The Mechanism of the Gas-phase Pyrolysis of Esters. Part 13.[1] The Very Strong Activating Effects of β-Trialkylmetal Groups

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The rates of gas-phase pyrolysis of β-substituted ethyl acetates $AcOCH_2CH_2X$ where X = $SiMe_3$, $SiEt_3$, $GeEt_3$, and $SiMe_2Ph$, and of 1-aryl-2-trimethylsilylethyl acetates have each been measured over a minimum of 50 °C, between 282 and 397 °C; the rates of pyrolysis of 2-aryldimethylsilylethyl acetates have been measured at 396.9 and 378.2 °C. The β-organometallic substituents are not themselves eliminated (except at considerably higher temperatures) but strongly accelerate the normal elimination of acetic acid, the relative rates per β-hydrogen at 327 °C for X being: H, 1.0; $SiMe_3$, 125; $SiEt_3$, 179; $GeEt_3$, 108; $SiMe_2Ph$, 144. These groups appear to activate by a combination of increasing the acidity of the β-hydrogen via stabilisation of the forming β-carbanion through $(p \longrightarrow d)\pi$ bonding, stabilisation of the incipient α-carbocation by C–X hyperconjugation, and steric acceleration. The effect of substituents in the aryl ring of 1-aryl-2-trimethylsilylethyl acetates gave an excellent correlation with σ^+ values with ρ – 0.52 at 327 °C. The lower ρ-factor for this reaction compared to that for 1-arylethyl acetates (–0.66) is consistent with either conjugative stabilisation of the α-carbocation or increased β-hydrogen acidity. Substituents in the aryl ring of 2-aryldimethylsilylethyl acetates gave a very small positive ρ-factor indicating that overall their effect on β-hydrogen acidity is larger than that on the forming carbocation. The product of pyrolysis of $AcO\cdot CH_2\cdot CH_2\cdot GeEt_3$ viz. $CH_2=CHGeEt_3$ underwent increasingly rapid elimination of successive moieties, believed to be ethylene, in a reaction of stoicheiometry 4.0, which did not occur with the silicon analogue.

THIS work was prompted by reports of the high reactivity of organotin esters towards thermal elimination.[2] Thus for example, 2-triphenylstannylethyl acetate decomposed on distillation,[2a] and a norbornyl derivative eliminated trimethyltin acetate on heating in aqueous acetone.[2b] (A seven-membered cyclic transition state has been proposed for the latter [2c] but the result can also be interpreted in terms of rearrangement followed by normal cis-β-elimination.) Carey and Toler [3] have recently described the liquid-phase pyrolysis of compounds $RCH(X)CH_2SiMe_3$ where X = $O\cdot CO\cdot NHPh$, $O\cdot CS\cdot NHPh$, $O\cdot CS\cdot SMe$, OSO_2NHCO_2Me, and OSO_2Me. Along this series (i) the basicity of X decreases, (ii) the leaving group ability of X increases, and (iii) the yields of vinylsilane $RCH=CHSiMe_3$ and alkene $RCH=CH_2$ decrease and increase, respectively. Thus there are two eliminations in competition as in equations (1) and (2). Carey and Toler interpreted their results in terms of rate-determining formation of ion pairs and assumed that the poorer leaving groups would give a more ionic transition state. Thus C–Si hyperconjugation would be more developed leading to a greater yield of the (conjugatively stabilized) vinylsilane, as observed. We cannot accept this explanation because not only are ion pairs not formed in gas-phase thermal eliminations [4] (and there is no evidence that the mechanism of thermal ester elimination differs between the gas- and liquid-phases), but also a poorer leaving group in these reactions leads to a less ionic transition state.[5] Furthermore, it has been shown that the stability of the reaction products is not an important factor in thermal eliminations.[6] We give an alternative explanation of these results below.

Carey and Toler did not pyrolyse acetates nor consider the possibility of the effects of the $SiMe_3$ group on β-hydrogen acidity. In order to examine these aspects we have made esters substituted at the β-position with silicon and germanium substituents and have carried out

kinetic and product studies. Our strategy was as follows. (i) To pyrolyse 2-trimethylsilylethyl acetate, and analyse the reaction products to see whether β-hydrogen or β-trimethylsilyl was the leaving group under gas-phase conditions. (ii) To investigate the relative rates of ethyl acetates containing $SiMe_3$, $SiEt_3$, $GeEt_3$, and $SiMe_2Ph$ as β-substituents. Comparison of the rates of the $SiMe_3$ and $SiEt_3$ compounds would give an indication of steric effects, while comparison of the $SiEt_3$ and $GeEt_3$ compounds would give a good indication of the importance of hyperconjugation from the electrons of the C^-MR_3 bond, and this would also be confirmed by comparison of the rates of the $SiMe_3$ and $SiMe_2Ph$ compounds. (iii) To investigate, via the Hammett equation, the effect of the α-aryl substituents in the compounds $ArCH(OAc)CH_2$-$SiMe_3$, and so assess the polarity of the reaction transition state compared with that for 1-arylethyl acetates. (iv) To investigate the relative rates (via the Hammett equation) on variation of the β-substituents $SiMe_2Ar$.

