Methanolysis of the Benzylideneaniline Derivatives ArC(MMe$_3$)=NAr′ (M = Si or Sn)

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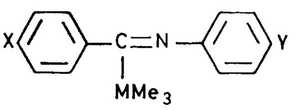
Rates of cleavage of compounds (I) and (II) of the type p-XC$_6$H$_4$C(MMe$_3$)=NC$_6$H$_4$Y-p, X = H, Y = OMe, Me, or Cl, or Y = H, X = H, OMe, Me, or Cl, in MeOH (to give the benzylideneanilines XC$_6$H$_4$CH=NC$_6$H$_4$Y) have been measured spectrophotometrically at 25 °C. The cleavages occur readily in methanol alone, but are catalysed by NaOMe and, at least for the tin compounds, by MeCO$_2$H. In the neutral cleavage the tin compound (IIa) is *ca.* 49 times as reactive as the corresponding silicon compound (Ia). The rate isotope effect (r.i.e.), the ratio of the rate constant in MeOH to that in MeOD, is *ca.* 1.3 for (II), and the product isotope effect (p.i.e.), given by the product ratio RH : RD on cleavage in 1 : 1 MeOH–MeOD is 1.1, while for the silicon compounds the r.i.e. is *ca.* 1.8. Electron release by X or Y increases the ease of reaction. The results are interpreted in terms of a cyclic mechanism in which transfer of a proton from an MeOH molecule to the nitrogen of the C=N bond is synchronous with formation of the M–OMe bond, and probably also with the breaking of the C–M bond, the proton transfer to the imine being considerably advanced in the transition state. In the base cleavage the tin compound (IIa) gives normal values for the r.i.e., p.i.e., and r.i.e. : p.i.e. ratio (*ca.* 0.96, 1.65, and 0.58, respectively), consistent with an electrophilically-assisted mechanism in which a proton is transferred from the solvent to the carbon atom of the imino-group as the C–Sn bond breaks. For the silicon compounds, the r.i.e. values, of *ca.* 1, are wholly abnormal, as is the fact that the silicon compound (Ia) is more reactive, by a factor of 2, than its tin analogue (IIa), and it is suggested that there is electrophilic assistance even for the silicon compounds, but involving proton transfer to nitrogen. For both tin and silicon compounds electron withdrawal in Y facilitates the base cleavage. Cleavage of (II) is catalysed 70 times as effectively by MeCO$_2$H as by MeONa, and in the media used oxonium ion does not compete with MeCO$_2$H as the catalyst.

As part of a series of investigations of the characteristics of base cleavages of R–MMe$_3$ bonds, where M = Si or Sn,[1-7] we have examined the methanolysis of the benzylideneaniline derivatives of types (I) and (II), which we usually refer to below as imino-compounds. These cleavages proved to be of special interest because in addition to catalysis by base there is also a ' spontaneous ' cleavage in neutral methanol. Furthermore, it is possible to vary the substituents in two parts of the molecule and so gain information about the charge distributions in the transition states.



(I) M = Si
(II) M = Sn

a; X = Y = H
b; X = OMe, Y = H
c; X = Me, Y = H
d; X = Cl Y = H
e; X = H, Y = OMe
f; X = H, Y = Me
g; X = H, Y = Cl

RESULTS AND DISCUSSION

The observed first-order rate constants, k, at various concentrations of sodium methoxide in methanol at 25.0 °C are shown in Table 1.

Cleavage occurs in neutral methanol in both cases, but is markedly faster for the tin compounds, the factor being 49 for the parent compounds (X = Y = H). In Table 2 the variation of k with the sodium methoxide concentration is shown in more detail for the parent tin compound (IIa), and it will be seen that the values of the second-order specific rate constant, k_s, for the base-

TABLE 1

Observed first-order rate constants, k, for cleavage of p-XC$_6$H$_4$C(MMe$_3$)=NC$_6$H$_4$Y-p compounds in MeOH or MeONa–MeOH at 25 °C

				10^5k/s^{-1}				
M	X	Y	[NaOMe]/M	0	0.200	0.500	1.00	2.00
Sn	H	H		67	98	127	195	380
	OMe	H		81	89	99	120	170
	Me	H		64	78	95	118	200
	Cl	H		60	170	305	590	1 260
	H	OMe		112		163	220	330
	H	Me		98	113	130	166	276
	H	Cl		33	143	280	570	1 270
Si	H	H		1.36		140	320	980
	OMe	H		2.78		45	114	320
	Cl	H		0.82		540	1 310	4 300
	H	OMe		5.30		124	305	910
	H	Me		2.90		104	230	760
	H	Cl		0.55		430	930	3 200

TABLE 2

Rate constants for cleavage of $PhC(SnMe_3)=NPh$ at various concentrations of NaOMe in MeOH at 25.0 °C

