritiation, in which steric effects are normally very small or non-existent, there is a small but significant degree of steric hindrance, because of the need for the $Me_3Si–CH_2$ bond to lie in a plane perpendicular to the ring, and consequent maximisation of the interaction between the substituent and the proton on the attacked carbon atom, and this would account for the fact that the (log f_o) : (log f_p) ratio is appreciably lower for the $Me_3Si[CH_2]_n{\cdot}C_6H_4{\cdot}{}^3H$ compounds with $n = 1$ than for those with $n = 2$—4 or for the $MeC_6H_4{\cdot}{}^3H$ compounds.

We have previously suggested that a set of substituent constants, $\sigma_{Ar}{}^+$, appropriate for correlations of rates of electrophilic aromatic substitutions, can be derived from the rates (or better, the rate factors) of detritiation in trifluoroacetic acid at 70°,[3] and the value for the $Me_3Si[CH_2]_n$ groups are shown in Table 1. The values for the *ortho*-substituents will, of course, be applicable only in favourable circumstances.[14]

The Electron-releasing Ability of the Me_3MCH_2 *Groups, and the Ease of Cleavage of* $Ar–MMe_3$ *Bonds*.—Ten years ago we drew attention to the analogy between the influence of the Me_3SiCH_2 group on the rate of detritiation of *p*-$Me_3SiCH_2{\cdot}C_6H_4{\cdot}{}^3H$ and the influence of the Me_3Si group on the ease of attachment of a proton at the carbon atom of the $Ph–SiMe_3$ bond (and thus on the ease of cleavage of the bond, since the proton attachment is rate determining);[7] the analogy, to which Berwin has recently re-directed attention,[8] is most simply revealed by comparison of the canonical forms (III) and (IV) of the relevant Wheland intermediates.*

In view of the large activating effect of the *p*-Me_3SiCH_2 group in detritiation, amounting to a factor of almost 10^5, it is easy to see why the $Ph–SiMe_3$ bond should be cleaved by acids so much more readily than the Ph–H bond (a factor of $>10^4$ applies in aqueous sulphuric acid at 25°) even though the Ph–Si bond is not broken in the rate-determining step. Since the influence of the substituents X on the rates of detritiation of $XC_6H_4{\cdot}{}^3H$ compounds correlates in most cases with the σ^+ constants of the X groups,[3] it follows from our analogy that the



(III) (IIIa) (IV) (IVa)

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* The analogy can be generalised, *i.e.*, the effect of a CH_2X group in detritiation or other electrophilic aromatic substitution should give a guide to the '*ipso* factors,' which refer to the ease of attack of an electrophile at the carbon atom of a Ph–X bond.[20] It does not in itself imply anything about the mechanism of the electron release or withdrawal by the X groups.

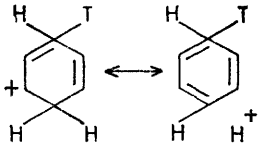
[18] A. R. Bassindale, C. Eaborn, D. R. M. Walton, and D. J. Young, *J. Organometallic Chem.*, 1969, **20**, 49.

[19] M. A. Cook, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1970, **24**, 293.

[20] C. L. Perrin and G. A. Skinner, *J. Amer. Chem. Soc.*, 1971, **93**, 3389; A. R. Butler and A. P. Sanderson, *J.C.S. Perkin II*, 1972, 989.

relative rates of electrophilic cleavage of Ph-MMe_3 bonds should correlate with the σ^+ constants of the *p*-CH_2MMe_3 groups. Directly determined σ^+ constants are not available for the groups with M = Ge, Sn, or Pb, but it is known that the frequencies of absorption of the charge transfer complexes between XPh and tetracyanoethylene correlate with σ^+ constants,[21] and thus the frequencies should be linearly related to the logarithms of the relative rates of cleavage of Ar-MMe_3 bonds, and this has been shown to be the case.[8] The importance of this observation lies in the fact that it discredits the possibility (which we initially proposed [22] but then later disfavoured [7,23]) that the observed very high reactivity of the Ph-MMe_3 bonds when M = Sn and Pb might reflect enhancement of the electron release from the C-MMe_3 bonds by co-ordination of hydroxylic solvent molecules to the metal centres, since if this were the case there would be no correlation with the charge transfer frequencies measured in chlorohydrocarbon media.

