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THE MECHANISM OF CLEAVAGE OF 3-PHENYLALLYL—SILICON AND—TIN BONDS BY METHANOLIC SODIUM METHOXIDE

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Summary

The compounds *trans*-PhCH=CHCH₂MR'₃ with M = Si or Sn and R' = Me or Et have been cleaved in methanolic sodium methoxide at 50°C to give the products *trans*-PhCH=CHCH₃ (I) and PhCH₂CH=CH₂ (II). (Small amounts of *cis*-PhCH=CHCH₃ sometimes obtained are thought to come mainly or exclusively from *cis*-PhCH=CHCH₂MR'₃ in the starting material.) At base concentrations of 0.02–0.40 M the I/II ratio is 1.53 for MR'₃ = SiMe₃ and 1.04 for MR'₃ = SnMe₃, but the ratio rises somewhat in both cases at higher base concentrations. The values of the product isotope effect, PIE, given by the product ratio PhCH=CHCH₃/PhCH=CHCH₂D obtained on cleavage in 1 : 1 MeOH/MeOD at 50°C, for formation of product I are as follows: (MR'₃ =) SiMe₃, 1.26; SiEt₃, 1.75; SnMe₃, 2.1; SnEt₃, 2.2. The corresponding values for the formation of II are 1.45, 2.0, 3.0 and 3.2. For formation of I the values of the rate isotope effect, RIE, given by the ratio of the rate in MeOH to that in MeOD, are 0.60 and 0.77 for MR'₃ = SiMe₃ and SnMe₃, respectively, and the corresponding values for formation of II are 0.65 and 1.14. The RIE: PIE ratios for MR'₃ = SiMe₃ are 0.48 and 0.45 for formation of I and II, respectively, and the corresponding ratios for MR'₃ = SnMe₃ are 0.37 and 0.38.

It is suggested that in all cases the cleavage proceeds by an electrophilically-assisted mechanism in which the proton transfers from the solvent to the C(1) or C(3) carbon atoms of the phenylallyl group are concerted with the cleavage of the metal–carbon bond.

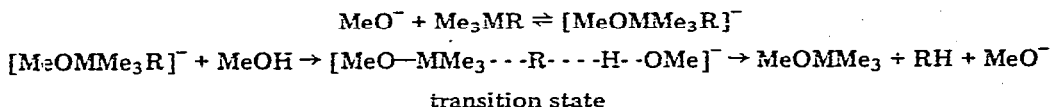
Introduction

We recently presented evidence, largely based on solvent isotope effects, that cleavage of a range of Me₃Si–R bonds (e.g., R = XC₆H₄CH₂, Ph₂CH, 9-fluorenyl,

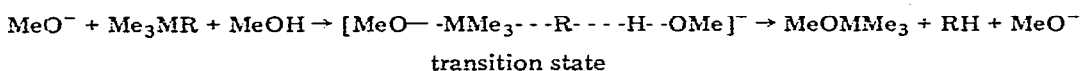
SCHEME 1

Mechanisms of Base Cleavage of $\text{Me}_3\text{M}-\text{R}$ Bonds by Methanolic Sodium Methoxide.

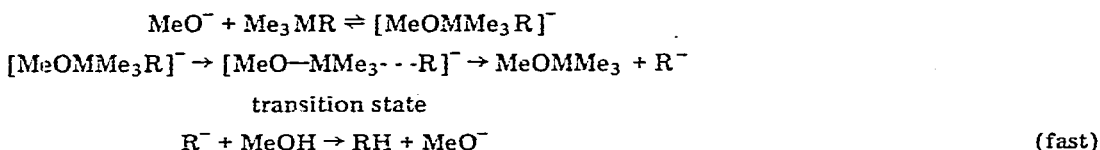
(1) Type A:



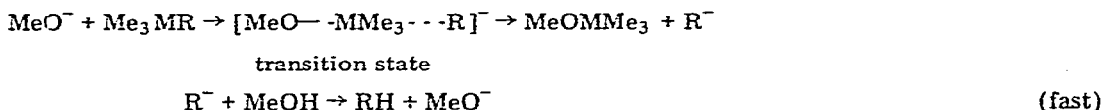
(2) Type A_s :



(3) Type B:



(4) Type B_s :



