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BASE-CATALYSED CLEAVAGE OF ALLYLIC DERIVATIVES OF GROUP IVA ELEMENTS

II. REACTIONS OF CINNAMYL AND BENZYL DERIVATIVES IN STRONGLY BASIC MEDIA

W. J. RENNIE* AND R. M. G. ROBERTS**
Department of Chemistry, University of Essex, Wivenhoe Park, Colchester, Essex (Great Britain)

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SUMMARY

The rates of cleavage of cinnamyl and benzyl derivatives of silicon, germanium and tin in strongly basic media have been measured spectrophotometrically. Correlations between these rates and acidity functions H_-, J_- and H_{R-} were made and kinetic solvent isotope effects evaluated. For the cinnamyl derivatives, the yield of allylbenzene (S'_E product) was much greater in aqueous alcohol than in aqueous DMSO. It was concluded that the transition states for the cleavages in DMSO solvent mixtures had much more carbanion character than those in aqueous alcohol. The tin transition states appeared to involve a greater degree of tin–oxygen bond formation than those of the silanes, where some evidence for an assisted pathway is presented. In the tin series, the transition state for the benzyl derivative has a greater ionic character than that of the cinnamyl analogue. There appears little evidence for any nucleophilic assistance in the latter case.

INTRODUCTION

The mechanism of these reaction types has already been discussed for aqueous alcoholic media[1]. It is the purpose of this paper to examine in greater detail and, in some cases, to re-evaluate previous data for such reactions in aqueous and alcoholic DMSO. The work will attempt to elucidate details of mechanism by using thermodynamic activation parameters, solvent isotope effects, Hammett and related acidity functions and product analyses.

RESULTS AND DISCUSSION

The reactions were followed spectrophotometrically in the presence of a large excess of base to ensure pseudo-first order kinetics. In all cases, the observed rate constant (k_{obs}) was dependent on the basicity of the medium, and the true second order

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* Present address: Department of Chemistry, University of Calgary, Calgary, Alberta, Canada.
** To whom further communications should be addressed.

rate constant (k_s) obtained by dividing k_{obs} by the base concentration. As in aqueous alcoholic media[1], the rates of cleavage were strongly dependent on the nature of the metal or metalloid element, resulting in the following reactivity sequence for the cinnamyl derivatives, the relative rates in 68.3 mole% aqueous DMSO at 40° appearing in parentheses.

$$Et_3Si\ (50) > Et_3Ge\ (1.0) \ll Et_3Sn\ (2.8 \times 10^5)$$

The trends are in agreement with those observed by Bott, Eaborn, and Swaddle[2] for cleavages of the benzyl analogues, and the sequence is in marked contrast to that obtaining for the corresponding acidolyses[3]. A rationalisation of these findings has already been offered. The reactivity sequence for base catalysis arises, it is thought, from a combination of opposing effects, namely the increase in nuclear shielding and the decrease in metal–carbon bond strength from silicon through germanium to tin.

In aqueous DMSO, the rate ratio of cinnamyl to benzyl for the triethyltin series is about 10^5. Simple molecular orbital treatment of the benzyl and cinnamyl anions[4] indicates that the latter is more stable by 0.66 β. Unfortunately the value of β for this system is not known with any accuracy. An alternative estimate of the relative anion stability can be obtained from the acidity of the corresponding carbon acids. Toluene[5] has a pK_a (α position) on the MSAD scale* of 35 but there appears to be no data for β-methylstyrene. An indirect assessment of the acidity can be made from the following hydrocarbon acidities. 1,3,3-Triphenylpropene[5] has a pK_a of 26.5. The corresponding values for triphenyl and diphenylmethane[6] are 31.5 and 33.1 respectively. It is seen that the replacement of each hydrogen by a phenyl group in toluene results in a decrease in pK_a of about 1.8 units. Using this crude approximation together with the value for 1,3,3-triphenylpropene, the pK_a of β-methylstyrene should be about 30. This in turn suggests that the cinnamyl anion is more stable than the benzyl anion by approximately 7 kcal·mole^{-1} at 25°. Thus if the cleavage of both triethylcinnamyl- and benzyl-tin compounds proceeds via a transition state of marked carbanionic character, a rate ratio of 10^5 could be accounted for in terms of carbanion stability alone. This, of course, would rule out homoallylic interaction in the transition states, but further discussion of this question is deferred until later.