RESULTS AND DISCUSSION

1 *Products of Pyrolysis of 2-Trimethylsilylethyl Acetate.* —The relative extents of the two possible eliminations [equations (1) and (2)] were determined by spectroscopic

$$CH_2=CH\cdot SiMe_3$$
$$+$$
$$MeCO_2H \qquad (1)$$

$$CH_2=CH_2$$
$$+$$
$$MeCO_2SiMe_3 \qquad (2)$$
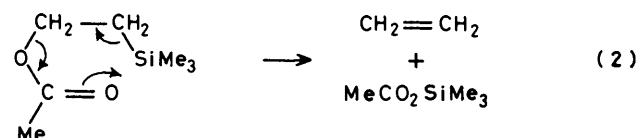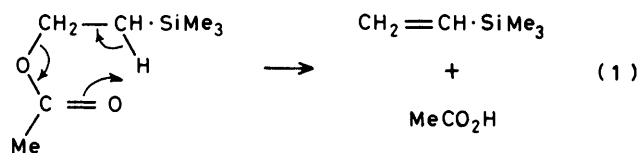
analysis of product runs (see Experimental section). The presence of acetic acid and trimethylvinylsilane would indicate reaction (1), whereas trimethylsilyl acetate would indicate reaction (2), ethylene being too volatile for satisfactory trapping. Runs were carried out at 660, 700, 750, and 800 K. At 600 K reaction (1) took place, but incompletely in the time taken for the ester to pass through the column of heated helices (ca. 20—30 s). This agrees with the kinetic data which give

these compounds are given in Table 1 along with the Arrhenius parameters for ethyl acetate.[7] The similarity of the log A values to that for ethyl acetate suggests that the reaction involves the normal six-centre process. The values are very slightly lower than that for ethyl acetate which may reflect the lower frequency of collision for the acetoxy-group with the (fewer) β-hydrogens. [Likewise the value for ethyl acetate is less than those (13.2 and 13.3, respectively) for isopropyl and t-butyl acetate,[7]

TABLE 1

Pyrolysis of compounds AcOCH$_2$CH$_2$MR$_3$

MR$_3$	T/K	$10^3 k$/s^{-1}	log(A/s^{-1})	E/kcal mol^{-1}	Corr. coeff.	log k at 600 K
(H)	696.9	2.68	12.496	48.05		−5.0085
	670.2	0.668				
	653.0	0.260				
	638.8	0.114				
SiMe$_3$	670.1	31.7	12.19	41.93	0.999 83	−3.0875
	653.0	14.45				
	636.7	6.33				
	621.2	2.76				
	606.2	1.22				
	593.1	0.525				
SiEt$_3$	670.2	43.5	12.17	41.48	0.999 78	−2.9317
	651.4	18.4				
	638.8	9.84				
	606.1	1.735				
	593.1	0.747				
GeEt$_3$	670.2	28.5	12.35	42.55	0.999 21	−3.1506
	651.4	12.1				
	638.8	6.01				
	620.7	2.64				
	606.2	0.981				
	595.1	0.535				
	593.1	0.441				
SiMe$_2$Ph	670.2	36.0	12.19	41.77	0.999 91	−3.0263
	651.4	15.1				
	638.8	8.13				
	593.1	0.618				

$t_{\frac{1}{2}}$ 40 s at this temperature. At 700 K, reaction (1) was complete but n.m.r. analysis of the products gave no evidence for reaction (2). At 750 K, reaction (2) was evident as a minor component; the peak in the n.m.r. attributed to trimethylsilyl acetate disappeared on washing the products with base as expected, as did that for acetic acid, produced by reaction (1). At 800 K reaction (2) took place to a greater extent but it was still only about one-third of the overall elimination. Thus reaction (2) will occur, but it has the higher activation energy and would not have taken place significantly at the temperatures used in our kinetic studies. These observations accord with those of Carey and Toler since acetate is a poorer leaving group than any which they studied.

Similar product runs were not carried out on 2-tri-ethylgermylethyl acetate because insufficient material was available. However, the absence of the analogue of reaction (2) is inferred from the kinetic data, described below.

Our explanation of the predominance of β-C–H over β-C–SiMe$_3$ cleavage in acetate elimination (and how the ratio of these cleavages varies with the nature of the leaving group) is given below.

2 The Relative Effects of the SiMe$_3$, SiEt$_3$, GeEt$_3$, and SiMe$_2$Ph Substituents.—The kinetic data for pyrolysis of

and reduced values for other β-substituted esters have been noted.[8]] The relative rates for the organometallic esters are given in Table 2 along with that for the corresponding CMe$_3$-substituted ester,[6] and the main features of the results are as follows.

