Cleavages of 1-Methyl-2-trimethylsilylbenzimidazole and 2-Trimethylsilylbenzothiazole in Methanol and Related Media

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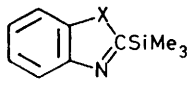
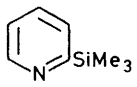
First-order rate constants k at 25 °C have been determined for the cleavage of 1-methyl-2-trimethylsilylbenzimidazole (I) and 2-trimethylsilylbenzothiazole (II) in MeOH, alone or containing NaOMe, and in 5 : 2 v/v MeOH–H_2O containing $HClO_4$. Compound (I) is cleaved rapidly by neutral methanol (10^3k 51 s^{-1}) (and also by H_2O, 10^3 k 110 s^{-1} or EtOH, 10^3 k 3.0 s^{-1}); very small amounts of NaOMe do not affect the rate (which thus refers to a spontaneous process), but larger amounts induce a base-catalysed process (10^2 k_s 63 l mol^{-1} s^{-1}). The data for the neutral cleavage of (I), including a rate isotope effect, r.i.e. [given by the ratio k(MeOH)/k(MeOD)], of 3.3, can be interpreted either in terms of the cyclic mechanism involving a solvent molecule previously proposed for cleavage of 2-trimethylsilylpyridine or one in which MeO^- attacks the protonated substrate. In base cleavage (I) gives an r.i.e. of 1.1, and this is interpreted in terms of proton transfer to the N of the N=C bond synchronous with breaking of the C–$SiMe_3$ bond, but (II) gives an r.i.e. of 0.46, suggesting that there is little if any such electrophilic assistance. The low product isotope effects (the product ratio RH/RD on cleavage in 1 : 1 MeOH–MeOD) of 1.2—1.3 for neutral cleavage of (I) and the base cleavages of (I) and (II) are attributed to the fact that the isotopic composition of the products is determined in a step involving transfer of hydrogen to a localized carbanion. Addition of acid greatly raises the rate of cleavage of (II) in 5 : 2 MeOH–H_2O, but reduces it for (I), for which the rate levels off at a value thought to refer to the fully protonated species. The acid-catalysed processes may involve attack of a solvent molecule at silicon in the protonated species.

As part of a systematic study of cleavage of C–Si bonds, especially those catalysed by base, we have examined the cleavages of the C–$SiMe_3$ bonds of 1-methyl-2-trimethylsilylbenzimidazole (I) and 2-trimethylsilylbenzothiazole (II), mainly by methanol or aqueous methanol. These compounds were shown previously by Jutzi and his colleagues to be cleaved by water in dichloromethane,[1,2] and a cyclic mechanism was suggested, similar to that proposed by Webster and his colleagues for neutral cleavages of 2-trimethylsilylpyridine (III) and related compounds (see below).[3,4] We have now confirmed by kinetic studies that (I) and (II) are cleaved by neutral methanol or aqueous methanol, and have shown, in addition, that both compounds also undergo base-catalysed and acid-catalysed cleavage.



(I) X = NMe
(II) X = S

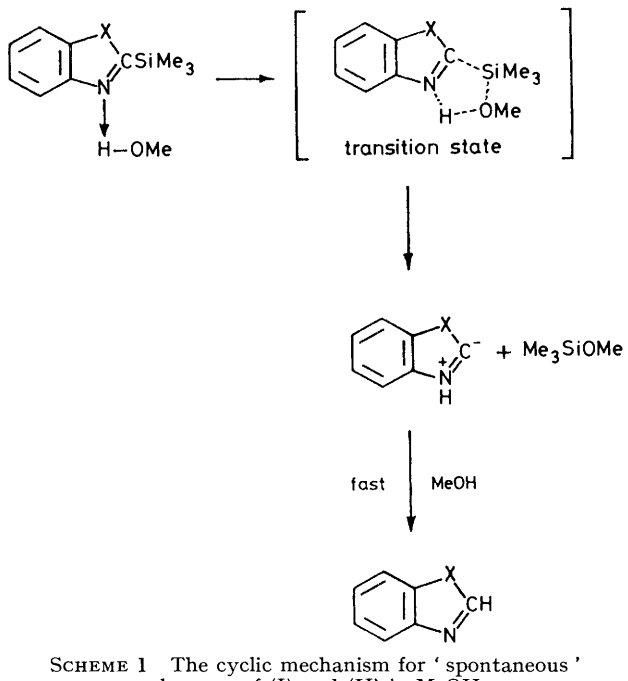


(III)