TABLE 1

SECOND ORDER RATE CONSTANTS (k_s, l·mole^{-1}·sec^{-1}) FOR THE CLEAVAGE OF TRIETHYLCINNAMYL-SILANE, -GERMANE AND -STANNANE ($XCH_2CH{:}CHPh$) AND FOR THE REARRANGEMENT OF ALLYLBENZENE IN AQUEOUS DMSO (x_{DMSO}=0.70)

X	T(°C)	k_s
Et_3Si	40.0	1.03
Et_3Ge	40.0	0.02
Et_3Sn	40.0	5.7×10^3 [a]
H	40.7	0.96×10^{-2} [b]
H	39.5	0.75×10^{-2} [c]

[a] Value extrapolated from solvent composition-rate data. [b] By GLC method. [c] By UV spectroscopy method.

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* McEwen–Streitwieser–Applequist–Dessy scale

Product analysis was complicated by the rather facile base catalysed rearrangement of allylbenzene to β-methylstyrene. It was demonstrated by independent experiments that the rate of the rearrangement in aqueous DMSO was slower than the cleavage of the silanes and stannanes by factors of 10^2 and 10^5 respectively, but only by a factor of 2 for the germanes, (Table 1). The results of product analysis appear in Table 2. In most cases, quantitative yields of β-methylstyrene were obtained within experimental error (standard deviation 1 %), with the notable exceptions of the cleavages in aqueous alcohol. A reinvestigation of our earlier results[1] for this solvent system has revealed an important discrepancy. Contrary to our original report that almost quantitative yields of β-methylstyrene were obtained from the cleavage of both silicon and tin derivatives, we now find that the respective yields of β-methylstyrene and allylbenzene were as follows; for $Me_3SiCH_2CH{=}CHPh$ 61, 39 %, for $Et_3SnCH_2CH{=}CHPh$ 53, 47 %. The significance of this data will be discussed in a later section. No traces of allylbenzene were found in any of the cleavages of the germanium derivative under conditions where rearrangement was known to be slow.

TABLE 2

PERCENTAGE YIELDS OF β-METHYLSTYRENE (I) AND ALLYLBENZENE (II) FROM THE BASE CATALYSED CLEAVAGES OF CINNAMYL DERIVATIVES OF SILICON, GERMANIUM AND TIN ($R_3MCH_2CH{:}CHPh$)

R	M	Added base	Solvent	x_{DMSO}	(I) (%)	(II) (%)
Me	Si	NaOH	aq. MeOH	[a]	61	39
Me	Si	NaOH	aq. DMSO	0.35	>98	<2
Me	Si	NaOH	aq. DMSO	0.80	92	8
Me	Si	NaOR'[b]	alc. DMSO	0.35–0.80	100	0
Et	Si	NaOH	aq. DMSO	0.35	>98	<2
Et	Si	NaOH	aq. DMSO	0.80	100	0
Et	Si	NaOR'	alc. DMSO	0.50	100	0
Et	Ge	NaOH	aq. DMSO	0.50	100	0
Et	Ge	NaOR'	alc. DMSO	0.50	100	0
Et	Sn	NaOH	aq. MeOH	[a]	53	47
Et	Sn	NaOH	aq. DMSO	0.50	93	7
Et	Sn	NaOR'	alc. DMSO	0.50	100	0

[a] $x_{MeOH} = 0.49$. [b] R' = methyl, ethyl, propyl, isobutyl, neopentyl.

Effects of changes in strongly basic media

The effect of changing from aqueous to alcoholic DMSO media can be seen in Table 3. The orders of reactivity are:

$\bar{O}Me < \bar{O}Et \sim \bar{O}\text{-n-Pr} \sim \bar{O}\text{-i-Bu} \sim \bar{O}\text{-neopentyl} < \bar{O}H$ for the silanes and

$\bar{O}Me < \bar{O}Et \sim \bar{O}\text{-n-Pr} < \bar{O}\text{-i-Bu} < \bar{O}\text{-neopentyl} < \bar{O}H$ for the stannanes.