$\text{PhC}\equiv\text{C}$) by sodium methoxide in methanol proceeds through generation of the carbanions, R^- , by a mechanism of the type B or B_s shown in Scheme 1 [1]. In contrast, cleavage of some tin-benzyl (and tin-aryl) bonds, e.g. in Me_3SnR with $\text{R} = \text{PhCH}_2$, 2-furyl, or 2-thienyl, seems to involve a rate determining step in which a proton is transferred from the methanol to the R groups as it separates, i.e. the mechanism is of the type A or A_s in Scheme 1 [2-4] *. For some Me_3SiR compounds with $\text{R} = \text{aryl}$, the kinetics do not distinguish between a type B or B_s mechanism and a type A or A_s mechanism in which there is only a small degree of proton transfer to the separating carbanion in the (rate-determining) transition state [3,4], but some substituent effects are more satisfactorily interpreted in terms of the A or A_s mechanisms [6].

We have now extended our studies to cleavage of the 3-phenylallyl-compounds, $\text{PhCH}=\text{CHCH}_2\text{MR}'_3$, with $\text{M} = \text{Si}$ or Sn and $\text{R}' = \text{Me}$ or Et . Base cleavage of these compounds has been previously examined by Roberts and his co-workers, who used as media both $\text{H}_2\text{O}/\text{MeOH}/\text{OH}^-$ [7] and $\text{ZOH}/\text{DMSO}/\text{ZO}^-$ with $\text{Z} = \text{H}$, Me , Et , Pr , $i\text{-Bu}$ and neopentyl [8]. They favour separation of a free carbanion for the tin compounds while, leaving open the possibility of some electrophilic assistance (i.e. a type A or A_s mechanism) with the silicon compounds. On the basis of our studies, and in the light of recent advances in this field [1-4], we have reached different conclusions for the cleavages by sodium methoxide in methanol.

* However, for R groups associated with more stable carbanions, e.g. $\text{R} = 9\text{-fluorenyl}$, the type B or B_s mechanisms may possibly apply to tin compounds also [5].

Results

Products

In cleavage by sodium methoxide in methanol, the trimethylsilyl compound *trans*-PhCH=CHCH₂SiMe₃ (which contained less than 0.2% of the *cis*-isomer) gave two products, the unrearranged *trans*-PhCH=CHCH₃, I, and the rearranged PhCH₂CH=CH₂, II. The ratio I/II is independent of the NaOMe concentration at low base concentrations (thus there is no detectable variation over the 20-fold change in base concentration between 0.02 and 0.4 M), but shows a definite increase at very high base concentrations (see Table 1). There is no significant difference between the product ratio for reaction in MeOD and that for reaction in MeOH.

The corresponding tin compound normally contained about 2% of the *cis*-isomer, and a third product, *cis*-PhCH=CHCH₃, *cis*-I, was detected. Neither the difference between the proportion of *cis*-I in the products and the proportion of *cis*-isomer in the starting material, nor the apparent variation in the proportion of *cis*-I in the products, is outside the limits of experimental uncertainty, and we suspect that *cis*-I comes exclusively from *cis*-PhCH=CHCH₂SnMe₃ but it is possible that a little isomerization does occur during the reaction.

When the PhCH=CHCH₂SnMe₃ sample contained larger quantities of the *cis*-isomer, there were larger proportions of *cis*-I in the products (Table 1). The latter proportions do not correspond directly with the former because some of the *cis*-substrate is converted into II. If the *cis*-PhCH=CHCH₂SnMe₃ were converted