RESULTS AND DISCUSSION

The observed first-order rate constants k for cleavage of (I) and (II) under various conditions are shown in Tables 1 and 2. For base-catalysed cleavages, values of the specific (second-order) rate constant k_s are also shown where appropriate. Solvent isotope effect data are given in Table 3; 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 $RSiMe_3$ in 1 : 1 MeOH–MeOD, in the presence of base where appropriate.

Neutral Cleavages.—The 1-methylbenzimidazole derivative (I) undergoes very ready cleavage in neutral methanol, *ca.* 1 750 times as rapidly as the pyridyl compound (III)[3] at 25 °C. The presence of up to at least 1×10^{-3}M-base does not affect the rate, which is thus constant over an appreciable pH range indicating that the cleavage in neutral methanol is a true 'spontaneous' process. The large negative entropy of activation (see Experimental section), *viz.* *ca.* —46 cal mol^{-1} K^{-1}, is noteworthy, and compares with a value of —36 cal



SCHEME 1 The cyclic mechanism for 'spontaneous' cleavage of (I) and (II) in MeOH

mol^{-1} K^{-1} observed for cleavage of (III) in MeOH.[3] (We used first-order rate constants to derive the value of $\Delta S^{\ddagger}$, and the value reported by Webster *et al.*[3] has been adjusted appropriately.)

Cleavage of (I) at 25 °C is 2.2 times as fast in H_2O and 17 times as slow in EtOH as in MeOH; the corresponding ratios for (III) are 10 (at 30 °C) and 157 (at 50 °C).[4]

There is no reason to believe that the neutral cleavages of (I) and (III) have different mechanisms, and so we first assume for (I) the route, starting from a hydrogen-bonded species, shown in Scheme 1,* analogous to that proposed for (III) by Webster *et al.*[3] There is one notable difference, however, between the results for (I) and (III), and that is that the r.i.e. observed for (I) in methanol, *viz.* 3.3, is markedly larger than that found for (III) in water, *viz.* 1.0—1.2,[3] which was very reasonably taken by Webster *et al.* to indicate that there was only a very small degree of proton transfer from the solvent molecule to the nitrogen atom in the (rate-determining) transition state. Since (III) is much less reactive than (I), the transition state would be expected to be further from the reactants, and so the proton transfer more advanced, for (III) than (I), for which the r.i.e. indicates substantial proton transfer, and we suggest that if both (I) and (III) do react by the cyclic mechanism, the near-unity value of the r.i.e. for (III) is to be associated not with a small degree of proton transfer but with almost complete transfer in the transition state. The large negative activation entropies in the reactions of (I) and (III) would then be associated not only with the binding of two reactant molecules into a rather rigid cyclic transition complex but also with ordering of the solvent molecules around the markedly polar transition state. The larger rate decrease for (III) than for (I) on changing from H_2O to MeOH to EtOH as solvent would be consistent with a more advanced (and more polar) transition state for (III). It is noteworthy that for the neutral cleavage of the imino-derivatives $ArC(SiMe_3)=NAr'$ in MeOH, which may have a similar mechanism, the effects

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

TABLE 1

First-order rate constants for cleavage of (I) and (II) in neutral and basic media at 25.0 °C

Compound	Solvent	10^4[Base]/M [a]	$10^5k/s^{-1}$ [b]	10^5k(B)/s^{-1} [c]	10^5k_s/l mol^{-1} s^{-1} [d]
(I)	MeOH	None	5 100		
		1.6	5 100		
		10	5 100		
		100	5 700	*ca.* 600	*ca.* 60 000
		1 000	11 600	6 500	65 000
		2 000	19 000	13 900	69 500
		3 000	26 000	21 900	70 000
	MeOD	None	1 550		
		1.6	1 550		
		10	1 610		*ca.* 60 000
		100	2 160	610	61 000
		1 000	7 800	6 250	62 500
		2 000	13 500	11 950	60 000
	EtOH	None	300		
	H_2O	None	11 000		
		1.0	11 000		
		10	11 500		
(II)	MeOH	10	950		950 000
		20	2 040		1 020 000
		50	5 100		1 020 000
		100	10 400		1 040 000
	MeOD	56.5	12 500		2 210 000