The alcohol content of the solutions was always high enough to preclude the formation of the dimsyl anion[7]. Bowden[8] has established the order of basicities of alkoxide solutions as:

$\bar{O}Me < \bar{O}H < \bar{O}Et < \bar{O}\text{-i-Pr} < \bar{O}\text{-t-Bu} < \bar{O}\text{-tert-pentyl}$

The anomalous position of hydroxide ion in the reactivity sequences can be explained in terms of its being less susceptible to steric effects in reactions which are essentially

TABLE 3

VALUES OF k_s ($\mathrm{l \cdot mole^{-1} \cdot sec^{-1}}$) FOR THE CLEAVAGE OF CINNAMYL DERIVATIVES ($R_3MCH_2CH{:}CHPh$) OF GROUP IVA ELEMENTS BY VARIOUS BASES $^-OR'$ IN $R'OH$/DMSO MIXTURES AT 40° [$x_{DMSO}=0.50$]

R_3M	^-OH	$^-OCH_3$	$^-OCH_2CH_3$	$^-OCH_2CH_2CH_3$	$^-OCH_2CH(CH_3)_2$	$^-OCH_2CH(CH_3)_3$
Me_3Si	6.93	0.341	0.442	0.447	0.424	0.492
Et_3Si	0.13	0.003	0.003			
Et_3Ge	0.001	0.07[a]				
Et_3Sn	128	0.282	4.22	4.93	7.45	26.6

[a] $x_{DMSO}=0.954$.

nucleophilic displacements at a sterically hindered reaction site. Steric effects do not appear to be important in simple protonation of the bases. The values of k_s(OH)/k_s(OMe) for the triethylsilanes and -stannanes are 43 and 450 respectively. Given the same degree of oxygen–metal(loid) bond formation in the transition state in each case, then, in terms of steric hindrance, the ratio should be greater for the silane than the stannane due to the differences in metal–carbon bond lengths (Si–C, 1.88; Sn–C, 2.18Å)[9]. From the observed ratios we conclude that bond formation in the transition state is more advanced for the stannanes than for the silanes. The reactivity sequences follow the relative basicities of the media for the lower alkoxide homologues for both stannanes and silanes, but anomalous behaviour is found for the higher members of the series in the case of the tin compounds. Only small differences in basicity occur for the β-alkylated bases[10,11] but nucleophilicity should decrease from ethoxide to neopentoxide due primarily to steric effects. Thus the reactivity sequence for the stannanes should be:

$$\bar{O}Et > \bar{O}\text{–n-Pr} > \bar{O}\text{–i-Bu} > \bar{O}\text{–neopentyl},$$

the exact reverse of the observed order. Without a more detailed investigation, no explanation other than a change in mechanism can be offered at present.

Acidity functions

A number of acidity functions have been derived for use in strongly basic media, and many correlations have been made between these functions and reaction rates to probe the finer details of mechanism[12,13,14,15]. We have adopted the H_- scale developed by Dolman and Stewart[14] for our calculation of J_- values.

Since the reactions described herein involve the addition of hydroxide or alkoxide to the substrate to form the transition state, the J_- and H_{R-} functions[16,17], which are measures of the ability of a basic solution to add hydroxide or alkoxide ions respectively to a neutral indicator, would seem to be more apposite for correlations with reaction rates. The slopes of these correlations appear in Table 4. Slopes of unity are expected only if the pattern of solvation of the indicators used to define H_- (J_-) and H_{R-} is similar to that of the transition states for the reactions concerned. Since these indicators (substituted diphenylamines, anilines and α-cyanostilbenes) have very different structures and hence solvation patterns compared with the substrates used, absolute values of the slopes cannot be interpreted. However, relative slopes should give some indication of the strength of base–metal(loid) bond formation in the transition state, higher relative values meaning stronger bonds[18]. For the reactions of the silanes in aqueous DMSO, plots of H_- and J_- against log $k_s{}^i/k_s{}^o$ (see Experimental section) showed slight curvature, slopes being greater at low than at high DMSO concentrations, implying a weakening of oxygen–silicon bonds in the transition states in the less aqueous media, (Table 5).

TABLE 4

SLOPES OF CORRELATIONS OF log k_s (40°) WITH VARIOUS ACIDITY FUNCTIONS FOR BENZYL (Bz) AND CINNAMYL (Cin) DERIVATIVES OF Si, Ge AND Sn

(a) Aqueous DMSO solutions

Compound	x_{DMSO}	$\frac{dk_s}{dH_-}$	$\frac{dk_s}{dJ_-}$
Me_3SiCin	0.28–0.40	0.80	0.94
Me_3SiCin	0.40–0.53	0.69	0.80
Et_3SiCin	0.38–0.50	0.69	0.76
Et_3SiCin	0.50–0.68	0.56	0.67
Et_3SiCin	0.24–0.34	0.85	1.02
Et_3SnBz[a]	0.45–0.60	0.63	0.76
Et_3SnBz[b]	0.45–0.60	0.67	0.81