TABLE I
PRODUCTS FROM CLEAVAGE OF PhCH=CHCH₂MR₃ BY METHANOLIC SODIUM METHOXIDE

MR ₃	[MeONa] (M)	Product composition (%)			I/II
		I	II	<i>cis</i> -I	
SiMe	0.020	60.4	39.6	—	1.53 ^a
	0.40	60.4	39.6	—	1.53 ^a
	2.00	62.1	37.9	—	1.64 ^a
	3.12	63.8	36.2	—	1.76 ^a
	6.06	64.6	35.4	—	1.82 ^a
	2.00	63.9	36.2	—	1.76 ^{a,b}
SiEt ₃	2.07	65.2	34.8	—	1.87 ^{a,c}
	2.07	65.9	34.1	—	1.93 ^{a,d}
	2.07	69.4	30.2	0.4	2.29 ^{a,e}
SnMe ₃	0.020	49.1	47.3	3.6	1.04 ^f
	0.100	48.9	47.7	3.4	1.03 ^f
	0.40	49.6	47.5	2.9	1.04 ^f
	1.52	50.6	45.6	3.8	1.11 ^f
	2.00	51.6	44.8	3.6	1.15 ^f
	3.03	53.5	42.2	4.3	1.27 ^f
	6.06	56.2	38.9	4.9	1.44 ^f
	6.100	57.1	37.9	5.0	1.51 ^{f,b}
	0.100	45.3	46.3	8.4	0.98 ^g
	0.100	32.5	41.3	26.2	0.79 ^h

^a <0.2% *cis*-isomer in starting material. ^b In MeOD. ^c After 64 h. ^e After 340 h. ^f Starting material contained 2% of *cis*-isomer. ^g Starting material contained 12.0% of *cis*-isomer. ^h Starting material contained 44% of *cis*-isomer.

TABLE 2

RATE CONSTANTS FOR CLEAVAGE OF $\text{PhCH}=\text{CHCH}_2\text{MR}_3$ COMPOUNDS BY METHANOLIC SODIUM METHOXIDE AT 50.0°C

MR_3	Medium	[NaOMe] (M)	$10^5 k^a$ (s^{-1})	$10^5 k_s^b$ ($\text{l mol}^{-1} \text{s}^{-1}$)	λ^c (nm)
SiMe ₃	MeOH	2.00	27.7	13.85	290
	MeOD	2.00	44.8	22.4	
SnMe ₃	MeOH	0.100	23.5	235	290
	MeOD	0.100	26.0	260	
SnEt ₃	MeOD	0.50	43.2	86.4	240
	MeOD	0.50	54	109	
	MeOH	2.02	290	144	
SiEt ₃	MeOH	2.07	0.137	0.066	260

^a Observed first order rate constant. ^b Specific rate constant, i.e. $k/[\text{NaOMe}]$. ^c Wave-lengths used in rate measurements.

only into *cis*-I and II, in 50 : 50 ratio (the ratio observed for I and II from *trans*- $\text{PhCH}=\text{CHCH}_2\text{SnMe}_3$), then for 46% of *cis*-substrate a product ratio of I/II/*cis*-I of 28 : 50 : 22 would be expected, compared with the 32 : 41 : 26 ratio observed. If *cis*- $\text{PhCH}=\text{CHCH}_2\text{SnMe}_3$ gave *cis*-I and II in 60 : 40 ratio, the expected ratio of I/II/*cis*-I would be 28 : 46 : 26, and this is close enough to the observed value to support our view that little if any *cis*-I is produced from *trans*- $\text{PhCH}=\text{CHCH}_2\text{SnMe}_3$, and little if any I from *cis*- $\text{PhCH}=\text{CHCH}_2\text{SnMe}_3$.

The product ratio I/II from $\text{PhCH}=\text{CHCH}_2\text{SnMe}_3$ showed no change over the 20-fold increase in base concentration from 0.02–0.4 M, but substantially higher ratios were found at much higher base concentrations (Table 1). The reliability of the product analysis is probably lower for the much less reactive triethylsilyl compound, $\text{PhCH}=\text{CHCH}_2\text{SiEt}_3$, and the apparent slight rise (from 65 : 35 to 69 : 30) in the I/II ratio as the reaction proceeds may not be real.

Isotope effects

The product isotope effect, denoted PIE, for cleavage of an Me_3MR compound in methanol is the ratio of the products RH/RD obtained upon cleavage in a 1 : 1 MeOH/MeOD mixture. For $\text{PhCH}=\text{CHCH}_2\text{MR}'_3$ cleavages, the PIE values must be determined separately for each of the isomeric products. The results are shown in Table 3. The most significant feature is that corresponding PIE values vary as MR'_3 is varied.