[a] Concentration of NaOMe or NaOH as appropriate. [b] Observed first-order rate constant. [c] For (I), observed value of k minus value in neutral solution. [d] k(B)/[NaOMe] for (I) and k/[NaOMe] for (II).

TABLE 2

First-order rate constants at 25.0 °C for cleavage of (I) and (II) in H_2O or 5 : 2 v/v MeOH–H_2O, either neutral or containing perchloric acid

Compound [a]	Solvent	10^4[$HClO_4$]/M [b]	$10^5k/s^{-1}$ [c]
(I)	H_2O	None	11 000
		3.5	84
		350	69
		3 500	40
	MeOH–H_2O	None	7 500
		5.1	1 410
		340	1 390
		680	1 060
(II)		None	8.7
		0.69	1 400
		1.71	4 100
		3.42	8 400
		134.2	*d*

[a] Concentration: (I) 46×10^{-5}M; (II) 60×10^{-5}M. [b] For MeOH–H_2O, the acid concentration is assumed to be two-sevenths of that of the aqueous $HClO_4$, 2 vol of which was mixed with 5 vol of methanol. [c] Observed first-order rate constant. [d] Too fast to measure.

TABLE 3

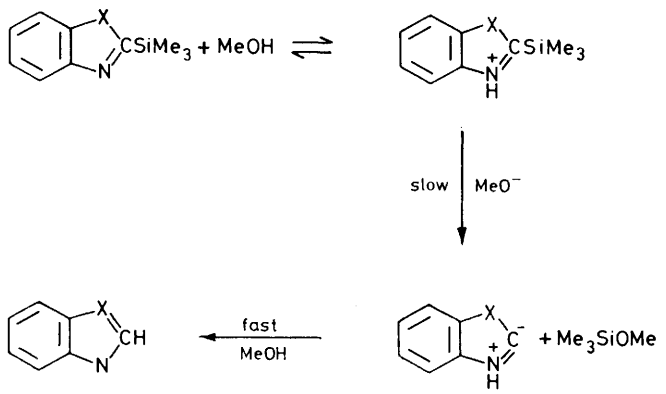
Solvent isotope effects in neutral and base cleavage in methanol or methanolic NaOMe at 25 °C

Compound	Medium	R.i.e.	P.i.e.[a]
(I)	MeOH	3.3 [b]	1.2
	MeONa–MeOH	1.1 [c]	1.3 [d]
(II)	MeONa–MeOH	0.46 [c]	1.3 [e]

[a] Ratio RH/RD of products of cleavage of $RSiMe_3$ in 1 : 1 CD_3OH–CD_3OD. [b] Ratio of rate constant in MeOH to that in MeOD. [c] Ratio of k_s in MeOH–MeONa to that in MeOD–MeONa. [d] Value for cleavage with 0.1 and 0.1M-base. [e] Cleavage was with 0.01M-base.

of substituents in the aryl groups show that substantial charge is developed around the C=N bond in the transition state.[5]

The available data for the neutral cleavage of (I), including the r.i.e. (see ref.6), are also consistent with an ' open ' process, shown in Scheme 2, in which the slow



SCHEME 2 Open mechanism for ' spontaneous ' cleavage of (I) and (II) in MeOH

step is attack of MeO^- on the protonated species (Ia). This is analogous to the mechanism believed to operate in hydrogen-exchange at the 2-position of benzimidazole.[7,8] This type of mechanism was not explicitly discussed by Webster *et al.* for (III), although it would fit all their kinetic data, but the cyclic mechanism has the advantage of providing a nice explanation of the retention of configuration at silicon in cleavage of appropriate 2-pyridyl compounds.[3] (It is, unfortunately, impossible to say with certainty that reaction by the mechanism shown in Scheme 2 would involve inversion of configuration.) On the other hand the cyclic mechanism has the disadvantage that it represents a departure from the useful generalization that cleavages of corresponding R–$SiMe_3$ and R–H bonds under similar conditions have analogous mechanisms. Hydrogen-exchange by a spontaneous process is known to occur at the 2-positions of pyridine,[9] benzimidazole,[8] and benzothiazole,[8] and mechanisms analogous to that in Scheme 2 are accepted for these reactions.