(b) Alcoholic DMSO solutions

Compound	x_{DMSO}	$\frac{dk_s}{dH_-(OMe)}$	$\frac{dk_s}{dH_{R-}(OMe)}$	$\frac{dk_s}{dH_-(OEt)}$	$\frac{dk_s}{dH_{R-}(OEt)}$
Me_3SiCin	0.47–0.79	1.08	0.74	0.86	0.74
Et_3SiCin	0.59–0.94	0.75	0.70	0.96	0.68
Et_3SnCin	0.25–0.72	1.12	0.79	0.69	0.85

[a] At 48°. [b] At 25°.

TABLE 5

VARIATION OF log k_s^i/k_s^o WITH H_- AND J_- FOR CLEAVAGE OF TRIMETHYL AND TRIETHYLCINNAMYLSILANE IN AQUEOUS DMSO AT 40°

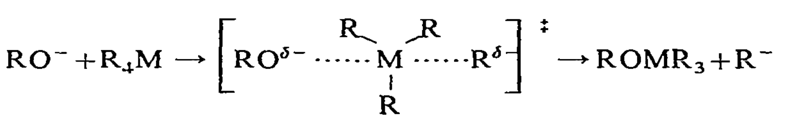
x_{DMSO}	H_-	log a_w	J_-	log $k_s{}^i/k_s^o$
For $Me_3SiCH_2CH{=}CHPh$				
0.280	15.30	1.19	16.49	13.51
0.311	15.62	1.12	16.74	13.77
0.345	15.96	1.04	17.00	14.05
0.386	16.37	0.95	17.32	14.34
0.430	16.80	0.85	17.65	14.68
0.479	17.28	0.74	18.02	14.96
0.533	17.82	0.62	18.44	15.34
For $Et_3SiCH_2CH{=}CHPh$				
0.385	16.37	0.95	17.32	12.11
0.430	16.80	0.85	17.65	12.38
0.480	17.31	0.74	18.05	12.74
0.538	17.88	0.60	18.48	13.07
0.603	18.53	0.46	18.99	13.46
0.680	19.30	0.28	19.58	13.79

The corresponding plots of H_{R-} were all linear. For the silanes, the average J_- slope is greater for the trimethyl than for the triethyl compound reflecting, it is thought, the easier approach of the nucleophile in the former. For the triethyl series the slope of the J_- correlation was greater for tin than for silicon suggesting stronger bond formation in the tin transition state. Similar trends are found in the H_{R-} correlations. The J_- slope for the benzyl derivative is much smaller than that for the cinnamyl analogue indicating weaker HO–Sn bonds in the benzyl transition state. Although the values of a_w used were calculated for 25°, no very significant differences in the slopes of the correlations were found between reactions conducted at 25 and 48°.

It is not as yet possible to distinguish between mechanisms (1) and (2) on the basis of H_- and J_- correlations alone but kinetic solvent isotope effects (*vide infra*)

$$RO^- + R_4M \overset{\text{fast}}{\rightleftharpoons} [ROMR_4]^-$$

$$[ROMR_4]^- \xrightarrow{\text{slow}} ROMR_3 + R^- \qquad (1)$$



$$RO^- + R_4M \rightarrow \left[RO^{\delta-}\cdots\cdots \underset{R}{\overset{R\quad R}{M}} \cdots\cdots R^{\delta-} \right]^{\ddagger} \rightarrow ROMR_3 + R^- \qquad (2)$$

favour the latter. Very recently, Schaal *et al.*[19] have determined the activity of the solvated proton in aqueous DMSO solutions using a series of buffers. pK_a values of indicators calculated from this data are at variance with those found by Stewart and Dolman[20] and until such discrepancies are accounted for, a quantitative interpretation of the numerical values of H_- and J_- rate correlations is not possible.

The role of water

According to Yagil and Anbar[21], the slope of log k_s *vs.* log C_w (C_w = concentration of "free" water) indicates the probable number of water molecules involved in the formation of the transition state. This solvation number decreases on raising the DMSO content of the medium as a result of effective scavenging of available water by DMSO, (Table 6).