Traylor and his colleagues [24] have documented evidence that after initially associating the large electron-releasing ability of the *p*-Me_3SiCH_2 group with hyperconjugation,[5,6] we later for a period doubted this explanation. (This is, indeed, the case, and we acknowledge that our support for the concept of hyperconjugation was reactivated by Traylor's work.[25,26]) In particular, they quote our 1960 comment that hyperconjugation from the C-PbR_3 bond in the case of an ion of type (IV) should be smaller than that from the analogously placed C-H bond in (V).[22] In 1960 evidence had accumulated to indicate that the electronegativity of lead in tetraorganometal compounds was markedly greater than that not only of silicon and germanium, but even that of hydrogen and carbon, and hence it seemed to us unlikely that for M = Pb, structures such as (IVa), in which a positive charge is placed on the metal, could be as important as those for M = Si or as structure (Va). We can now appreciate that even if the electronegativity values do provide a reliable guide to the ease of placing a positive charge on the metal atoms in structures such as (IVa) (which is doubtful), the influence of the change of the location of the charge on going from (IV) to (IVa) or (V) to (Va) is less important than that of the change in energy on replacing the C-MR_3 σ-bond by a C-C π-bond. Thus the extent of hyperconjugation from the CH_2-$SiMe_3$ bond will increase with decreasing strength of the bond, *i.e.* will be in the sequence Si < Ge ≪ Sn ≪ Pb. (We came close to this concept in 1961 when considering the high reactivity of the Ar-Sn bond, by suggesting that ' the electrons of the weak, highly polarisable Ar-Sn bond are readily available to help in the formation of the Ar-HOM bond.' [23]) This accounts nicely for the fact that the relative ease of cleavage reflects the strengths of the Ph-MMe_3 bonds even though these are not broken in the rate-determining step, a feature which has led some authors to doubt our conclusions about the nature of this step.[27]



(V) (Va)

In paying tribute to the dominant role played by Traylor in establishing the importance of σ–π conjugation from C-metal bonds, we question his conclusion that this conjugation has an insignificant influence on ground state properties,[24] and operates more on demand than do other kinds of delocalisation. This view was based on a comparison of values of σ_R constants, which are derived from ground state properties, with those of σ^+ constants, but in our opinion this does not provide a reliable guide because σ^+ constants are a composite of polar and resonance effects. Table 2 shows the values of two sets of resonance constants, *viz.* $\sigma_R{}^0$ constants, applicable to some ground state properties (*e.g.* the ^{19}F chemical shifts of *p*-$XC_6H_4 \cdot F$ compounds), and $\sigma_R{}^+$ constants, applicable to reactions which generate carbonium ion centres conjugated with the substituents.[26] It will be seen that in terms of the free energy change on going from the parent

TABLE 2

Values and ratios of various substituent constants of *para*-substituents X

X	$\sigma_R{}^0$	$\sigma_R{}^+$	$\sigma_R{}^+ : \sigma_R{}^0$
NH_2	−0·52	−1·75	3·4
OMe	−0·45	−1·02	2·3
CH_2SiMe_3	−0·20 [a]	−0·50 [b]	2·5
CH_2SnMe_3	−0·26 [a]	−1·0 [c]	3·8
CH_3	−0·11	−0·25	2·4
Ph	−0·11	−0·30	2·7
F	−0·34	−0·57	1·7
Cl	−0·23	−0·36	1·6
CH_2HgCH_2Ph	−0·24 [d]	−1·7 [e]	7·0

[a] N. Cutress, A. R. Katritzky, C. Eaborn, D. R. M. Walton, and R. D. Topsom, *J. Organometallic Chem.*, 1972, **43**, 131; N. Cutress, T. B. Grindley, A. R. Katritzky, C. Eaborn, D. R. M. Walton, and R. D. Topsom, *ibid.*, 1974, **65**, 17. [b] Approximate value derived from the relationship $\sigma^+ = \sigma_I + \sigma_R{}^+$ (S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Progr. Phys. Org. Chem.*, 1973, **10**, 1) using a σ_I value of −0·04. [c] Derived by assuming that (i) $\sigma^+{}_{p\text{-}CH_2SiMe_3}/\sigma^+{}_{p\text{-}CH_2SnMe_3} = \sigma^+{}_{CT}(p\text{-}CH_2SiMe_3)/\sigma^+{}_{CT}(p\text{-}CH_2SnMe_3)$,[8] giving a σ^+ value of −1·04, and (ii) σ_I has the same value as for *p*-CH_2SiMe_3. [d] D. N. Kravtsov, B. A. Kvasov, E. N. Fedin, B. A. Fainger, and L. S. Golovshenko, *Izvest. Akad. Nauk. S.S.S.R., Ser. khim.*, 1969, 536. This value and the corresponding σ_I value refer to $FC_6H_4CH_2HgCH_2$, but the error introduced by this is insignificant. [e] Calculated from σ^+ *ca.* 1·7,[3] by using $\sigma^+ = \sigma_I + \sigma_R{}^+$.