TABLE 2

Relative rates per β-hydrogen at 600 K for pyrolysis of AcOCH$_2$CH$_2$MR$_3$

| MR$_3$	k_{rel}
(H)	1.0
CMe$_3$	2.5
SiMe$_3$	125
SiEt$_3$	179
GeEt$_3$	108
SiMe$_2$Ph	144

(i) The SiMe$_3$ group activates strongly and increases the rate 125-fold per β-hydrogen at 600 K. Only two other groups have been found to have a larger effect. These are β-acetyl[9] (338-fold at 600 K) and β-methoxy-carbonyl-[1] (144-fold at 600 K). These latter substituents are believed to activate mainly as a result of conjugative electron withdrawal which increases the acidity of the β-hydrogen (I),[8,10] and the effect of SiMe$_3$ can in principle be similarly explained.

However, this explanation seems quantitatively inadequate because the σ_p^- values for COMe, CO$_2$Me, and

SiMe₃ are 0.82,[11] 0.74,[11] and 0.19;[12] the former two values accord reasonably with the quantitative effects of these substituents, but that for SiMe₃ does not. On the other hand the SiMe₂Ph substituent is more activating than SiMe₃, consistent with this interpretation, although it can be equally well interpreted in another way (below).


(1)
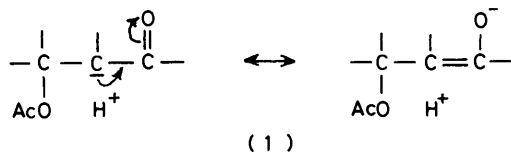
The importance of β-hydrogen acidity is apparent from the results of Carey and Toler[3] on pyrolysis of the S-methylxanthate (II) of 1-trimethylsilyloctan-2-ol. This gave more of the vinylsilane (III) than the allylsilane (IV) the ratio being 2—3 : 1.
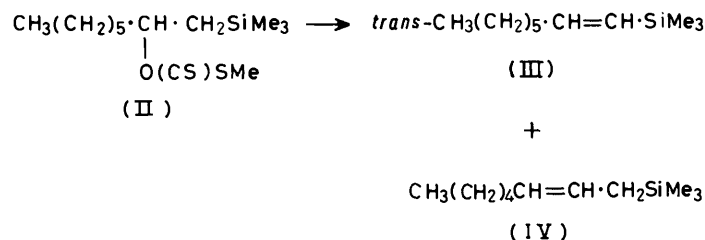
(ii) The SiEt₃ substituent is more activating than the SiMe₃ substituent which suggests that steric acceleration plays a role in governing the elimination rate. Steric acceleration was first proposed as a factor in ester elimination by Benkeser et al.[13] and one of us later provided confirmatory evidence.[6,10,14] Other workers have since explained their results in terms of steric acceleration.[15] Steric acceleration would likewise explain the relative activation by the SiMe₃ and SiMe₂Ph substituents.

(iii) One mode of action which could produce the large β-substituent effects is stabilisation of the incipient α-carbocation by hyperconjugation involving the electrons of the C–MR₃ bond (V), since hyperconjugation involving carbon–metal bonds is known to be very strong.[16,17] In

(V)
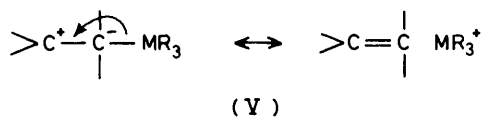
previous work, the β-deuterium isotope effect (leading to lower rates) has been attributed in part to poorer hyperconjugative stabilisation of the incipient α-carbocation, in the presence of β-C–D bonds.[18,19] However, this effect is not as great as in reactions in solution which involve a fully developed carbocation, not only because of the smaller charge, but also because the electrons of the C–MR₃ bond are constrained at an angle of 30—60° away from that required for maximum hyperconjugation.[18] Moreover the effect is least with primary esters where there is less charge developed on the α-carbon.[19] The

present results tend to suggest that C-MR₃ hyperconjugation is not the dominant factor in the present esters since the GeEt₃ substituent, from which hyperconjugation is normally strongest, is less activating than the SiEt₃ substituent, and SiMe₃ is less activating than SiMe₂Ph. The overall effect of these β-substituents is likely therefore to be a composite one, in keeping with the concerted nature of the transition state in which charge develops at a number of sites. It is possible that there is a synergetic process such that electrons of the C–MR₃ bond hyperconjugate with the incipient α-carbocation so increasing the elimination rate, at the same time as the electron-withdrawing resonance effect assists C–H bond breakage. Combined with this there is almost certainly some steric acceleration. The effects of steric acceleration and hyperconjugation are difficult to distinguish, and we note here that the accelerating effects of alkyl groups when attacked to the β-carbon[10] could

equally well be explained in terms of the greater importance of C-C (VI) than of C-H hyperconjugation (VII).[20]

(VI)