TABLE 6

VALUES OF y FOR THE RELATION $\log_{10} k_s = y \log_{10} C_w$ FOR VARIOUS CINNAMYL (Cin) AND BENZYL (Bz) DERIVATIVES

Compound	x_{DMSO}	y
Me_3SiCin	0.28–0.40	5.6
Me_3SiCin	0.40–0.53	4.6
Et_3SiCin	0.38–0.50	4.7
Et_3SiCin	0.50–0.68	3.2
Et_3GeCin	0.68–0.80	3.2
Et_3SnCin	0.24–0.34	6.0
Et_3SnBz[a]	0.45–0.60	4.5
Et_3SnBz[b]	0.45–0.60	4.6

[a] At 48° [b] At 25°.

Kinetic solvent isotope effects (KSIE)

Values of KSIE appear in Table 7. Although Bunton and Shiner[22] have attempted to quantify these effects through a hydrogen bonding approach, interpretation of their theory is by no means straightforward due to neglect of entropy differences caused by solvent structure reorganisation on going from H_2O to D_2O[23].

TABLE 7

VALUES OF k_{H_2O}/k_{D_2O} FOR CINNAMYL (Cin) AND BENZYL (Bz) DERIVATIVES OF Si, Ge AND Sn IN AQUEOUS DMSO

Compound	x_{DMSO}	k_{H_2O}/k_{D_2O}
Me_3SiCin	0.317	0.73
Me_3SiCin	0.392	0.88
Me_3SiCin	0.490	0.87
Et_3SiCin	0.535	0.84
Et_3GeCin	0.683	0.95
Et_3SnCin	0.314	0.76
Et_3SnBz	0.450	0.94
Et_3SnBz	0.500	0.95
Et_3SnBz	0.550	0.94
Et_3SnBz	0.600	0.92

In the present study, all values of k_{H_2O}/k_{D_2O} were less than unity, precluding any significant proton transfer to the incipient carbanion in the transition state. In view of the dependence of rate on base concentration, it is clear that the reactions are all bimolecular. A limited number of KSIE values have been reported for S_N2 displacements by hydroxide ions. The observed k_{H_2O}/k_{D_2O} for the displacement of the benzenesulphonate ion from methyl benzenesulphonate[24] is 0.86, and includes a contribution of about 1.09 due to differential solvent structure reorganisation, yielding a true KSIE of 0.77. Since S_N1 solvolyses have KSIE values of greater than unity, values for S_N2 approaching unity would imply a high degree of bond fission in the transition state. Thus, Pritchard and Long[25] found a KSIE of 0.96 for the alkaline hydrolysis of propylene oxide (S_N2), from which they conclude that the transition state is reached before bond making is far advanced. KSIE values in aqueous and alcoholic DMSO solutions seem to correlate fairly well with acidity function data. For example, in the case of cleavage of trimethylcinnamylsilane J_- plots showed higher slopes at lower DMSO concentrations, at the same time KSIE values are lower in the more aqueous solvent. It is, therefore, tempting to interpret the two sets of data together, that is, on changing to a more aqueous solvent less bond fission and more bond formation occurs in the transition states. It is particularly significant, in this context, that, in the cleavage of trimethylcinnamylsilane in aqueous methanol[1], a low KSIE value of 0.5 was accompanied by relatively high yields of allylbenzene (39%), contrasting strongly with the low yields (< 1%) obtained from the protonation of the cinnamyl anion (*vide infra*).

Bearing in mind the dependence of KSIE on solvent composition, the relative amount of bond fission in the transition states for the triethyl series appears to be:

$$Et_3Ge > Et_3Si \sim Et_3Sn$$

The value of the KSIE for triethylbenzyltin is close to unity, indicating pronounced carbanionic character in the transition state. This, coupled with the J_- data, suggests a highly ionic transition state. Very recently, Eaborn[26] has found that in the base catalysed cleavages of benzyl–silicon and benzyl–tin bonds, the product isotope effect is much closer to unity in aqueous DMSO than in aqueous MeOH. A change to more polar media evidently increases the stability of the incipient carbanion.

Mechanism (1) cannot be disregarded but in view of the fact that most base catalysed reactions of this type have KSIE values of slightly greater than unity[24] it seems unlikely.