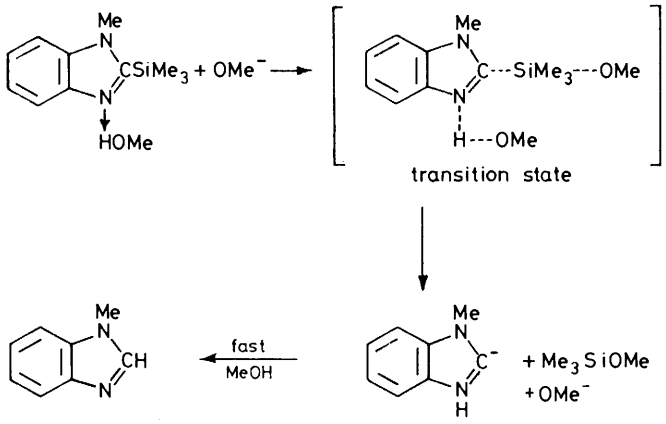
The value of the p.i.e. for (I), *ca.* 1.3, when taken along with the r.i.e. value of 3.3 indicates that the isotopic composition of the products is not determined in the rate-limiting step. This is consistent with either of the mechanisms shown in Schemes 1 and 2, since after the formation of the ylid the proton transfer from nitrogen to carbon will presumably take place *via* the solvent, and a p.i.e. close to 1 can be expected for interaction of a 2-carbanion with the solvent, as discussed for the base cleavage below.

The cleavage of the benzothiazole derivative (II) was inconveniently slow in neutral MeOH at 25 °C (there was roughly 10% of cleavage in 4 h), and was mainly examined in 5 : 2 v/v MeOH–H_2O, in which it is 870 times slower than that of (I), and can be estimated to be roughly three times slower than that of (III). Since acid and base (in MeOH) catalyse so strongly, we have no firm evidence that there is a genuine spontaneous process, with a rate independent of pH, and certainly the rate of such a process must be very much lower than that for (I). This lower reactivity can be associated with the much lower base strength of (II) (assuming that the relative base strengths of the silicon derivatives $RSiMe_3$ reflect those of the parent RH species), and thus with a poorer ability to accept a proton at N from the solvent during (Scheme 1) or before the cleavage of the C–$SiMe_3$ bond. This will be to some extent offset by the greater tendency of (II) to generate carbanionic charge at the 2-position (see the discussion of base cleavage below), but this will be less important than the relative ability of (I) and (II) to accept a proton if, as seems likely, the transfer of the light H atom is markedly more advanced in the transition state than the breaking of the C–$SiMe_3$ bond. The influence of the relative stabilities of the 2-carbanion shows up in the much greater reactivity of (I) than of (III); these compounds can be assumed to have similar base strengths, as have the corresponding RH species,[10] and so could be expected to undergo cleavage at similar rates if the ease of proton transfer to N were the only factor, but the acidity of the 2-position of 1-methylbenzimidazole is much greater than that of the 2-position of pyridine, and thus generation of carbanionic charge by splitting of the C–$SiMe_3$ bond will be much easier for (I) than for (III) [(I) is much more reactive than (III) in base-catalysed cleavage] and this makes (I) much more reactive overall than (III).