(VII)
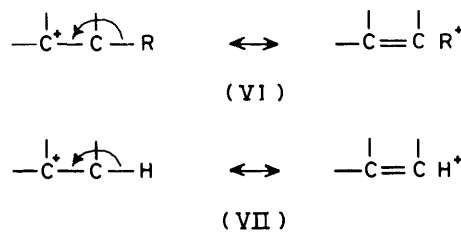
We are now in a position to reinterpret the results of Carey and Toler.[3] Along their series of compounds noted above, the transition state for the elimination will become more El- and less Eᵢ-like.[21] This has two consequences. (a) The breaking of the β-C–H bond will become less kinetically significant.[21] Thus the importance of the increased β-hydrogen acidity arising from the presence of the SiMe₃ group diminishes, so that the advantage in loss of β-hydrogen rather than β-SiMe₃ likewise diminishes. (b) The extent of double-bond formation between the α- and β-carbons in the transition state will diminish, along with the importance of hyperconjugative stabilisation of this bond by the SiMe₃ group, so the advantage favouring formation of vinylsilane along the series will decrease, as observed. This also explains the preferential loss of SiMe₃ in pyrolysis of β-SiMe₃-substituted alkyl chlorides,[22] because these reactions have a more El-like transition state than that for ester pyrolysis. An additional factor is that although the differences in standard themochemical bond energies predict that

loss of SiMe₃ will be favoured in both reactions (by 54 and 36 kJ mol⁻¹ * in halide and ester pyrolysis, respectively) these values predict a greater tendency towards loss of SiMe₃ in the former reaction, as observed.

(iv) The pyrolysis of 2-trimethylgermylethyl acetate differed from that of the other esters in that a second

but this was slow and not of the same kinetic form as that for the germanium-containing ester. This does not however entirely rule out a similar decomposition, because at this temperature the secondary decomposition of acetic acid is very significant and could have altered the kinetic form.

TABLE 3

Pyrolysis of compounds XC₆H₄·CH(OAc)·CH₂·SiMe₃

$10^3k/s^{-1}$

T/K	X = p-Me	m-Me	H	p-Cl	m-Cl
620.7				184	123
606.2	141	108	99.2	88.5	60.1
595.1	83.4	62.6	57.1	49.9	32.9
593.1	75.2	57.2	50.6	42.2	29.3
580.3	37.1	27.6	25.0	21.8	14.3
570.4	22.4	15.5	13.8	11.9	7.94
555.0	9.67	6.46	5.75		
Correlation coefficient	0.999 81	0.999 82	0.999 87	0.999 76	0.999 94
E/kcal mol⁻¹	35.23	37.15	37.49	38.00	38.40
log (A/s⁻¹)	11.85	12.44	12.52	12.72	12.62
log k_{rel} (600 K)	0.158	0.042	0	−0.059	−0.232

reaction commenced shortly after completion of the primary elimination. The rate of this increased to a maximum and then decreased during which time the pressure increased 2.5-fold making the stoicheiometry including the primary elimination 5-fold overall. The product of the primary elimination evidently undergoes a further decomposition, and the two possible products that could decompose further are triethylgermyl acetate or triethylvinylgermane produced from the analogue of reactions (2) and (1), respectively. Triethylgermyl acetate was prepared and pyrolysed under the conditions used for 2-triethylgermylethyl acetate. Although it underwent decomposition this was very slow and of a quite different kinetic form to that observed above, so this compound cannot be the reaction product which rules out pathway (2) which was also ruled out for the silicon-containing ester. Triethylvinylgermane was unavailable, so tetraethylgermane was pyrolysed as a model. It pyrolysed very slowly (and is reported to give hydrogen, germanium, and various hydrocarbons [23] in a reaction which commences via homolysis to Et₃Ge· and Et· [24]) but both the kinetic form and rate were quite different from that of the reaction product. It would seem therefore that the vinyl group is crucial to the secondary elimination, and a possible reaction is shown in (VIII) which bears a relationship to the pyrolysis of vinyl ethers (IX). In this process all three molecules of ethylene would be lost leaving vinylgermane in a reaction with the correct overall stoichemistry. Because the rate-determining step would be largely influenced by breaking of the carbon–metal bond, the failure to observe a similarly rapid reaction with the corresponding silicon ester follows. To ascertain whether any reaction could be observed with the latter, it was pyrolysed at ca. 40 K higher than the maximum used in the kinetic studies. Under these conditions a secondary reaction did occur,

* 4.184 J = 1 cal.

3 The Effects of Substituents in Pyrolysis of 1-Aryl-2-trimethylsilylethyl Acetates, ArCH(OAc)·CH₂·SiMe₃.— The kinetic data are given in Table 3 and these gave excellent Arrhenius plots as shown by the correlation coefficients. The log k_{rel} values also gave an excellent

(VIII)