Except for the relatively unreactive Et_3Si compound, first order rate constants were measured for each compound in MeOH and in MeOD at a fixed base concentration (see Table 2). The ratio $k(\text{MeOH})/k(\text{MeOD})$, which we refer to as the overall rate isotope effect, and denote RIE [1] *, has to be split into the separate components associated with each of the products. Thus for cleavage of $\text{PhCH}=\text{CHCH}_2\text{SiMe}_3$ by 2.0 M NaOMe in MeOH, 62% of the observed specific rate constant of $13.8 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$ is associated with the formation of I, so the specific rate constant, k_s , for formation of I is $(0.62 \times 13.8) \times 10^{-5} = 8.6 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$. Similarly, k_s for II is $5.2 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$. The corresponding

* We previously used KIE to denote this ratio [3].

TABLE 3

ISOTOPE EFFECTS FOR PRODUCTS OF CLEAVAGE OF $\text{PhCH}=\text{CHCH}_2\text{MR}_3$ COMPOUNDS BY METHANOLIC SODIUM METHOXIDE AT 50.0°C

MR ₃	[MeONa] (M)	Product I			Product II			cis-I PIE ^b
		RIE ^a	PIE ^b	RIE/PIE	RIE ^a	PIE ^b	RIE/PIE	
SiMe ₃	2.00	0.60	1.26	0.48	0.65	1.45	0.45	—
SiEt ₃	2.00		1.75			2.0		—
SnMe ₃ ^c	0.100	0.77	2.1	0.37	1.14	3.0	0.38	2.3
SnEt ₃	0.5	<i>d</i>	2.2		<i>d</i>	3.2		

^a $k(\text{MeOH})/k(\text{MeOD})$ ^b RH/RD product ratio from cleavage in 1 : 1 MeOH/MeOD ^c The same RIE and PIE values for I, II, and cis-I were obtained with starting material containing 12 and 44% of the cis-isomer, respectively. ^d Overall RIE for disappearance of starting material is ca. 0.80.

constants for cleavage in MeOD are calculated in the same way. The results are shown in Table 3, along with those for the tin compounds. The RIE:PIE ratios associated with each product are also shown.

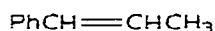
Possible side reactions

When reactions were carried out in 1 : 1 MeOH/MeOD, samples of $\text{PhCH}=\text{CHCH}_2\text{MR}_3$ recovered before reaction was complete were found to contain no deuterium. No detectable deuterium incorporation occurred when *cis*- or *trans*- $\text{PhCH}=\text{CHCH}_3$ was treated with 2 M NaOMe in 1 : 1 MeOH/MeOD for 14 h at 50°C . No change in the composition of a 6 : 94 mixture of *cis*- and *trans*- $\text{PhCH}=\text{CHCH}_3$ occurred during 1 h at 50°C in MeOH containing 6.06 M NaOMe, the most basic conditions used for the cleavages.

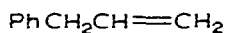
Discussion

We first note that the product compositions considered separately do not in themselves rule out the carbanion mechanism for any of the reactants. Ela and Cram, starting from allylbenzene or propenylbenzene, found that equilibrations in *t*-BuOH/KOBu-*t* at 97°C via the carbanion gave a mixture of $\text{PhCH}=\text{CHCH}_3$ (*cis* and *trans*) and $\text{PhCH}_2\text{CH}=\text{CH}_2$ containing only 0.32% of the latter [9], and Rennie and Roberts seem to argue from this that generation of the free carbanion during the cleavage of *trans*- $\text{PhCH}=\text{CHCH}_2\text{MR}_3$ would lead to almost 100% of I (+*cis*-I) [8]. But Ela and Cram also showed that in *t*-BuOH at 25°C the *trans*-anion III (which we assume would be generated from *trans*- $\text{PhCH}=\text{CHCH}_2\text{MR}_3$ compounds if they gave carbanions during the cleavage) undergoes protonation at C(1), to give $\text{PhCH}=\text{CHCH}_3$, I, only 2–4 times as rapidly as it does at C(3), to give $\text{PhCH}_2\text{CH}=\text{CH}_2$, II. If the same factor applied in MeOH we should expect the anion III to give a I/II ratio of between 66 : 33 and 80 : 20. In fact the more acidic MeOH might well be less selective than *t*-BuOH, so the observed I/II ratios of between 50 : 50 and 65 : 35 would be readily reconcilable with reaction via the free carbanions.