Activation parameters

For reactions of triethylbenzyltin in aqueous DMSO, increasing the water content of the solvent increases $\Delta H^{\ddagger}$ and makes $\Delta S^{\ddagger}$ more positive (Table 8). Due to the low reactivity and lack of solubility of the germanium derivative, it was not possible to obtain activation parameters in the standard solvent 50 mole% DMSO, but an approximate value of $\Delta H^{\ddagger}$ of 23 kcal · mole^{-1} is obtained by assuming a similar medium dependency. The lack of reactivity of the germanes is therefore due mainly to a $\Delta H^{\ddagger}$ effect.

TABLE 8

ARRHENIUS PARAMETERS FOR THE CLEAVAGES OF CINNAMYL AND BENZYL DERIVATIVES OF Si, Ge AND Sn IN AQUEOUS DMSO.

Compound	x_{DMSO}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger a}$
$Me_3SiCH_2CH{=}CHPh$	0.50	10.4±0.3	−21.8±0.9
$Me_3SiCH_2CH{=}CHPh$	0.50[b]	10.9±0.1	−23.0±0.3
$Et_3SiCH_2CH{=}CHPh$	0.50	12.6±0.3	−22.4±0.9
$Et_3GeCH_2CH{=}CHPh$	0.80	15.0±1.0	−14.8±3.3
$Et_3SnCH_2CH{=}CHPh$	0.50	11.2±0.4	−13.2±1.3
Et_3SnCH_2Ph	0.45	21.1±0.5	− 3.6±1.1
Et_3SnCH_2Ph	0.50	18.9±0.4	− 9.4±0.4
Et_3SnCH_2Ph	0.55	18.4±0.3	− 9.4±0.4
Et_3SnCH_2Ph	0.60	16.9±0.3	−12.5±0.4

[a] Calculated for T=25°; [b] Iso-butanol DMSO ($x_{DMSO}=0.50$).

Comparing data for the triethyl-silanes and -stannanes (Table 8), the rate difference is due principally to a more favourable $\Delta S^{\ddagger}$ for the tin compound. If, as suggested by J_- and KSIE data, the transition state for cleavage of the silanes is more ionic than that of the stannanes, $\Delta S^{\ddagger}$(Si) should be less negative or at least very similar to $\Delta S^{\ddagger}$(Sn) which evidently it is not. This anomaly could be explained by homoallylic interaction in the silane transition state, such effects in the initial state having now been largely discounted[27,28]. The more positive the reaction site, as a result of less bond formation and greater bond fission in the transition state, the more probable such interaction becomes. Thus one might anticipate a smaller interaction in the stannanes compared with the silanes. One consequence of the donor–acceptor phenomenon in the cinnamyl system is that proton attack at C(3) will be strongly inhibited, resulting in quantitative yields of β-methylstyrene. Cram's[29] elegant and intensive study of the rearrangement of allylbenzene in tert-butoxide/tert-butanol and in tert-butoxide/DMSO gave 99.67 and 99.95% yields of β-methylstyrene respectively. In such strongly basic media, the reaction almost certainly involves a carbanion intermediate.

The accuracy of our analyses (standard deviation 1 %) did not permit a distinction to be made between the purely carbanionic and the assisted mechanisms, though it must be added that where quantitative yields of β-methylstyrene are indicated, no allylbenzene could be detected using a very sensitive setting on the GLC chromatogram. It is clear from the analyses in DMSO that less charge separation occurs for tin than for silicon in the triethyl series with the result that some protons attack at C(3) rather than at C(1). In aqueous alcoholic media, there is presumably much less carbanionic character in the transition state and hence much more allylbenzene is formed. As stated previously, KSIE values[1] in this solvent system suggest much stronger bonds in the transition state and hence less likelihood of reaction via an assisted pathway.

Supporting this thesis, is the observation that the reactions of the silanes in both solvent systems showed small negative salt effects in keeping with charge dispersal in the transition state, but in the absence of any data concerning the effect of added salts on the activities of the substrates, this evidence should be treated with some caution.

The difference in reactivity between the benzyl- and cinnamyltin compounds is due primarily to a difference of nearly 8 kcal·mole^{-1} in $\Delta H^{\ddagger}$, remarkably and perhaps fortuitously close to the calculated difference in corresponding carbanion stabilities. The transition state for the benzyl derivative seems, however, to be more ionic, with less bond formation than that of the cinnamyl derivative and we cannot attribute the $\Delta H^{\ddagger}$ difference entirely to the difference in incipient carbanion stability. It is not clear at present why such transition state differences occur. Taken as a whole this evidence suggests that, for the tin compounds at least, homoallylic interaction in the transition state is absent in base catalysed cleavage reactions.