Base Cleavage.—We first consider the results for the benzothiazole compound (II), for which there is no significant competition from the spontaneous process. The base cleavage is very fast; the value of k_s is *ca.* 90 times as large as that for *p*-nitrobenzyl- or fluoren-9-yl-trimethylsilane [11,12] and *ca.* 1.5×10^6 and 3×10^6 times as large as those [13,14] for benzothien-2-yl- [13] and thien-2-yl-trimethylsilane,[14] respectively. The observed r.i.e. of 0.46 is in the usual range for cleavages of R–$SiMe_3$ bonds, consistent with separation of the carbanion R^- in the rate-determining step.[11,12]

The low p.i.e. value, of *ca.* 1.3 for (II) would have been puzzling for a compound of such high reactivity [compare the p.i.e. of 10 observed for inden-1-yl-trimethylsilane, which is about nine times less reactive than (11) [12]], if we had not recently observed values in the range 1.0—1.2 for some substituted thienyltrimethylsilanes, X·C_4H_2·$SiMe_3$-2, which have k_s values ranging from *ca.* 10^6 times smaller than that for (II) to one (for X = 3-NO_3) very similar to that for (II).[13] On the basis of those results we suggested that for carbanions derived from RH species of similar equilibrium acidities, those in which the carbanionic charge is conjugatively stabilized will discriminate more effectively between MeOH and MeOD than with those in which the carbanionic charge cannot be so delocalized. The charge in the 2-carbanion derived from benzothiazole, like those in the thienyl anions, cannot be conjugatively delocalized, except possibly for a minor interaction between the lone pair and the *d*-orbitals of the sulphur atom.

For cleavage of (I) in MeONa–MeOH the value of the first-order rate constant in the neutral solvent has to be subtracted from the observed first-order rate constant k to give the first-order rate constant k(B) for the base-catalysed process. The values of the specific rate constant k_s given by k(B)/[NaOMe], are then effectively constant over the base concentration range 10^{-2}—3×10^{-1}M. The mean value of k_s is $63\,000 \times 10^{-5}$ l mol^{-1} s^{-1}, which means that (I) is *ca.* 16 times less reactive than (II) in base cleavage, and this order of reactivity is consistent with the greater stabilizing effect of a sulphur than of a (neutral) nitrogen atom on an adjacent carbanionic centre. The stability of the forming carbanion is not the only relevant factor, however, since the r.i.e. for base cleavage of (I) is 1.1, which indicates that there is electrophilic assistance involving proton transfer from the solvent to (I) as the C–$SiMe_3$ bond breaks.[14,15] It is most unlikely that this proton transfer is to the separating carbanionic centre, since this seems to be very rare for cleavage of R–$SiMe_3$ bonds, though normal for cleavage of R–$SnMe_3$ bonds;[14,15] the only example of such transfer for a silicon compound involves the allyl derivative $PhCH{=}CHCH_2SiMe_3$, in which the relevant organic group is especially prone to attack by electrophiles.[16] It is much more likely that the proton transfer is to the nitrogen atom in the leaving group, as in Scheme 3,



SCHEME 3 Proposed mechanism of the base cleavage of (I)

especially in view of the mechanism proposed for the neutral cleavage. Furthermore, if the electrophilic assistance did arise from proton transfer to the separating carbon, an r.i.e. value of 1 would be expected to be associated with p.i.e. value in the region of 2,[14,15] whereas a p.i.e. of *ca.* 1.2 is found. For the mechanism shown in Scheme 2, the p.i.e. would not be determined in the rate-determining step, but during the subsequent proton transfer from nitrogen to the carbanionic centre, and since this would no doubt go *via* the solvent, and is to a localized carbanionic centre, a p.i.e. in the region of 1 would be expected. It is noteworthy that a high r.i.e., of 1.05, is also observed in the base cleavage of the imino-compounds $ArC(SiMe_3){=}NAr'$, and can be explained in that case also in terms of electrophilic assistance involving proton transfer to the nitrogen atom.[5]

In the light of the results for (I), it is necessary to consider why electrophilic assistance is absent or contributes only to an undetectable extent in the base cleavage of the benzothiazole compound (II). This can be understood in terms of the greater stabilization of the carbanion derived from (II) than of that derived from (I), the difference being attributable to the well established greater stabilization of a carbanion by a neighbouring sulphur than a neighbouring neutral nitrogen atom. Because of this greater stability of the carbanion from (II), no electrophilic assistance is needed; a parallel can be found in the cleavage of tin compounds $RSnMe_3$, for which electrophilic assistance is normal but which change to a mechanism involving separation of the carbanion when the stability of the latter (and the acidity of RH) is raised sufficiently.[15] However, we cannot rule out the existence of a little electrophilic assistance in the cleavage of (II), too small to have a detectable influence on the r.i.e., and this is an attractive possibility in view of the fact that solvent could already be hydrogen-bonded to the N atom when attack of the MeO^- began.