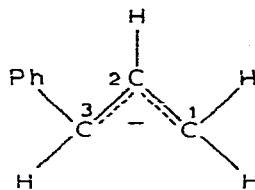
The product compositions are also compatible with the existence of electrophilic assistance in the rate-determining step, since if there is much carbanion character in the separating allylic entity in the transition state (as seems likely



(I)



(II)



(III)

by analogy with related systems [2-4]), the relative amounts of proton attachment at C(1) and C(3) could be expected to be rather similar to those for proton attachment to the anion III.

Likewise, none of the PIE values considered separately can be taken to rule out the free-carbanion mechanism. Cleavage of $\text{PhCH}=\text{CHCH}_2\text{SiMe}_3$ is about three times as fast as that of $\text{Ph}_2\text{CHSiMe}_3$, and if the reaction did have the carbanion mechanism this would imply that $\text{PhCH}=\text{CHCH}_3$ is of similar acidity to Ph_2CH_2 , and thus the anion III might give rise to a PIE similar to that for the Ph_2CH^- anion, viz. 2.2 [1]. However, the highly delocalized carbanion III might not fit the usual pK_a -PIE relationship, and the two PIE values to which it would give rise might well fall anywhere in the range of the observed values, viz. 1.26-3.2 (see Table 3).

What is revealing about both the product compositions and PIE values is that they vary significantly from compound to compound, since if a free carbanion were generated in all cases then product composition and PIE values would be properties of this anion, and so constant throughout. Thus the substantial differences in both product composition and PIE values for the $\text{PhCH}=\text{CHCH}_2\text{MR}'_3$ compounds with $\text{MR}'_3 = \text{SiMe}_3$ and SnMe_3 rule out the possibility that both compounds react by the carbanion mechanism. Either both must react by the assisted mechanism (A or A_s) or one by the assisted and the other by the carbanion mechanism (B or B_s). The significant difference between the PIE values for the compound with $\text{MR}'_3 = \text{SiEt}_3$ and those for the corresponding SiMe_3 compound is strong evidence against the carbanion mechanism for the silicon compounds. On the other hand, the difference is consistent with an assisted mechanism, since the considerable reactivity difference between the two compounds implies a significantly different position of the (rate-determining) transition state along the reaction coordinate. The absence of a difference between the PIE values for the tin compounds with $\text{MR}'_3 = \text{SnMe}_3$ and SnEt_3 is consistent either with a free carbanion mechanism or (since the reactivity difference is so small) an assisted mechanism. It is most unlikely however, that the tin compounds would react by the free carbanion mechanism if the silicon compounds did not, since over a wide range of compound types tin derivatives have shown a markedly greater tendency than silicon derivatives to react by the assisted mechanism [1-5]. Indeed, the RIE values of 0.77 and 1.1 observed for $\text{PhCH}=\text{CHCH}_2\text{SnMe}_3$ virtually preclude a carbanion mechanism for this compound, since such a mechanism is unlikely to be associated with RIE values much greater than 0.5 [1-4]. Even the RIE values of 0.60 and 0.65 observed for $\text{PhCH}=\text{CHCH}_2\text{SiMe}_3$ argue against the carbanion mechanism; the highest observed RIE value associated with what we believe to be a carbanion mechanism is that

of 0.57 for cleavage of 9-fluorenyltrimethylsilane, and that value must be regarded as anomalously high [1].

Our results are best explained in terms of the assumption that both silicon and tin react by the assisted mechanism, of type *A* or *A_s*. For $\text{MR}'_3 = \text{SiMe}_3$, the RIE: PIE ratios for both C(1) and C(3) protonation fall clearly into the expected range of ca. 0.42–0.50 [1–4]. The corresponding ratios for $\text{MR}'_3 = \text{SnMe}_3$ fall slightly outside the previously observed range of 0.40–0.50, but if the RIE for C(1) protonation, for example, were 2.8 instead of 3.0, a difference probably within the experimental uncertainty, the RIE: PIE ratio would be 0.41.