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[21] W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, 1970, **92**, 829.

[22] C. Eaborn and K. C. Pande, *J. Chem. Soc.*, 1960, 1566.

[23] C. Eaborn and J. A. Waters, *J. Chem. Soc.*, 1961, 542; R. W. Bott, C. Eaborn, K. C. Pande, and T. W. Swaddle, *ibid.*, 1962, 1217.

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compounds with X = H to the substituted compounds, the resonance effect of the p-CH_2SiMe_3 group on the relevant ground state properties, as measured by $\sigma_R{}^0$, is almost twice that of the p-CH_3 group, and almost half of that of the p-OMe group, and this seems to us to indicate a substantial resonance effect. Furthermore, the value of the ratio $\sigma_R{}^+ : \sigma_R{}^0$ for the p-CH_2SiMe_3 group is similar to that for the p-OMe, p-CH_3, and p-Ph groups, but markedly smaller than that for the p-NH_2 group and markedly larger than that for the p-F and p-Cl groups, while the ratio for p-CH_2SnMe_3 is slightly larger than that for the p-NH_2 group. [The same pattern necessarily emerges from examination of the ratio $(\sigma_R{}^+ - \sigma_R{}^0) : \sigma_R{}^0$, which measures the response of the resonance effect to the additional electron demand relative to the resonance effect in the ground state.] Thus for the range of groups considered above no clear distinction can be drawn between (σ–π) and (n–π) or (π–π) conjugation in terms of differential operation of resonance effects in carbonium ions and ground states. However, there is an anomaly for the $PhCH_2HgCH_2$ substituent,[24] for which the $\sigma_R{}^+ : \sigma_R{}^0$ ratio is much larger than in the other cases.

That the (σ–π) conjugative effects of the CH_2–metal bonds operate in ground states also follows from the fact that, by Koopmans theorem, the ionisation potentials of benzene derivatives are equal to the negative of the energy of the highest occupied orbital. (For a discussion, see ref. 4.) In other words, the whole of the electronic effects revealed by the ionisation potentials of $PhCH_2M$ compounds is necessarily present in the ground state molecules. The contribution of these effects to the *total* energy of the ground state molecule, and thus to the stabilities of the neutral molecules, may be fairly small, of course, as Traylor *et al.* conclude,[24] and certainly markedly smaller than those to the energy of the positively charged systems.

EXPERIMENTAL

[4- and 2-^{3}H]Benzyltrimethylsilane.—The Grignard reagent from p-bromotoluene (21·5 g, 0·125 mol) in ether was treated with tritiated water (2·3 ml, 0·25 mol; 100 mCi ml^{-1}) followed by an excess of aqueous hydrochloric acid. The usual work-up, culminating in fractional distillation, gave [4-^{3}H]toluene (70%). Some of this (6·9 g, 0·075 mol) was heated under reflux for 12 h with N-bromosuccinimide (13·3 g, 0·075 mol) in chloroform. Filtration followed by fractionation gave [4-^{3}H]benzyl bromide, b.p. 198°. The product was diluted five-fold with inactive material, and a sample (8·5 g, 0·050 mol) converted in dilute ether solution at 0° into the Grignard reagent. Chlorotrimethylsilane (5·4 g, 0·050 mol) in ether was added. The mixture was boiled under reflux for 30 min, then worked-up in the usual way, culminating in fractional distillation, to give [4-^{3}H]-benzyltrimethylsilane, b.p. 186—189°. The sample used for rate measurements was purified by preparative g.l.c., using a 5 m column of 20% PEGA on 80—100 mesh Chromosorb P at 130°.

The 2-isomer was prepared analogously.