A mechanism involving simple proton abstraction from the neutral substrate, with generation of the carbanion, has been proposed for the corresponding base-catalysed hydrogen-exchange at the 2-position of thiazole at high base concentrations,[8] but as far as we are aware no-one has specifically sought evidence for synchronous proton attachment to nitrogen in this exchange or in that of imidazole systems.

We cannot adequately explain one striking feature of the base cleavage, namely the anomalously high reactivity of (II) in relation to the kinetic or equilibrium acidity of benzothiazole. The pK_a of the latter (in $CsNHC_6H_{11}$–$C_6H_{11}NH_2$) is 28.08,[17] and if the usual relationship between log k_s for the cleavage of $RSiMe_3$ and the pK_a of RH applied,[12,18] (II) would be expected to be 30 times less reactive than 9-trimethylsilylfluorene (pK_a 23.04 [19]) whereas it is actually almost 100 times more reactive. Compound (II) would also be expected to be somewhat less reactive than 9-trimethylsilylfluorene from consideration of the rates of hydrogen-exchange for benzothiazole and fluorene in MeONa–MeOH, in which fluorene is about six times the more reactive. (The second-order rate constant for deuteriodeprotonation of benzothiazole in MeONa–MeOD at 25 °C is 1.21×10^{-4} l mol^{-1} s^{-1},[20] while a value of *ca.* 7×10^{-4} l mol^{-1} s^{-1} can be estimated for the corresponding reaction of fluorene from the value of 0.31×10^{-4} l mol^{-1} s^{-1} reported for protiodetritiation.[21]) The anomaly can be viewed in another way by noting that the ratio of the k_s value for cleavage of the R–$SiMe_3$ to that for cleavage of the corresponding R–H bond (in the notional protiodeprotonation), both in MeONa–MeOH at 25 °C, is 170 000 for R = benzothiazol-2-yl and only 300 for R = fluoren-9-yl. Electrophilic assistance involving proton transfer to nitrogen, such as that we have postulated for (I) would have provided a nice explanation for the exceptionally high reactivity of (II), but we have seen that there cannot be much, if any, such assistance, and almost

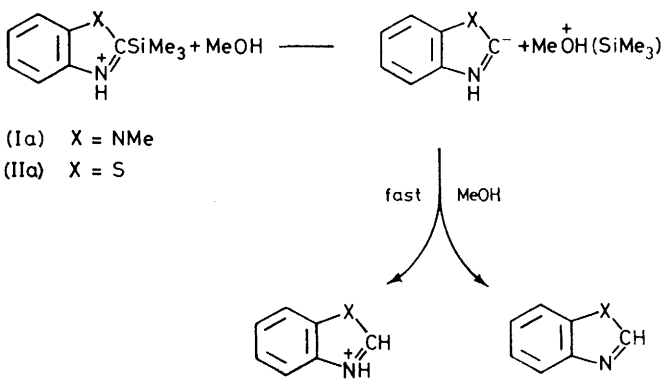
certainly not enough to enhance the rate by a factor of 10. It is possible that steric hindrance significantly lowers the reactivity of 9-trimethylsilylfluorene which would be inherent in the stability of the carbanion, but again the factor could not be large because the reactivity of this compound is in line with the pK_a of fluorene when viewed along with the data [12,18] for other $RSiMe_3$ compounds for which steric hindrance would be smaller (*e.g.* R = inden-1-yl, *p*-$O_2NC_6H_4CH_2$, or PhC≡C). However, if a little electrophilic assistance in the case of (II) and a little additional steric hindrance in the case of 9-trimethylsilylfluorene together accounted for a factor of 50, the remaining anomaly would be fairly small.