λ/nm [a]	10^3[MeONa]/M	10^5k/s^{-1} [b]	10^5k(B)/s^{-1} [c]	10^5k_s/l mol^{-1} s^{-1} [d]
310	0	67		
310	18	69	2	111
410	87	78	11	126
310	182	89	22	121
310	505	128	61	121
410	870	168	101	116
310	1 000	195	128	128
310	1 820	339	272	149
310	2 010	385	318	158

[a] Wavelength used to monitor reaction. [b] Observed first-order rate constant. [c] Rate constant for base-catalysed process, after deduction of rate constant for [NaOMe] = 0. [d] Specific second-order rate constant for base-catalysed reaction, given by k(B)/[NaOMe].

catalysed process (after allowance for the neutral process at each base concentration) are effectively constant up to 1M-base and then increase somewhat up to 2M-base, as is normal for base cleavage of organotin compounds.[6] In Table **3** are shown the rate constants, k(B) for the base-catalysed process at various base concentrations after deduction of the rate constant for the neutral process. The values of k(B) for the silicon compounds vary with [NaOMe] in the expected manner; thus the average factor for the increase in k(B) on going from 0.5 to 2M-base is 7.6, effectively the same as in cleavage of m-$ClC_6H_4CH_2SiMe_3$ at 50 °C.[6]

The effects of the substituents X and Y on the rates of the spontaneous and base-catalysed reactions are shown separately in Tables 4 and 5 as values of k_{rel}, the rate relative to that of the appropriate parent compound (X = Y = H), the values shown being the mean of those observed for 1.0M and 2.0M-base. Also shown, where relevant, for the neutral cleavages are the values of (log k_{rel})/σ and (log k_{rel})/σ^+.

Rate constants at various temperatures and the derived activation parameters are shown for some representative compounds in Table 6, and solvent isotope effect data in Table 7. In the latter Table the rate isotope effect (r.i.e.) is that given by the ratio of the rate constant in MeOH to that in MeOD under similar conditions, and the product isotope effect (p.i.e.) is that given by the product ratio RH : RD obtained on cleavage of $RMMe_3$ in 1 : 1 MeOH–MeOD (with or without base, as appropriate); unfortunately p.i.e. values could not be determined for the imino-silicon compounds because these could not be obtained free from the corresponding benzylideneanilines.

TABLE 3

First-order rate constants for base-catalysed cleavage of p-$XC_6H_4C(MMe_3)=NC_6H_4Y$-p in MeONa–MeOH at 25.0 °C

				10^5k(B)/s^{-1} [a]			
M	X	Y	[NaOMe]/M	0.200	0.50	1.00	2.00
Sn	H	H		31	60	128	315
	Me	H		8	18	39	89
	Me	H		14	31	54	136
	Cl	H		110	244	530	1 200
	H	OMe			51	107	215
	H	Me		15	32	68	178
	H	Cl		110	250	540	1 240
Si	H	H			139	320	980
	OMe	H			42	111	315
	Me	H					
	Cl	H			540	1 310	4 300
	H	OMe			119	300	905
	H	Me			101	225	760
	H	Cl			430	930	3 200

[a] Rate constant for base-catalysed process after deduction of rate constant for [NaOMe] = 0.

TABLE 4

Effects of substituents X and Y on the rates of cleavage of p-$XC_6H_4C(MMe_3)=NC_6H_4Y$-p in methanol alone at 25.0 °C

M	X	Y	k_{rel}	log k_{rel}/σ	log k_{rel}/σ^+
Sn	H	H	1.00		
	OMe	H	1.21		
	Me	H	0.96		
	Cl	H	0.90		
	H	OMe	1.67	0.82	
	H	Me	1.46	0.96	
	H	Cl	0.49	1.3	
Si	H	H	1.00		
	OMe	H	2.04	1.15	0.4
	Cl	H	0.60	0.98	1.9
	H	OMe	3.90	2.2	0.8
	H	Me	2.13	1.9	1.0
	H	Cl	0.40	1.8	3.5

TABLE 5

Effects of substituents X and Y on the rates of cleavage of p-$XC_6H_4C(MMe_3)=NC_6H_4Y$-p in NaOMe–MeOH at 25.0 °C

X	Y	k_{rel}(M = Sn) [a]	k_{rel}(M = Si) [a]
H	H	1.0	1.0
OMe	H	0.29	0.33
Me	H	0.43	
Cl	H	3.97	4.25
H	OMe	0.76	0.93
	Me	0.55	0.74
	Cl	4.05	3.09

[a] Rate constants relative to that for X = Y = H; the value shown in each case is the mean of the values for 1M and 2M-base.