In summary, we conclude that in aqueous and alcoholic DMSO, the transition states have appreciable carbanionic character especially in the case of the germanes. There appears to be more bond formation in the transition states for the stannanes than for those of the silanes where it is possible that at least part of the reaction proceeds via an assisted pathway.

EXPERIMENTAL

Purification of solvents

Methanol, ethanol, propanol and isobutanol were purified by standard procedures[30]. Neopentanol was refluxed with sodium for 1 h, then fractionally distilled Reagent grade dimethylsulphoxide was reacted with calcium hydride until gas evolution ceased. The filtered solvent was allowed to stand over molecular sieves (Grade 4A) for two days then fractionated in an inert atmosphere. Mixed solvents were made up by weight.

Preparation of base solutions

Sodium hydroxide solutions were prepared from 1.0 *M* carbonate-free sodium hydroxide by dilution with boiled out, CO_2-free water. The alkoxide solutions were prepared by bubbling CO_2-free nitrogen through the corresponding alcohol under reflux and adding carefully the required quantity of clean dry metallic sodium.

Deuterated compounds

Methanol-d_1 (isotopic purity >99 atom% D), deuterium oxide (isotopic purity < 99.7 atom % D) and sodium deuteroxide, 40% in D_2O, pure (>99 atom % D) were obtained from Koch–Light Laboratories Ltd.

Preparation of substrates

The cinnamyl derivatives were prepared via the Grignard reagents using a slightly modified technique[1]. Triethylbenzyltin was prepared in 68% yield by a standard Grignard method.

Kinetic technique and analysis of data

Reactions were followed spectrophotometrically, as described previously[1], by measuring the decrease in absorption due to substrate in the range 280–310 nm for the cinnamyl derivatives and at 270 nm for the benzyltin compound. In most cases the spectrum of the completed reaction solution was identical with synthetic mixtures of the anticipated products. A large excess of base was used to ensure pseudo first order kinetics and the observed first order rate constants related by the usual equations, k_s being the true second order rate constant:

$$k_1^{(\text{obs})} = \frac{2.303}{t} \cdot \log_{10} \frac{(D_0 - D_\infty)}{(D_t - D_\infty)} = k_s \cdot [\text{base}] \qquad (3)$$

and D_0, D_t, D_∞ the optical densities of the reaction solutions at times $t=0$, t, ∞. Linear plots were obtained to well over 80% reaction with a standard deviation in k_1^{obs}, calculated for each point, of 2%.

Rates of reaction were insensitive to a change to anaerobic conditions. The rearrangement of allylbenzene was followed in a similar fashion.

Kinetic solvent isotope effects

Since it proved difficult to reproduce exactly, solvent compositions on changing from H_2O to D_2O, values of k_{H_2O}/k_{D_2O} were obtained by interpolation from rate constant–solvent composition plots (log k_s *vs.* x_{DMSO})* which were linear over the ranges used.

Product analysis

Products were detected using a Perkin–Elmer F11 chromatogram with a non-polar column (silicone oil MS 555 + Bentone oil on Chromosorb W, DE 210) at 150°. Under these conditions, allylbenzene and β-methylstyrene had retention times of 5.5 and 9.5 min respectively. Solutions of substrate (10^{-2} M) and base (10^{-1} M) were mixed and 1 μl of the reaction mixture injected immediately. Further injections were made to determine when reaction was complete. Synthetic mixtures of the two hydrocarbon products were used as calibrants. The rates of rearrangement of allylbenzene could be measured using this method and checked against values obtained by the spectroscopic technique (Table 1). The standard deviation for k_1^{obs} thus obtained was 8%.

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* x_{DMSO} = mole fraction DMSO.

Acidity functions and correlations with reaction rates

The H_- functions used for aqueous and alcoholic DMSO solutions were those developed by Stewart[13,14,31] and Bowden[12]. The J_- function[16] was obtained from the equation $J_- = H_- + \log_{10} a_w$, using McTigue's values for the activity coefficient of water in aqueous DMSO mixtures[32] and "normalised" water concentrations[21]. The H_{R-} function of Kroeger and Stewart[17] was used for methanol/DMSO mixtures.

Reaction rates were correlated with the acidity functions described above by plotting $\log_{10} k_s^i/k_s^0$ against the appropriate function, k_s^i and k_s^0 being the values of the second order rate constant (k_s) at H_- values of H_-^i and zero respectively.

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