It is attractive to seek to relate the anomalous behaviour of (II) to the fact that the benzothiazolyl anion is unusual among the more stable carbanions in not being conjugatively delocalized, but arguments along these lines lead in the wrong direction. It is known that the relationship between kinetic and equilibrium acidity can break down badly for localized carbanions and thus, for example, PhC≡CH has a much higher kinetic acidity than would be expected from its pK_a,[22] whereas the rate of base cleavage of $PhC{\equiv}CSiMe_3$ is in accord with that pK_a.* By analogy the reactivity of (II) would be expected to be more accurately related to the pK_a of benzothiazole rather than to its kinetic acidity, whereas the opposite appears to be the case.

Acid Catalysis.—The effects of acid were examined in MeOH–aqueous perchloric acid (5 : 2 v/v) For (I), which is soluble in water; a few runs were also carried out in wholly aqueous solutions. The results are shown in Table 2.

For (II) the neutral cleavage does not compete effectively with the acid-catalysed process, and the observed first-order constant is roughly proportional to the concentration of acid (in the mixture) up to *ca.* 3.4×10^{-4}M, beyond which it is too high for convenient measurement. A separate spectrophotometric study showed that benzothiazole itself at 0.47×10^{-4}M concentration in 5 : 2 MeOH–H_2O was virtually unprotonated in 1.5×10^{-4}M and roughly 10% protonated in 7×10^{-1}M-acid. The silicon derivative (II) will have a rather similar base strength, and it is unlikely that more than a few percent of it is protonated even at the highest acid concentration used in the rate studies. Two possible mechanisms have thus to be considered.

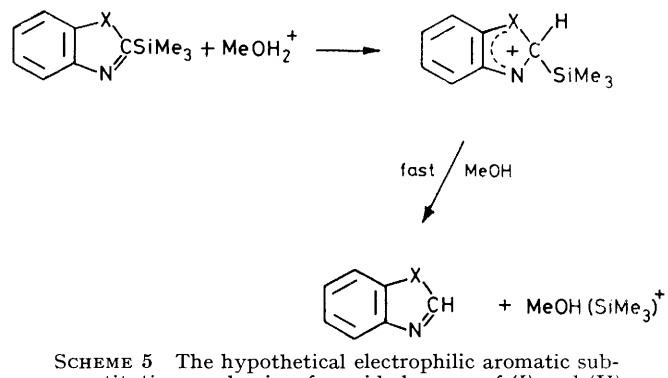
The first possibility, depicted in Scheme 4, is related to those considered for the neutral and base cleavage above, and involves rate-determining nucleophilic attack of a solvent molecule on the Me_3Si group in the protonated species (IIa). The second, shown in Scheme 5, is a completely different process, involving rate-determining proton transfer from oxonium ion to the 2-carbon atom to give a Wheland intermediate; that is, it is a straightforward electrophilic aromatic substitution. We can rule out this possibility, however, by making a comparison with data for acid cleavage of 2-trimethylsilylthiophen. Values of σ^+ of −0.80 and +0.26 have been derived for the 2-positions of thiophen and thiazole, respectively,[23] and so 2-trimethylsilylthiazole should be cleaved by this mechanism *ca.* 10^5 times less readily than 2-trimethylsilylthiophen in 5 : 2 MeOH–H_2O containing



SCHEME 4 Proposed mechanism of acid-catalysed cleavage of (I) and (II)

perchloric acid (the ρ value is *ca.* 5) and (II) will probably be even less reactive. (Compare the lower reactivity of 2-trimethylsilylbenzothiophen than of 2-trimethylsilylthiophen.[24]) 2-Trimethylsilylthiophen gives a rate constant of 19.6×10^{-5} s^{-1} at 25 °C in MeOH–0.56M aqueous perchloric acid (5 : 1 v/v),[24] and so the rates observed for (II) at much lower acid concentrations are at least 10^{10} times as large as would be expected for the mechanism shown in Scheme 5.