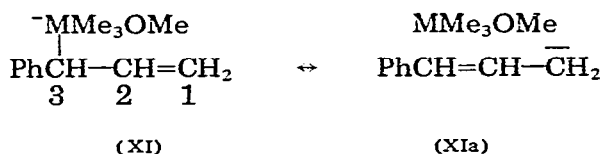
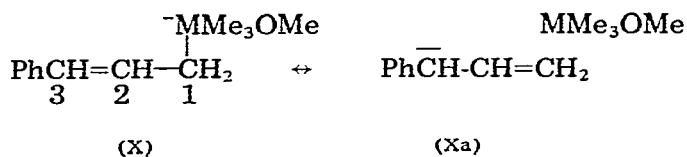
The conclusion that for the phenylallyl-derivatives both the tin and silicon compounds probably react by a type *A* or *A_s* mechanism raises the question of why the mechanism for these silicon compounds is different from that for silicon compounds of the benzylic type, e.g. $\text{Ph}_2\text{CHSiMe}_3$. An answer can be found in the fact that attack of an electrophile into the π -cloud of the allyl system is especially easy, as the very ready acid cleavage of $\text{RCH}=\text{CHCH}_2\text{MR}'_3$ compounds illustrates. (This point is considered again below.) In this, the allyl- MR'_3 compounds resemble aryl- MR'_3 more than benzyl- MR'_3 compounds (cf. ref. 4).

We have yet to account for the variation in the I/II product ratios with base (Table 1) in terms of the above proposals. The variations only become evident at very high base concentrations, and can thus reasonably be associated with differing medium effects on the rate constants for formation of I and II from any one compound. It is known that the specific rate constants for cleavage of Me_3MR compounds in methanol show marked deviations from proportionality to the NaOMe concentration at high base concentrations [4], and that in mixed media the medium dependence can vary considerably from compound to compound [10]. For reactions by mechanisms *A* or *A_s*, reactions having differing PIE's (reflecting differing degrees of proton attachment in the transition state) may well differ in their dependence on the methoxide concentration at high concentrations in methanol. Thus since the PIE for formation of I is different from that for formation of II from either $\text{PhCH}=\text{CHCH}_2\text{SiMe}_3$ or $\text{PhCH}=\text{CHCH}_2\text{SnMe}_3$, the respective rates are expected to show a different dependence on the sodium methoxide concentration at high base concentrations. Furthermore the difference should be greater for the tin than for the silicon compound, in line with the differences between the two PIE values in each case [10], and so the greater variation in the I/II ratio for the tin compound is understandable.

A major difficulty arises, however, when some of the results obtained by Rennie and Roberts are considered in the light of our proposals. Their results for aqueous-methanolic media are wholly consistent with ours for methanol, in so far as there is overlap. However, for cleavage in ZOH/DMSO/ZO^- ($\text{Z} = \text{Me}$, Et , etc.) they obtained exclusively the unrearranged product, I [8]. (For $\text{Z} = \text{H}$, there may have been up to 2% of II.) If a type *A* or *A_s* mechanism operated in these media, it would be very difficult to explain why proton transfer from ZOH to C(1) should now be so greatly favoured over that to C(3). We have previously suggested, for the particular case of $\text{Z} = \text{H}$, that electrophilic assistance might be less effective in ZOH/DMSO/ZO^- media than in methanol [11], and it is conceivable that the mechanism would change to the unassisted *B* or *B_s* type in such media, but if a free carbanion were indeed formed one would expect, in the light

that change to DMSO as solvent led to a marked fall in the amount of the product they associate with cleavage of isomer V [12]. The increase in the ratio I/II at high base concentrations could then be attributed to more effective competition of reaction 2 with reaction 3 as $k_2 [\text{OMe}^-] [\text{I}]$ rises relative to $k_1 [\text{I}]$. The variation in the product composition in acid-cleavage of IV was accounted for in just this way [12].

There are two major difficulties associated with this hypothesis. First, there is no obvious reason why cleavage of VIII should involve proton-attachment exclusively at C(1) and that of IX attachment exclusively at C(3). In so far as the allyl group in the transition state resembled a carbanion, comparable amounts of attack at C(1) and C(3) would be expected, as discussed above. In so far as the allyl group in the transition state resembled that in the Sn^{v} intermediates X and XI, proton transfer from the solvent might be expected to be of the type associated with $\text{S}_{\text{E}}2'$



processes, i.e. for X exclusively at C(3) and for XI exclusively at C(1); this is because of the importance of the hyperconjugative interactions represented by resonance structures Xa and XIa, which lead to a substantial excess of electron density at C(3) in X and C(1) in XI*. (There is a close analogy to the proton transfer from oxonium ions to neutral allytin compounds as discussed by Kuivila and his colleagues [12].) If this were so, then the rearranged product II would come exclusively from unrearranged VIII, while I would come exclusively from the rearranged IX, the reverse of the situation represented in Scheme 3. However, if only one product appeared in ZOH/DMSO/ZO⁻ media, this would now be expected to be II (from unrearranged starting material), not I as found by Rennie and Roberts.