(IX)
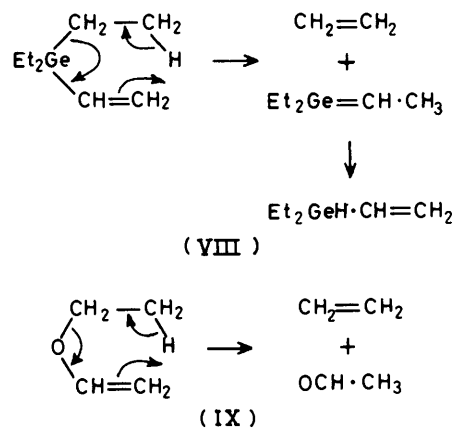
plot (r 0.999) against σ⁺ values (Figure) from which the ρ factor is obtained as −0.52 at 600 K.* This is smaller than for pyrolysis of the corresponding 1-arylethyl acetates (− 0.66),[25] which could be taken to imply that the transition state is less polar but this is not necessarily the case. If there is hyperconjugative stabilisation of the incipient α-carbocation by the SiMe₃ group, there will be less nett charge to be stabilised by the aryl group: similar arguments account for the magnitude of the ρ-factor in pyrolysis of 1-aryl-1-methylpropyl acetates.[26] The situation is certainly not straightforward as is clear from considering Schemes 1 and 2 where the numbers indicate the increase in reactivity in the direction of the arrows.

* By contrast, a plot against σ values has a correlation coefficient of only 0.964.

Hammett correlation for pyrolysis of
1-aryl-2-trimethylsilylethyl acetates at 600 K
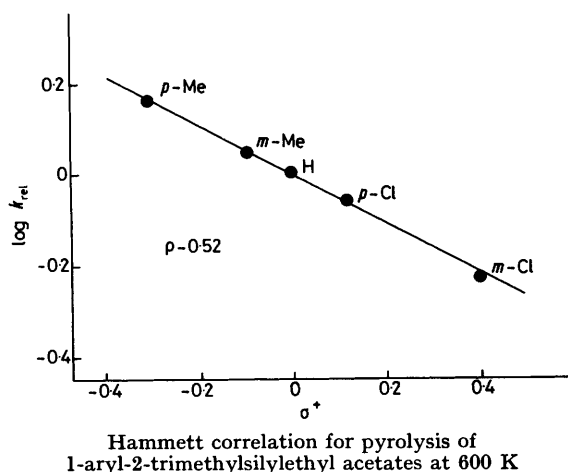
Consider first the reactivity ratios in Scheme 2.

(i) *1-Phenylethyl acetate compared to ethyl acetate.*
The former is **63** times more reactive due to stabilisation
of the incipient α-carbocation by the phenyl group.

(ii) *2-Phenylethyl acetate compared to ethyl acetate.* The
former is more reactive due to enhancement of the β-
hydrogen acidity, and since this step is kinetically less
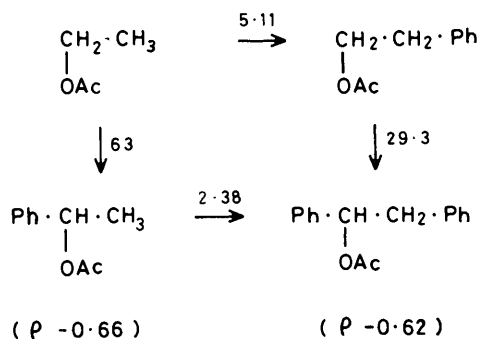
SCHEME 1   Relative reactivities towards pyrolysis at 600 K
and ρ factors (for the 1-arylethyl compounds)

important,[25] the rate increase (5.1-fold) is smaller than in
(i).

(iii) *1,2-Diphenylethyl acetate compared to 1-phenyl-
ethyl acetate.* The former is 2.38 times more reactive.
This factor is smaller than observed in (ii) because
β-C–H bond breaking is less kinetically significant for
secondary esters.[21]

(iv) *1,2-Diphenylethyl acetate compared to 2-phenyl-
ethyl acetate.* The former is 29.3 times more reactive.
This factor is smaller than observed in (i) because there is
a smaller charge on the α-carbocation, shown by the
smaller ρ factor for the 1-aryl-2-phenylethyl acetates
(−0.62),[25] *cf.* −0.66 for 1-arylethyl acetates.[25]

These data are thus all self-consistent. Consider now
the results in Scheme 1.

(v) *1-Phenylethyl acetate compared to ethyl acetate.* As
in (i).

(vi) *2-Trimethylsilylethyl acetate compared to ethyl
acetate.* The former is 77.5 times more reactive. This
factor is much larger than observed in (ii) as a result of

one or more of the following: increase in β-H acidity,
C–Si hyperconjugation, and steric acceleration.

(vii) *1-Phenyl-2-trimethylsilylethyl acetate compared to
1-phenylethyl acetate.* The former is 107 times more
reactive than the latter so the effect is larger than in (vi).
This is at first sight anomalous because we would expect
the phenyl group to produce a *smaller* rate increase than
in (vi), *cf.* the transformation (iii) *versus* (ii) in Scheme 2.
On the other hand, if C–Si hyperconjugation is important
this result *would* follow, because there is more charge on
the α-carbocation for the secondary phenylethyl acetate
than for the primary ethyl acetate.
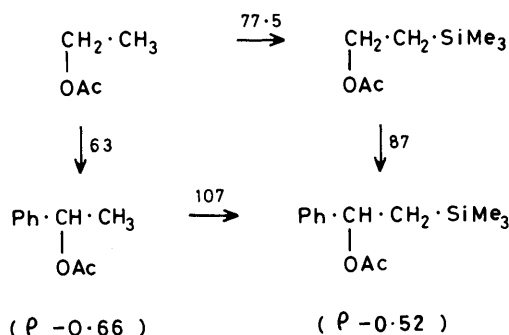
SCHEME 2   Relative reactivities towards pyrolysis at 600 K
and ρ factors (for the 1-arylethyl compounds)