For the tin compounds the base-catalysed cleavage was also studied in a 4 : 1 v/v mixture of Me_2SO and 0.01M aqueous NaOH. In this medium the spontaneous cleavage is negligibly slow (a similar observation was made for cleavage of 2-trimethylsilylpyridine [5]), but in the case of the chloro-compounds there was some hydrolysis of the formed imines, p-$ClC_6H_4CH=NPh$ and $PhC=NC_6H_4Cl$-p to the corresponding aldehydes and amines, and this had to be taken into account in determining the rate constant. The results are shown in Table 8, and since the pattern of substituent effects is not significantly different from that in MeONa–MeOH they are not specifically discussed below.

TABLE 6

Activation parameters for neutral and base-catalysed cleavages of $PhC(MMe_3)=NPh$

	M	θ/°C	[NaOMe]/M	10^5k/s^{-1}	E_a/kcal mol^{-1}	$\Delta S^‡$/cal mol^{-1} K^{-1}
(a) In MeOH						
	Sn	25.0	0	69	15.9	−22
		35.0	0	175		
		45.0	0	370		
	Si	25.0	0	1.36	10.0	−49
		40.0	0	3.12		
		45.0	0	5.03		
(b) In MeONa–MeOH						
	Sn	25.0	2.01	316 [a]	14.1	−25
		35.0	2.01	667 [a]		
		45.0	2.01	1 415 [a]		
	Si	25.0	0.502	149	14.6	−25
		35.0	0.502	319		
		50.0	0.502	1 000		

[a] After allowance for neutral reaction.

Some rate constants observed for the parent tin compound in methanol (or MeOD) containing small concentrations of acetic acid alone or in the presence of sodium acetate to provide buffer solutions and lithium perchlorate to maintain the ionic strength constant are shown in Table 9, along with values of the rate constant k(A), given by deducting from the observed value the value in neutral methanol, and of the specific rate constant $k(A)/[MeCO_2H]$. The rates are virtually unaffected by changing from MeOH to MeOD.

TABLE 7

Solvent isotope effects for cleavage of p-$XC_6H_4C(MMe_3)=NC_6H_4Y$-p in MeOZ at 25.0 °C

M	X	Y	Z	[MeONa]/M	10^5k/s^{-1}	R.i.e.[a]	P.i.e.[b]
Sn	H	H	H	0	67	1.3	1.1
			D	0	53		
			H	1.00	195	0.93 [c]	1.5
			D	1.00	190		(1.7)
			H	2.00	383	1.0 [c]	1.5
			D	2.00	365		(1.6)
Si	H	Cl	H	0	0.55	1.83	
			D	0	0.30		
	H	OMe	H	0	5.30	1.75	
			D	0	3.03		
	MeO	H	H	0	2.78	1.74	
			D	0	1.60		
	H	Cl	H	2.00	3 200	0.94	
			D	2.00	3 400		
	H	OMe	H	2.00	910	1.03	
			D	2.00	880		
	MeO	H	H	2.00	320	1.07	
			D	2.00	298		

[a] $k(MeOH)/k(MeOD)$. [b] Product rate RH/RD on cleavage of $RMMe_3$ in 1 : 1 MeOH–MeOD; the values in parentheses are those obtained after allowing for the neutral process. [c] After allowance for contribution of neutral process.

Neutral (*Spontaneous*) *Cleavage*.—There is an obvious analogy between these spontaneous cleavages and those observed for 2-pyridylMMe$_3$ compounds by Webster and his co-workers.[8-10] The $C_6H_5C(MMe_3) : NC_6H_5/2$-$C_5H_4N\cdot MMe_3$ reactivity ratios are 0.45 and 30 for M = Si and Sn, respectively. Spontaneous cleavage was also observed recently for 2-trimethylsilyl-benzothiazole and -1-methylbenzimidazole.[7]

For the pyridine compounds Webster *et al.* discussed the mechanism in terms of Scheme 1,* involving, in step a, conversion of the hydrogen-bonded species (III) into the (possibly hypothetical) intermediate (IV), which then breaks down directly to the final products with migration of H from N to C as the C–M bond breaks (route b) or initially gives the zwitterion (V), which then rapidly isomerizes to pyridine (route c + d). Because of the smallness of the isotope effect on changing from H_2O to D_2O (or MeOH to MeOD) they favoured rate-determining formation of the intermediate (IV), but could not rule out the possibility that process b or c is synchronous with a.

Because of the analogy between the pyridine and

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* In the Schemes, N→H denotes hydrogen-bonding.

imine systems, we shall first assume that the imino-compounds are also cleaved by a cyclic mechanism, although, while there are definite similarities between the results in the two systems there are also some clear differences, as revealed in the following comparisons.*

TABLE 8

Rates of cleavage of p-X·$C_6H_4C(SnMe_3)$=NC_6H_4Y-p in NaOH–Me_2SO–H_2O at 25.0 °C [a]

X	Y	$10^5k/s^{-1}$	k_{rel}
H	H	440	1.00
OMe	H	170 [b]	0.39
Me	H	220	0.50
Cl	H	2 370	5.4
H	OMe	320 [b]	0.73
H	Me	270	0.61
H	Cl	2 550	5.8

[a] The medium was Me_2SO–0.0100M-NaOH (4 : 1 v/v). [b] A wavelength of 330 nm was used to monitor the reaction.