The second difficulty associated with Scheme 3 is that it seems unlikely to apply for M = Si, since, to be significant, the value of k_1 would have to be of the same order of magnitude as that for the tin compound**. (The value of $k_2 \times [\text{OMe}^-] [\text{VIII}]$ would have to be much the same for both Si and Sn, since $[\text{OMe}^-]$ was adjusted in all cases to give conveniently measurable rates.) The only observation which we cannot satisfactorily explain either in terms of Scheme 1 or

* An equivalent explanation, of course, can be given in terms of the transition state for the proton transfer.

** We note that our results within themselves would be consistent with the possibility that the tin compounds react partly via rearrangement while the silicon compounds do not.

Scheme 3 (or less probably, operation of Scheme 1 for $M = \text{Si}$ and Scheme 3 for $M = \text{Sn}$) is the exclusive formation of I observed by Rennie and Roberts for cleavage in ZOH/DMSO/ZO^- , and this must remain an anomaly*.

Some secondary aspects of the results have still to be discussed. The first concerns the magnitude of the $\text{Me}_3\text{Si}/\text{Et}_3\text{Si}$ reactivity ratio for the $\text{PhCH}=\text{CHCH}_2\text{SiR}'_3$ compounds. We have previously suggested that, other things being equal, this ratio, which primarily reflects steric influences, should increase with the reactivity of the $\text{Me}_3\text{SiR}'$ compound, as the rate-determining step moves closer to the (real or notional) Si^v intermediate, $[\text{Me}_3\text{SiR}'(\text{OMe})]^-$ [13]. Rennie and Roberts reported an $\text{Me}_3\text{Si}/\text{Et}_3\text{Si}$ ratio of $>10^3$ for cleavage in aqueous alcohol, which is greater than that observed for the much more reactive 9-fluorenyl SiR'_3 compounds [14]. Even taking account of the probable difference in mechanism in the two cases (A or A_s for the phenylallyl- and B or B_s for the 9-fluorenyl-compounds) a ratio of 10^3 seemed to us surprisingly high. Our value, viz. 213, compares with a ratio of 440 observed for the $\text{Ph}_2\text{CHSiR}'_3$ compounds [14], which have reactivities rather similar to those of the $\text{PhCH}=\text{CHCH}_2\text{SiR}'_3$ compounds. (Rennie and Roberts observed $\text{Me}_3\text{Si}/\text{Et}_3\text{Si}$ reactivity ratios of 60–140 for cleavage of $\text{PhCH}=\text{CHCH}_2\text{SiMe}_3$ in ZOH/DMSO/ZO^- media [8].) As usual, the corresponding $\text{Me}_3\text{Sn} : \text{Et}_3\text{Sn}$ ratio is much smaller, viz. 3, for $\text{PhCH}=\text{CHCH}_2\text{SnR}'_3$.

Our final point concerns the relationship between the reactivity of $\text{PhCH}=\text{CHCH}_2\text{SiMe}_3$ and the acidity (at C(1)) of $\text{PhCH}=\text{CHCH}_3$. Unfortunately the $\text{p}K_a$ of the latter is not available; Rennie and Roberts estimated it from the $\text{p}K_a$ of 26.5 recorded [15] for 1,3,3-triphenylpropene, $\text{PhCH}=\text{CHCHPh}_2$, by using $\text{p}K_a$'s of 35, 33.1, and 31.5, respectively, for PhCH_3 , Ph_2CH_2 , and Ph_3CH , and noting that each additional Ph group increased the acidity of toluene by ca. 1.8 pK units; by analogy, the $\text{p}K_a$ of $\text{PhCH}=\text{CHCH}_3$ would be roughly $26.5 + 3.6$, i.e. 30, a value which would imply that even without any electrophilic assistance $\text{PhCH}=\text{CHCH}_2\text{SiMe}_3$ should be more reactive towards base than $\text{Ph}_3\text{CSiMe}_3$. However, the $\text{p}K_a$ of toluene is now thought to be ca. 41, and on the same scale Ph_2CH_2 and Ph_3CH have pK's of 33.4 and 31.5 [16], and so on this crude reasoning the $\text{p}K_a$ of $\text{PhCH}=\text{CHCH}_3$ should be at least $26.5 + 9.5$, i.e. 37. (An even higher estimate, perhaps 39, would be reached by taking account of the fact that for steric reasons the three Ph groups in Ph_3CH cannot exercise their normal delocalizing power.) If $\text{PhCH}=\text{CHCH}_2\text{SiMe}_3$ reacted by a carbanion mechanism, its reactivity, which is a little greater than that of $\text{Ph}_2\text{CHSiMe}_3$, would imply a $\text{p}K_a$ of 33.5 for $\text{PhCH}=\text{CHCH}_2\text{SiMe}_3$ **, However, the electrophilic assistance might make a contribution equivalent up to about 2–3 pK units, and we predict a value in the region of 35 ± 2 for the acidity of $\text{PhCH}=\text{CHCH}_3$.