4-[p-^{3}H]Phenylbutyltrimethylsilane.—The Grignard reagent was prepared by the entrainment method, 1,2-dibromoethane (4·05 g, 21·6 mmol) in ether (50 ml) being added during 30 min to a gently refluxing, well-stirred mixture of 4-p-bromophenylbutyltrimethylsilane (6·15 g, 21·6 mmol), magnesium (1·15 g, 47·4 mg atom), and ether (80 ml). After an additional 15 min reflux, the mixture was treated with tritiated water (0·4 ml, 200 mCi ml^{-1}) followed by aqueous ammonium chloride. The usual work-up, gave, on fractionation, 4-[p-^{3}H]phenylbutylmethylsilane, b.p. 77—78° at 1 mmHg. This was refractionated before use.

4-[o-^{3}H]Phenylbutyltrimethylsilane.— 4-o-Chlorophenylbutyltrimethylsilane in tetrahydrofuran was added to lithium foil in tetrahydrofuran during 15 min with vigorous stirring and the stirred mixture was boiled under reflux for 2 h. Subsequent treatment as for the p-isomer gave 4-[o-^{3}H]phenylbutyltrimethylsilane, b.p. 60—62° at 4—5 mmHg. This was refractionated before use.

2-[o- and -p-^{3}H]Phenylethyl- and 3-[o- and -p-^{3}H]Phenylpropyl-trimethylsilane.—The corresponding $Me_3Si[CH_2]_n\cdot C_6H_4SiMe_3$ compounds [2] were heated at 50° for 2 h with tritiated aqueous perchloric acid in methanol; the silane : acid (9M) : methanol ratio was 1 : 4 : 10, and the mixture was not homogeneous, but the cleavage occurred at approximately the expected rate.[2] The usual work-up, culminating in fractional distillation, gave the required products.

Rate Studies.—A good commercial sample of trifluoroacetic acid was fractionally distilled from silver oxide and then from sulphuric acid.

For detritiation rate measurements the usual technique [28] was used, except that (i) the ampoules containing the samples were sealed under vacuum (with cooling in liquid nitrogen), and (ii) in the extraction the amount of sodium hydroxide used was just sufficient to neutralise the trifluoroacetic acid, and the mixture of aqueous and organic phases was mechanically shaken for 20 min, then set aside for 24 h before the toluene layer was taken off for counting. (This procedure was necessary because the phases separated very slowly, the effect being especially marked for the compound with $n = 3$. When the usual excess of sodium hydroxide was used, a yellow colour developed which persisted in the toluene layer.) Part of the toluene extract was used for counting in the ordinary way, and part for g.l.c. determination of the change in the concentration of the tetraorganosilane. For the latter samples (10 μl) were injected on to 2 m × 5 mm column of 5% SE 30 on 100—120 mesh Chromosorb G at 125—170°, the temperature being higher the higher the value of n.

Excellent first-order plots were obtained for the detritiations to >90% reaction, and for the loss of tetraorganosilane in the *ca.* 20% reaction studied. Values of k_T were reproducible to within ±2%.

Product Analyses.—A solution of 4-phenylbutyltrimethylsilane in trifluoroacetic acid was kept for three weeks in an ampoule at 70°. Extraction as above, but with spectroscopic quality hexane, was followed by g.l.c. examination of the extract. G.l.c. at 80° gave a substantial peak with a retention time identical with that for n-butylbenzene. Linked g.l.c.–mass spectrometry revealed features as follows: (i) a small peak giving m/e values of 147 and 73, thought to correspond to $Me_3SiOSiMe_2{}^+$ and Me_3Si^+ ions from hexamethyldisiloxane; (ii) a peak giving an m/e value of 134, thought to be the parent ion from n-butylbenzene; (iii) a peak corresponding to unchanged starting material

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(m/e = 206, with fragments at 191, 176, and 163 formed by loss of methyl groups, and at 73 corresponding to Me_3Si^+); and (iv) a large peak of long retention time and with long tail-off giving fragments with m/e values of (*a*) 190, 191, 192, and 193, probably corresponding with loss of H, OH, and CH_3 combinations from n-butylhydroxytrimethylsilane; (*b*) 175—177, 162—163, 147—149, and 132, corresponding with further expected losses of fragments from this species, and (*c*) 75 (fairly intense), corresponding to Me_3SiOH.

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