(a) The activation entropies, $\Delta S^‡$, have large negative values, *viz.* —49 and —22 cal mol^{-1} K^{-1}, respectively, for PhC($SiMe_3$)=NPh and PhC($SnMe_3$)=NPh, compared with —30 for both of the 2-C_5H_5N·MMe_3 compounds. (We have calculated $\Delta S^‡$ values on the basis of first-order rate constants, and an adjustment of +6 units has been made to the values derived by Webster *et al.* by use of second-order constants.[8]) Such values are consistent with a rather rigid cyclic transition state formed from two reactant molecules, and the larger negative value for the silicon compound would be consistent with the development of a greater degree of charge in the transition state (see below).

(b) The tin compound PhC($SnMe_3$)=NHPh is more reactive than the corresponding silicon compound by a factor of 49. For the pyridine derivatives Webster *et al.* found the silicon and tin compounds to react at similar rates in MeOH, but in H_2O and EtOH the tin compound was *ca.* 20 times the more reactive.[8]

TABLE 9

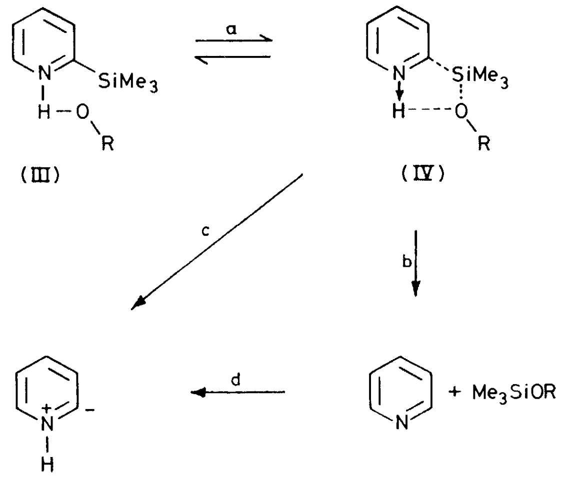
Acetic acid-catalysed cleavage of PhC($SnMe_3$)=NPh in MeOH or MeOD at 25.0 °C

Solvent	10^3[AcOH]/M [a]	10^3[NaOAc]/M	10^3[$LiClO_4$]/M	$10^5k/s^{-1}$	$10^5k(A)/s^{-1}$ [b]	10^5k(A)/ [AcOH]/ l mol^{-1} s^{-1}
MeOH	0.00			67		
	5.00			460	390	7 800
	15.00			1 260	1 190	7 900
	45.00			3 520	3 450	7 700
	5.00	5.0	38.5	465	400	8 000
	10.00	10.00	33.5	865	800	8 000
	15.00	15.00	28.5	1 265	1 200	8 000
	30.00	30.00	13.5	2 440	2 370	7 900
MeOD	0.00			53		
	5.00			445	390	7 800
	15.00			1 230	1 180	7 900
	45.00			3 540	3 490	7 800

[a] In MeOD, AcOD was used. [b] Observed k minus value in neutral solvent.

(c) The r.i.e. has a value of 1.3 for methanolysis of the parent imino-tin compound, which compares with values of 1.0—1.25 observed for hydrolysis of the pyridyl-silicon and -tin compounds. However, the r.i.e.s for the several iminosilicon compounds examined are distinctly larger, *viz. ca.* 1.8, and too large to be associated with absence of breaking of the O–H bond, as were the r.i.e. values for the pyridine compound.[8] A value of 3.3 was observed for 2-trimethylsilyl-1-methylbenzimidazole.[7]

(d) The cleavages of the imino-compounds are catalysed by base, and those of the iminotin compounds, at least, also by acid (the effect of acid on the imino-silicon compounds was not examined), whereas Webster *et al.* found that the cleavages of the pyridine compounds were markedly retarded by acid and little affected by base.[8] In this respect the cleavages of the imino-compounds show a closer similarity to those of 2-trimethylsilyl-benzothiazole and -1-methylbenzimidazole,[7] and to methanolysis of anilinotrialkylsilanes.[11]



SCHEME 1

The most revealing features of the results for the imino-compounds are the effects of the substituents X and Y. It will be seen from Table 4 that for the imino-silicon compounds electron-releasing substituents in either ring increase the rate while the electron-withdrawing substituent p-Cl lowers it, the effects being larger for variation of Y. At first sight this might seem to indicate