Experimental

Preparation of phenylallyl derivatives

The $\text{PhCH}=\text{CHCH}_2\text{MR}_3$ compounds were made essentially by the methods described by Roberts and Faiq el Kaissi [7], and purified by fractionation in a

* An obvious suggestion, that conversion of II \rightarrow I occurred after cleavage, is apparently ruled out by Rennie and Roberts' demonstration that such rearrangement is much slower than the cleavage [8].

** The reasonable assumption is involved that the cleavage does not proceed to the extent of more than 90% through rearrangement to $\text{PhCH}(\text{SiMe}_3)\text{CH}=\text{CH}_2$.

Perkin—Elmer Model 151 Annular Still. The proportion of *cis*-isomer (if any) was determined in each case by GLC analyses.

Product analyses

Products were analyzed by use of Varian 1400 GL Chromograph fitted with a 2m Carbowax 20M column kept at 90°C. Relative retention times were PhCH₂CH=CH₂, 4.96; *cis*-PhCH=CHCH₃, 7.13; *trans*-PhCH=CHCH₃, 10.72.

A solution of 3-phenylallylsilane (0.5 ml) in MeOD (4.0 ml) containing sodium methoxide (2*M*) was left at 50°C for 20 h. The solution was cooled and added to ice/water, and the organic material extracted with pentane. The pentane extracts were washed with water and dried, and the solvent was removed. Preparative GLC gave two products with NMR spectra (CCl₄ solution, 100 Hz) as follows: (i) (larger component) 3-deutero-1-phenylpropene, δ 7.15 (ArH) (m, 5H); δ 6.35, H(1) (doublet of triplets, 1H; *J*(12) 15.5 Hz, *J*(13) 1.0 Hz); δ 6.08, H(2) (6 sets of triplets with one set rather weak, 1H; *J*(21) 15.5 Hz, *J*(23) 6.0 Hz, *J*(2D) 0.9 Hz); δ 1.83, H(3) (4 sets of triplets, 2H; *J*(32) 6.0 Hz, *J*(31) 1.0 Hz, *J*(HD) 2.2 Hz). (ii) 3-deutero-3-phenylpropene, δ 7.13 (ArH) (m, 5H); δ 5.92, H(2) (24 line multiplet, 1H; *J*(HD) 0.9 Hz; δ 5.0, H(1) (complex multiplet, 2H); δ 3.32, H(3) (m, 1H).

Rate studies

Reactions were followed spectrophotometrically as previously described [4]. However, the rate constants for PhCH=CHCH₂SiEt₃ were based on only the first 20% of reaction, and may be in error by as much as $\pm 15\%$.

PIE measurements

The method was as previously described [4], cleavages being carried out in 1 : 1 MeOH/MeOD in all cases.

Control experiments

Analyses revealed that no significant amount of deuterium was incorporated in any case in the organometallic reagent recovered after incomplete cleavage, and that no exchange occurred between MeOD and either PhCH=CHCH₃ or PhCH₂CH=CH₂ under cleavage conditions.

No change in the *cis/trans* ratio occurred when a mixture of *cis*- and *trans*-PhCH=CHCH₃ was treated with 6 *M* MeONa in MeOH for 1 h at 50°C.

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