(viii) *1-Phenyl-2-trimethylsilylethyl acetate compared to
2-trimethylsilylethyl acetate.* The former is 87 times more
reactive so the effect is larger than in (v). This appears
anomalous [*cf.* (iv) *versus* (i)] because the polarity of the
transition state for the 2-trimethylsilyl compounds
should be smaller than for the unsubstituted ester and
this is confirmed by the smaller ρ factor for the 1-aryl-2-
trimethylsilylethyl acetates (−0.52) compared to 1-
arylethyl acetates (−0.66).

It appears then that an effect operates to make 1-
phenyl-2-trimethylsilylethyl acetate exceptionally reac-
tive, and it is possible that this is either C–Si hypercon-
jugation, or steric acceleration, or both.

4 *The Effects of Substituents in Pyrolysis of 2-Aryldi-
methylsilylethyl Acetates,* $AcOCH_2 \cdot CH_2 \cdot SiMe_2Ar$.—The
kinetic data are given in Table 4 and rates were measured

TABLE 4

Pyrolysis of compounds $AcOCH_2CH_2SiMe_2 \cdot C_6H_4X$

		$10^3 \; k/s^{-1}$			
T/K	X = *p*-OMe	*p*-Me	H	*p*-Cl	*m*-Cl
670.1	35.7	36.5	36.0	38.5	37.05
651.4	15.35	15.0	15.2	15.4	16.0
Average k_{rel}	0.997	1.014	1.0	1.053	1.036

at two temperatures only once it became apparent that
the substituent effects were very small. The data gave a
ρ-factor which is at most very slightly positive (*ca.* 0.02)
and this is inconsistent with β-C–SiMe₂Ar bond breakage,
but is consistent with β-C–H bond breakage. For 2-
arylethyl acetates, ρ + 0.2,[7] so with the extra atom
through which the substituent effects operate in the

silicon-containing compounds, a very small positive ρ-factor of *ca.* 0.2/2.8 (*i.e.* 0.07) would be expected.[27]

EXPERIMENTAL

The kinetic apparatus and general technique have been described.[28]

Product analysis of 2-trimethylsilylethyl acetate pyrolysis was carried out by passing the ester in a nitrogen stream down a column of heated helices and condensing the products in a coil cooled in dry ice–acetone, as previously described.[29] The products were rinsed from the trap with carbon tetrachloride and analysed by n.m.r. which gave the following data indicative of the consituents shown, τ (CCl$_4$) 3.87—4.72 (3 H, m, CH=CH$_2$), 9.95 (9 H, s, Me$_3$Si) (Me$_3$SiCH=CH$_2$); 6.08 (2 H, t, CH$_2$O), 8.20 (3 H, s, COCH$_3$), 9.18 (2 H, t, CH$_2$SiMe$_3$), 9.95 (9 H, s, Me$_3$Si) (Me$_3$SiCH$_2$CH$_2$OCOMe); 8.10 (s, COCH$_3$) (CH$_3$COOH); 7.97 (3 H, s, COCH$_3$), 9.95 (9 H, s, Me$_3$Si) (CH$_3$COOSiMe$_3$). Where the Me$_3$Si peaks coincided, the peak area gave a total of nine hydrogens relative to the peak areas of the other hydrogens of the various constituents.

2-Trimethylsilylethyl Acetate—2-Trimethylsilylethanol, prepared by the method of Speier *et al.*,[30] was acetylated with pyridine and acetic anhydride to give, after work up, 2-trimethylsilylethyl acetate (44%), b.p. 66—67 °C at 30 mmHg, n_D^{25} 1.4132 (lit.,[27] 52—53 °C at 12 mmHg, n_D^{20} 1.4162).

2-Triethylsilylethyl Acetate.—2-Triethylsilylethanol, prepared by the method of Speier *et al.*,[30] was acetylated as above to give 2-triethylsilylethyl acetate (67%), b.p. 64—65 °C at 0.8 mmHg, n_D^{25} 1.4412 (lit.,[31] 87—88 °C at 3.0 mmHg, n_D^{20} 1.4438).

2-Triethylgermylethyl Acetate.—Triethylgermane (5.0 g, 0.03 mol) (prepared according to the literature[32]), vinyl acetate (4.5 g, 0.052 mol), and chloroplatinic acid in ethanol (0.5 ml of a 0.04M solution) were heated at reflux under nitrogen during 5 h. The mixture was extracted with ether, filtered, concentrated under vacuum and fractionally distilled to give 2-triethylgermylethyl acetate (3.0 g, 39%), b.p. 82—87 °C at 0.8 mmHg, n_D^{20} 1.4556 (Found: C, 48.4; H, 8.9. C$_{10}$H$_{22}$GeO$_2$ requires C, 48.65; H, 9.0%).