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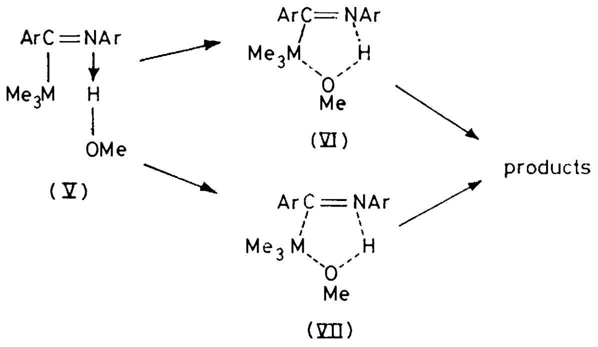
* The cyclic mechanism implies an *E*-configuration for the imino-compounds. This may not be the preferred state, but we assume that configurational interchange occurs very readily, as usual for imine derivatives.

the generation of positive charge at both ends of the C=N linkage on going to the (highest energy) transition state, but we note that the pK_a values of $\mathrm{XC_6H_4C{=}\overset{+}{N}HBu^t}$ vary substantially with variation of X, the ρ value being 1.6;[12] moreover σ^+ constants have to be used, showing that there is marked conjugative delocalization of the positive charge on the protonated nitrogen atom into the aromatic ring. Furthermore, the free energies of formation of the hydrogen-bonded complexes between $\mathrm{XC_6H_4CH{=}NC_6H_4Y}$ and p-$\mathrm{O_2NC_6H_4OH}$ show a greater variation for change of X than of Y,[13] and it is likely that this would be the case also for formation of the protonated species. Thus if in the reactions of the imino-compounds positive charge were developed at the N of the C=N bond and no charge at C, then the effects of varying X could be expected to be greater than those of varying Y. If a substantial positive charge were developed at N, with a small negative charge at C, then electron release by the substituents X would still increase the rate, though rather less than that by the substituents Y, which is what is observed.

For the three substituents the effects of varying X and Y correspond to very rough ρ values of −1.1 and −1.9, respectively. Since the ρ value for variation of Z in the equilibrium protonation of the benzylideneaniline derivative p-$\mathrm{Me_3\overset{+}{N}C_6H_4CH{=}NC_6H_4Z}$ in water is only −1.5,[14] the value of −1.9 for variation in Y in the cleavage implies a substantial development of positive charge at the N atom, *i.e.* in cyclic processes [starting from the H-bonded species (V)] such as those depicted in Scheme 2, the proton transfer from O to N must be considerably advanced in the transition state, and the r.i.e. value of 1.8 is to be associated with a degree of formation of the N=H bond which has largely compensated for the breaking of the O–H bond. We thus envisage the transition state as being either (VI) or (VII) (Scheme 2). In (VI), there is some formation of the O–Si bond without breaking of the C–Si bond, and some of the negative charge developed at Si will be relayed to the attached C of the C=N bond. If, as we favour, there is also a small amount of breaking of the C–Si bond, as in (VII), this will put a rather larger, but still small, negative charge on the C atom.



SCHEME 2

A minor difficulty associated with this picture is that the effects of the X groups are better related to their σ than their σ^+ constants; Table 4 shows that while there is reasonable agreement between the log k_{rel}/σ ratios for X = p-OMe and p-Cl, there is marked disagreement between the log $k_{\mathrm{rel}}/\sigma^+$ ratios. This may be related to the smallness of the ρ value.

With the imino-tin compounds (II) less charge is developed on both aromatic rings on going to the transition state, and the effects of X are very small. Since the r.i.e. of 1.3 is smaller than that for the silicon compounds, the degree of proton transfer must be even greater (if, as we suggest, the low r.i.e. values are to be attributed to large rather than small degrees of proton transfer), and the effect of this must be offset by significantly greater degree of C–M bond breaking. The p.i.e. value of *ca.* 1.1 observed for the parent tin compound is consistent with the mechanism depicted in Scheme 2 since the zwitterion (ylid) initially produced would not be expected to show a kinetic isotope effect significantly larger than 1 in its reaction with MeOH and MeOD.