In the case of (I) (4.6×10^{-4}M) the presence of as little as 5.1×10^{-4}M-acid caused a 5.3 fold decrease in rate and a further 130 fold increase in the acid concentration caused only a further 1.3 fold decrease, and it is likely that the residual rate in the strongest acid used, about one-seventh that in neutral solution, is that for the fully protonated species. [A separate spectrophotometric study confirmed that 1-methylbenzimidazole, and thus (I), would be almost fully protonated even in the weakest acid used in the rate studies.] The assignment of the mechanism shown in Scheme 4 to the cleavage of (I) in acid is consistent with the ease of decomposition of 1-methyl-2-trimethylsilylbenzimidazolium iodide in



SCHEME 5 The hypothetical electrophilic aromatic substitution mechanism for acid cleavage of (I) and (II)

* The log k_s values for cleavage of 2-trimethylsilyl-thiophen, -benzofuran, and -benzothiophen, all of which give localized carbanions, lie reasonably close to the usual log k_{rel}–pK_a plot.[14]

protic solvents.[2] Taking account of the probable degree of protonation in the acid used, the fully protonated species (IIa) must be at least 200 times as reactive as (Ia). This is consistent with the expected order of stabilities of the ylids derived from (Ia) and (IIa), and with the greater reactivity of (II) than of (I) in the base-catalysed process.

EXPERIMENTAL

Preparations.—Compounds (I) [25] and (II) [1] were prepared as previously described.

Rate Studies.—The general method has been described.[11,12,14] The stopped-flow method was used for base cleavage of (II). Wavelengths of 290 and 302 nm, respectively, were used to monitor the progress of reactions of (I) and (II), which were used in *ca.* 4.6×10^{-4} and *ca.* 6×10^{-4}M concentration, respectively. The u.v. spectrum of the product was identical in all cases with that of the corresponding solution of the expected 1-methylbenzimidazole or benzothiazole, and good first-order kinetics were observed. Rate constants were reproducible to within ±3%.

The 5 : 2 v/v MeOH–H_2O solutions were made up by mixing 5 vol of methanol with 2 vol of aqueous NaOH or $HClO_4$, and the acid or base concentration in the mixture is assumed to be two-sevenths of that in the aqueous solution. In the case of (II), the organosilane was dissolved in the methanol before the mixing, but for (I), which reacts rapidly with methanol, 1 μl of a solution in n-heptane was dissolved in the MeOH–H_2O mixture at the reaction temperature.

Activation Parameters.—For cleavage of (I) in MeOH alone, values of 10^5k of 3 600, 5 100, and 5 800 s^{-1} were obtained at 16.9, 25.0, and 30.0 °C, respectively. These data give an approximate value of 6.1 kcal mol^{-1} for the activation energy, of 3.2 for log A, and of −46 cal mol^{-1} K^{-1} for the activation entropy.

Protonation of 1-Methylbenzimidazole and Benzothiazole.—(a) A 1.24×10^{-4}M solution of 1-methylbenzimidazole in MeOH (5 vol) was mixed with water or aqueous perchloric acid (2 vol) and the u.v. spectrum of the mixture was recorded. The optical density at 282 nm when 1.2×10^{-2} or 0.24M aqueous acid was used was in each case *ca.* 10% of that when water (or 1×10^{-2}M NaOH) was used, indicating that protonation was complete even with the 1.2×10^{-2}M-acid. With 2.4×10^{-4}M aqueous acid the corresponding optical density was 62% of that with water alone, and with 4.8×10^{-4}M acid it was 36% indicating that protonation was roughly 40% complete in the weaker acid and *ca.* 70% in the stronger.

(b) The optical density at 272 nm remained constant for mixtures of 5 vol of a 1.6×10^{-4}M solution of benzothiazole in methanol with 2 vol of water or 2.4×10^{-4} or 6×10^{-4}M aqueous perchloric acid. The optical density rose to 450% of that first value on using 12M-acid, with which protonation is complete. The corresponding value with 0.24M-acid was 128%, indicating *ca.* 8% protonation.

Product Isotope Effects.—The n.m.r. method [11] was employed to determine the RH/RD product ratio in cleavage of $RSiMe_3$ in 1 : 1 CD_3OH–CD_3OD (see ref. 26) with or without NaOMe, the signal from the proton in the 2-position being used. The values are not accurate to better than ±0.2. For (II) the same RH/RD ratio was obtained by use of an Applied Chromatography Systems Organic Analyzer MPD850 linked to a gas chromatograph.[14]

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