2-Dimethylphenylsilylethyl Acetate.—2-Dimethylphenylsilylethanol (8.85 g, 0.05 mol),[33] was acetylated as above to give, after work-up, 2-dimethylphenylsilylethyl acetate (8.0 g, 73%), b.p. 73 °C at 0.3 mmHg, n_D^{25} 1.4976 (Found: C, 65.4; H, 8.05. C$_{12}$H$_{18}$O$_2$Si requires C, 64.8; H, 8.2%), τ(CCl$_4$) 2.55—2.85 (5 H, m, ArH), 5.97 (2 H, t, CH$_2$O), 8.18 (3 H, s, COCH$_3$), 8.87 (2 H, t, CH$_2$Si), and 9.73 (6 H, s, SiMe$_2$).

2-Dimethyl-(p-methoxyphenyl)silylethyl Acetate.—2-Dimethyl-(*p*-methoxyphenyl)silylethanol[33] was acetylated as above to give, after work-up, 2-dimethyl-(p-methoxyphenyl)silylethyl acetate (83%), b.p. 110 °C at 0.3 mmHg, n_D^{25} 1.5058 (Found: C, 62.2; H, 8.0. C$_{13}$H$_{20}$O$_3$Si requires C, 61.9; H, 8.0%), τ (CCl$_4$) 3.02 (4 H, q, ArH), 5.87 (2 H, t, CH$_2$O), 6.38 (3 H, s, OMe), 8.23 (3 H, s, COCH$_3$), 8.97 (2 H, t, CH$_2$Si), and 9.83 (6 H, s, Me$_2$Si).

2-Dimethyl-(p-methylphenyl)silylethyl Acetate.—2-Dimethyl-(*p*-methylphenyl)silylethanol[33] was acetylated as above to give, after work-up, 2-dimethyl-(p-methylphenyl)-silylethyl acetate (70%), b.p. 103—104 °C at 0.08 mmHg, n_D^{25} 1.4972 (Found: C, 66.0; H, 8.4. C$_{13}$H$_{20}$O$_2$Si requires C, 66.05; H, 8.5%), τ(CCl$_4$) 2.90 (4 H, q, ArH), 6.05 (2 H, t, CH$_2$O), 8.13 (3 H, s, CH$_3$), 8.25 (3 H, s, COCH$_3$), 8.97 (3 H, t, CH$_2$Si), and 9.82 (6 H, s, SiMe$_2$).

2-Dimethyl-(m-methylphenyl)silylethyl Acetate.—2-Dimethyl-(*m*-methylphenyl)silylethanol[33] was acetylated as above to give, after work-up, 2-dimethyl-(m-methylphenyl)-silylethyl acetate (79%), b.p. 84 °C at 0.35 mmHg, n_D^{25} 1.4998 (Found: C, 66.6; H, 8.3%), τ(CCl$_4$) 2.77—2.97 (4 H, m, ArH), 5.97 (2 H, t, CH$_2$O), 7.67 (3 H, s, CH$_3$), 8.13 (3 H, s, COCH$_3$), 8.87 (2 H, t, CH$_2$Si), and 9.72 (6 H, s, SiMe$_2$).

2-Dimethyl-(p-chlorophenyl)silylethyl Acetate.—2-Dimethyl-(*p*-chlorophenyl)silylethanol[33] was acetylated as above to give, after work-up, 2-dimethyl-(p-chlorophenyl)-silylethyl acetate (50%), b.p. 102 °C at 0.3 mmHg, n_D^{25} 1.5108 (Found: C, 56.4; H, 6.7. C$_{12}$H$_{17}$ClO$_2$Si requires C, 56.1; H, 6.7%), τ (CCl$_4$) 2.71 (4 H, q, ArH), 6.00 (2 H, t, CH$_2$O), 8.17 (3 H, s, COCH$_3$), 8.88 (2 H, t, CH$_2$Si), and 9.73 (6 H, s, SiMe$_2$).

2-Dimethyl-(m-chlorophenyl)silylethyl Acetate.—2-Dimethyl-(*m*-chlorophenyl)silylethanol[33] was acetylated as above to give, after work-up, 2-dimethyl-(m-chlorophenyl)-silylethyl acetate (71%), b.p. 102 °C at 0.4 mmHg, n_D^{25} 1.5110 (Found: C, 55.7; H, 6.2%), τ (CCl$_4$) 2.62—2.73 (4 H, m, ArH), 5.98 (2 H, t, CH$_2$O), 8.17 (3 H, s, COCH$_3$), 8.88 (2 H, t, CH$_2$Si), and 9.70 (6 H, s, SiMe$_2$).