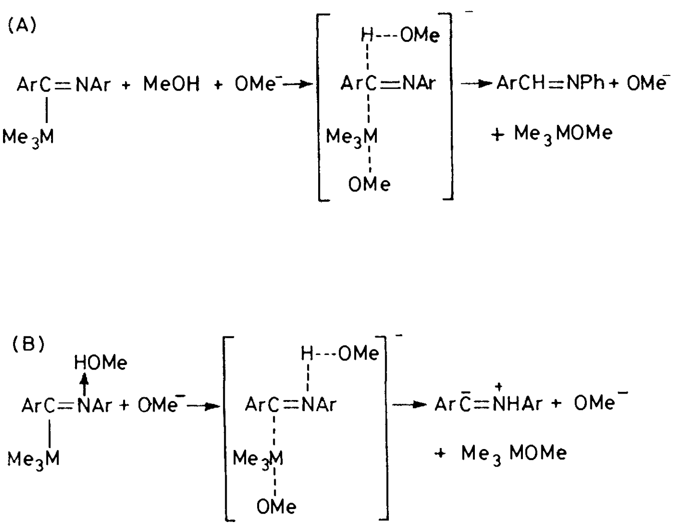
It is of interest to look again at the results for the pyridine compounds in the light of the above discussion. We differ from Webster *et al.* in concluding that the small solvent isotope effects for the imino-compounds arise from a large degree of proton transfer, rather than a small degree, as they suggested for the pyridine compounds.[8] It seems rather unlikely that there is such a drastic difference between the positions of the transition states if the same cyclic mechanism operates for both sets of compounds, especially in view of the similarity in the rates of reaction, and so we suggest that there is also fairly complete proton transfer from oxygen in the transition state for the reactions of the pyridine compounds. Anderson and Webster found that a methyl substituent in the various positions of the pyridine ring had only small effects on the rate, implying a fairly small development of charge, but there could be a greater degree of C–$\mathrm{MMe_3}$ bond breaking, so that there is little overall charge created on the ring. Interestingly, Anderson and Webster found that whereas 4- and 6-Me substituents increased the rate a 5-Me substituent slightly lowered it;[10] this would be consistent with development of a small positive charge at the nitrogen atom and of a smaller *negative* charge at the 2-carbon atom, as would be expected if a significant amount of C–$\mathrm{SiMe_3}$ bond breaking accompanied the proton transfer. However, Anderson and Webster chose not to argue along these lines because of the substantial variations in the activation entropies associated with the methyl substitutions.

It remains to consider briefly non-cyclic mechanisms for the cleavages of the imino-compounds. Such mechanisms were not explicitly considered by Webster and his colleagues in the case of pyridine compounds, for which the cyclic process offers such a satisfactory explanation of the observed retention of configuration at the silicon atom during the cleavage.[9] A variety of mechanisms (see, for example, ref. 15) can be written for ‘spontaneous’ processes involving the solvent, all of which would be consistent with the observed kinetics, although some can be readily excluded; *e.g.* attack by MeOH on the silicon atom of free imino-compound (since MeOH could not be that effective as a nucleophile relative to MeO^-), or rate-determining proton transfer to the nitrogen atom of an M^V complex $[PhC(MMe_3OMe)=NPh]^-$. The simplest alternative to the cyclic process is that in which there is pre-equilibrium formation of the N-protonated species, followed, as a result of attack by MeO^-, by rate-determining cleavage of the C–M bond, possibly with simultaneous proton migration from N to C. This would be consistent with the kinetic data (including the isotope effects [15,16]), and with the substituent effects, since the distribution of charge around the C=N bond could be much the same as proposed for the cyclic process.

Base Cleavage.—The solvent isotope effects in the base cleavages are especially revealing since the r.i.e. and p.i.e. are fairly normal for the one tin compound studied but the r.i.e.s for the silicon compounds are quite abnormal. (No p.i.e.s are available for the latter.)

We first note that the p.i.e.s of 1.5 observed for the cleavage of the parent tin compound in 1M and 2M-NaOMe–MeOH refer to the products of both neutral and base-catalysed processes; allowance for the contribution from the neutral process leads to slightly higher values of 1.7 and 1.6 for the base-catalysed process at 1M and 2M-base, respectively. R.i.e.s of *ca.* 0.96 or more are common in the base cleavages of $R–SnMe_3$ bonds, and are accompanied by p.i.e. values of *ca.* 2 or higher, the ratio r.i.e. : p.i.e. having a value in the region of 0.5. Such behaviour is as expected for a process involving electrophilic assistance in the rate-determining proton transfer from the solvent to the separating R group.[1-3] For the imino-tin compound the r.i.e. : p.i.e. ratio of 0.58 is a little higher than usual, but cannot be regarded as abnormal, especially in view of the magnitude of the possible errors in the p.i.e. values. Thus the data are consistent with the usual mechanism for tin compounds, shown as route (A) in Scheme 3. (In this Scheme, for convenience we have shown only processes involving synchronous C–M breaking and M–OMe bond making, but it should be appreciated that we cannot rule out the possibility that M^V species are formed as real intermediates.[1-3]) However, for the imino-compounds the electrophilic assistance might in principle involve proton transfer to N rather than C, as in route (B) of Scheme 3, but in this case the p.i.e. would be determined in the interaction of the ylid $Ph\overset{-}{C}=\overset{+}{N}HPh$ with the solvent, and a value of *ca.* 1.0 (as observed for the neutral cleavage) would be expected, rather than the observed 1.6.

For base cleavages of $RSiMe_3$ compounds r.i.e. values in the region of 0.5 are normal, and are consistent with a transition state in which the methoxide ion is fully or almost fully attached to the silicon atom, with no assistance from proton transfer to the R group.[1,2,5] (It is likely, however, that there is some electrophilic assistance in cleavage of $PhCH=CHCH_2SiMe_3$, in which the leaving group is highly susceptible to attack by electrophiles, and slightly higher than usual values of 0.60—0.65 are observed for the r.i.e.[3]) The r.i.e. values of *ca.* 1.05 observed for the two imino-silicon compounds studied suggest that there is substantial electrophilic assistance. Direct electrophilic attack at the C of the C=N bond should not be especially easy, and it seems likely that the assistance is to be associated with the presence of the nitrogen atom, and the simplest assumption is that there is proton transfer to N as in process (B) of Scheme 3. It is significant, in this connection, that the silicon compounds are cleaved by base more readily than the corresponding tin ones, by a factor of *ca.* 2. This is the first time that we have observed such an order for cleavage of Me_3MR compounds in MeONa–MeOH; $Me_3Si–R$ bonds are generally less readily cleaved than $Me_3Sn–R$ ones when protons are readily available (as in MeOH) to provide the usual electrophilic assistance for the tin compounds, but more readily in media in which protons are less readily available [17,18] (*e.g.* in MeOH–Me_2SO or H_2O–Me_2SO mixtures containing a large proportion of Me_2SO [17]). The reversal of the usual reactivity sequence in the case of the imino-compounds can be nicely attributed to the opposite effect, namely the operation of electrophilic assistance for the silicon as well as the tin derivatives.

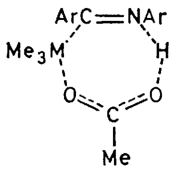


SCHEME 3

The close similarity of the activation parameters for the base-catalysed cleavages of the imino-tin and -silicon compounds in association with rather similar rates of reaction is in keeping with the view that both sets of compounds react by an electrophilically assisted mechanism, but it cannot be taken as positive support for an identity of mechanism since $RSiMe_3$ and $RSnMe_3$ compounds known to react by different mechanisms do not show consistently different activation parameters.[1,2]

The effects of substituents on the base-catalysed reactions remain to be discussed. We first note that the proton transfer responsible for the electrophilic assistance would, whether to C or N, be expected to be much less advanced than the $C–MMe_3$ bond breaking, as in electrophilically assisted base cleavage of X·$C_6H_4CH_2$–$SnMe_3$ bonds.[19] Thus since the development of negative charge at the C atom of the C=N bond will greatly dominate in determining the substituent effects, the quite marked acceleration by the *p*-Cl group in both rings is understandable. (The carbanionic charge will be relayed into the aryl-N ring by polarization of the π-system, and the effects of substituents in that ring on this charge could be comparable with those of substituents in the aryl-C ring; at the same time the small degree of proton transfer to N would be affected, in the opposite sense, to comparable extents by substituents in both rings, as we saw in discussing the neutral cleavage, and so overall the effects of the *p*-Cl group could be similar from both rings, as observed.) Furthermore, this dominance of the influence of the carbanionic charge would mean that the substituent effects could be similar for the tin and silicon compounds even if for the tin compounds the proton transfer were to carbon, as usual, and for the silicon compounds to nitrogen. The unusually small deactivating effects of the *p*-OMe and *p*-Me groups in the aryl-N group are also understandable, since it has been shown that this pattern accords with observation and calculations for other carbanions, *viz.* the phenyl and thienyl anions $XC_6H_4^-$ and $XC_4H_2S^-$, in which the negative charge is dispersed over the ring by π-polarization rather than conjugation.[4] The effects of the *p*-OMe and *p*-Me groups in the aryl-C ring relative to those of the *p*-Cl groups are more normal, suggesting that there is some conjugative delocalization of the forming carbanionic charge into this ring, associated with twisting of the ring from coplanarity with the C=N bond; evidence for delocalization of the lone pair of the N atom into the aryl-N ring of benzylideneanilines gives support to this possibility.[20]

Acid Cleavage.—We investigated the possibility of acid catalysis for the parent tin compound PhC($SnMe_3$)=NPh only. The results in Table 9 show that there is very marked catalysis by acetic acid, which is *ca.* 70 times as effective as sodium methoxide. The r.i.e. for the acid-catalysed process is 1.0. It is clear from the detail of the results that at the low oxonium ion concentrations involved the acetic acid is effectively the sole catalyst.



(VIII)

(This contrasts with the results for solvolysis of *m*-$MeC_6H_4NHSiPr^i_3$ in a similar medium, which indicate specific oxonium ion catalysis.[11]) It is attractive to attribute this great effectiveness of acetic acid to a seven-centred cyclic process, (VIII), corresponding to that for the spontaneous cleavage in MeOH alone. If that is so, the acetic acid is *ca.* 3 000 times as reactive a reagent as MeOH, and the isotope effect of unity might reflect a transition state close to the reagents. A more detailed study of the acid-catalysed process in these and related reactions seems to be necessary, and we hope to undertake it.