1-Phenyl-2-trimethylsilylethyl Acetate.—1-Phenyl-2-trimethylsilylethanol (4.0 g, 0.02 mol), prepared according to the literature method,[34] was acetylated as above to give, after work-up, 1-phenyl-2-trimethylsilylethyl acetate (2.9 g, 58%), b.p. 89—90 °C at 1.0 mmHg, n_D^{25} 1.4851 (Found: C, 66.3; H, 8.5. C$_{13}$H$_{20}$O$_2$Si requires C, 66.05; H, 8.5%), τ (CCl$_4$) 2.93 (5 H, s, ArH), 4.40 (1 H, t, CH), 8.63 (3 H, s, COCH$_3$), 9.05 (2 H, d, CH$_2$Si), and 10.22 (9 H, s, SiMe$_3$).

1-(p-Methylphenyl)-2-trimethylsilylethyl Acetate.—The general literature method[34] was used to prepare 1-(p-methylphenyl)-2-trimethylsilylethanol (73%), b.p. 83 °C at 0.45 mmHg, τ (CCl$_4$) 2.97 (4 H, s, ArH), 5.45 (1 H, t, CH), 7.33 (1 H, s, OH), 7.73 (3 H, s, CH$_3$), 9.01 (2 H, d, CH$_2$Si), and 10.17 (9 H, s, SiMe$_3$). Acetylation as above and work-up gave 1-p-methylphenyl-2-trimethylsilylethyl acetate (73%), b.p. 90 °C at 0.4 mmHg, n_D^{25} 1.4879 (Found: C, 67.1; H, 8.85. C$_{14}$H$_{22}$O$_2$Si requires C, 67.15; H, 8.85%), τ (CCl$_4$) 2.25 (4 H, q, ArH), 4.30 (1 H, t, CH), 7.77 (3 H, s, CH$_3$), 8.17 (3 H, s, COCH$_3$), 9.17 (2 H, d, CH$_2$Si), and 10.17 (9 H, s, SiMe$_3$).

1-(m-Methylphenyl)-2-trimethylsilylethyl Acetate.—The general method[34] was used to prepare 1-(m-methylphenyl)-2-trimethylsilylethanol (42%), b.p. 88 °C at 0.65 mmHg, m.p. 34—37 °C, τ (CCl$_4$) 3.00 (4 H, s, ArH), 5.38 (1 H, t, CH), 7.70 (3 H, s, CH$_3$), 8.17 (1 H, s, OH), 8.98 (2 H, d, CH$_2$Si), and 10.1 (9 H, s, SiMe$_3$). Acetylation as above and work-up gave 1-(m-methylphenyl)-2-trimethylsilylethyl acetate (74%), b.p. 92 °C at 0.45 mmHg, n_D^{25} 1.4903 (Found: C, 67.1; H, 8.85%), τ (CCl$_4$) 2.97 (4 H, s, ArH), 4.32 (1 H, t, CH), 7.73 (3 H, s, CH$_3$), 8.15 (3 H, s, COCH$_3$), 8.83 (2 H, d, CH$_2$Si), and 10.17 (9 H, s, SiMe$_3$).

1-(p-Chorophenyl)-2-trimethylsilylethyl Acetate.—The general method[34] was used to prepare 1-(p-chlorophenyl)-2-trimethylsilylethanol (67%), b.p. 87 °C at 0.15 mmHg, n_D^{25} 1.5166, τ (CCl$_4$) 2.87 (4 H, s, ArH), 5.47 (1 H, t, CH), 6.83 (1 H, s, OH), 9.1 (2 H, d, CH$_2$Si), and 10.17 (9 H, s, SiMe$_3$). Acetylation as above and work-up gave 1-(p-chlorophenyl)-2-trimethylsilylethyl acetate (92%), b.p. 84 °C at 0.25 mmHg, n_D^{25} 1.4980 (Found: C, 57.5; H, 7.1. C$_{13}$H$_{19}$ClO$_2$Si requires C, 57.65; H, 7.1%), τ (CCl$_4$) 2.72 (4 H, s, ArH), 4.23 (1 H, t, CH), 8.05 (3 H, s, COCH$_3$), 8.75 (2 H, d, CH$_2$Si), and 10.03 (9 H, s, SiMe$_3$).

1-(m-Chlorophenyl)-2-trimethylsilylethyl Acetate.—The

general method [34] was used to prepare 1-(m-*chlorophenyl*)-2-*trimethylsilylethanol* (44%), b.p. 93 °C at 0.3 mmHg, τ (CCl$_4$) 2.80—2.90 (4 H, m, ArH), 5.40 (1 H, t, CH), 7.40 (1 H, s, OH), 9.03 (2 H, d, CH$_2$Si), and 10.15 (9 H, s, SiMe$_3$). Acetylation as above and work-up gave 1-(m-*chlorophenyl*)-2-*trimethylsilylethyl acetate* (59%), b.p. 88 °C at 0.25 mmHg, n_D^{25} 1.4983 (Found: C, 57.7; H, 7.1%), τ (CCl$_4$) 2.70—2.83 (4 H, m, ArH), 4.25 (1 H, t, CH), 8.02 (3 H, s, COCH$_3$), 8.75 (2 H, d, CH$_2$Si), and 10.03 (9 H, s, SiMe$_3$).

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