EXPERIMENTAL

Preparation of C-(*Trimethylstannyl*)*benzylideneanilines.*—The compounds *p*-$XC_6H_4C(SnMe_3)$=NC_6H_4Y-*p* were prepared from the corresponding *C*-chlorobenzylideneanilines and Me_3SnLi as described by Jappy and Preston.[21] However, we did not, as they did, use column chromatography for purification because in our hands this caused some decomposition. After distillation the products were recrystallized from light petroleum, b.p. 60—80 °C.

Physical constants and analyses were as follows: (a) X = H; (Y =) H, b.p. 143 °C at 0.3 mmHg, m.p. 50 °C (lit.,[21] m.p. 47 °C); OMe, b.p. 150 °C at 0.05 mmHg, m.p. 49—50 °C (Found: C, 54.5; H, 5.6; N, 3.7. $C_{17}H_{21}ONSn$ requires C, 54.6; H, 5.7; N, 3.7%); Me, m.p. 54 °C (Found: C, 57.2; H, 5.8. $C_{17}H_{21}NSn$ requires C, 57.0; H, 5.9%); Cl, b.p. 133 °C at 0.01 mmHg, m.p. 85—86 °C (Found: C, 51.2; H, 4.8. $C_{16}H_{18}ClNSn$ requires C, 50.8; H, 4.8; N, 3.7%); (b) Y = H, (X =) OMe, b.p. 160 °C at 0.1 mmHg, m.p. 68—69 °C (Found: C, 55.0; H, 5.7%); Me, b.p. 150 °C at 0.5 mmHg, m.p. 62—63 °C (Found: C, 57.5; H, 6.9%); Cl, b.p. 133 °C at 0.1 mmHg (Found: C, 51.6; H, 4.9; N, 3.8%).

The ^1H n.m.r. spectra were all as expected.

Preparation of C-(*Trimethylsilyl*)*benzylideneanilines*, p-$XC_6H_4C(SiMe_3)$=NC_6H_4Y-p.—The appropriate *C*-chlorobenzylideneaniline (0.1 mol) in tetrahydrofuran (100 cm^3) was added slowly under nitrogen with stirring to a mixture of magnesium turnings (0.1 g atom), chlorotrimethylsilane (0.1 mol), and tetrahydrofuran (100 cm^3) containing hexamethylphosphorotriamide (0.1 mol), the temperature being kept at *ca.* 0 °C throughout. The mixture was then allowed to warm to room temperature and stirred until all the magnesium had been consumed. Saturated aqueous ammonium chloride was added, and the product extracted with light petroleum. The extract was washed, dried (Na_2SO_4), and fractionally distilled at low pressure, the b.p.s at specified pressures (mmHg) being: (a) X = H; (Y =) OMe, 130 °C at 0.3; Me, 130 °C at 0.7; Cl, 119 °C at 0.5; (b) Y = H, (X =) OMe, 145 °C at 0.6; Cl, 162—164 °C at 2; H, 120 °C at 0.1.

The mass and ^1H n.m.r. spectra confirmed the identities of the products, but they all contained appreciable quantities of the corresponding benzylideneanilines, XC_6H_4CH=NC_6H_4Y; attempts to remove these seemed to cause further decomposition and the impure products were used for the cleavages since the presence of the benzylideneanilines does not interfere with the rate studies. The identity of the u.v. spectra of the cleavage products in MeOH with those of corresponding solutions of the appropriate benzylideneanilines confirmed that the latter were the only significant impurities.

Rate Measurements.—These were carried out spectrophotometrically with a Hitachi–Perkin-Elmer model 323 u.v. spectrophotometer; a wavelength of 310 nm was used unless otherwise indicated. The general procedures have been described previously,[1,2] but because the imino-compounds react with methanol alone, a solution of the appropriate quantity of the substrate in n-heptane (1 μl) was added to 3 cm^3 of MeOH or MeONa–MeOH contained in the absorption cell situated in the thermostatted cell-holder, the cell being briefly removed for shaking; automatic recording of the absorption was then begun. For reactions in Me_2SO–H_2O, 0.0100M aqueous NaOH (1 vol) was mixed with Me_2SO (4 vol); because of hydrolysis of the imino-cleavage products the Swinbourne method[22] was used to determine the rate constants in the case of the *p*-chloro-compounds. Rate constants were reproducible to within ±3%.

Except for the *p*-chloro-compounds, the u.v. spectra of the solutions after 10 half-lives were identical to those of the expected cleavage products.

Product Isotope Effects.—The general procedures have been described.[1,2] The n.m.r. method was used to determine the ArCH=NAr′/ArCD=NAr′ ratios obtained from $ArC(SnMe_3)=NAr'$ compounds, the intensity of the signal from the CH proton being compared with that of an internal standard. The signal was absent, as expected, when 100% MeOD was used for the cleavages.

The p.i.e.s could not be satisfactorily obtained for the silicon compounds because of the presence in them of the ArCH=NAr′ species.

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