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BASE-CATALYSED CLEAVAGE OF ALLYLIC DERIVATIVES OF GROUP IVA ELEMENTS. I

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SUMMARY

The mechanism of alkali cleavage of 3-phenallyl derivatives of silicon, germanium and tin in aqueous alcoholic media has been studied spectrophotometrically Both solvent isotope and primary salt effects are consistent with a rate determining S_N2 attack on the metal or metalloid atom with the expulsion of a carbanion. The product of reaction is β-methyl styrene, indicating that proton attack on the carbanion has occurred in the 3 position. The reaction appears to be subject to rather large steric effects.

In aqueous alcohol, the triethyl tin derivatives reacted faster than either the silicon or germanium analogues, the latter two reacting too slowly to enable an estimate of relative rates to be made. In aqueous dimethyl sulphoxide the order of reactivity was found to be $Et_3Sn \gg Et_3Si > Et_3Ge$. Some spectroscopic evidence for homoallylic interaction in the 3-phenallyl series is presented. This interaction has been invoked to explain the greater reactivity of 3-phenallyl compounds compared with their benzyl analogues.

INTRODUCTION

The mechanism of alkali cleavage of ethynylsilanes has been investigated in some detail by Eaborn and Walton[1]. More recently, Kraihanzel and Poist[2] have studied the cleavage of ethynylsilanes by alcoholic solutions of alkali halides, interpreting their results in terms of nucleophilic attack by alkoxide ions generated in solution. In addition, Bott, Eaborn and Swaddle[3] have presented a detailed account of the alkali cleavage of benzyl, (diphenylmethyl), (triphenylmethyl) and fluorenyl derivatives of silicon, germanium and tin. Little, however, is known of the analogous cleavage of allylic derivatives of these elements, though Kuivila and Verdone[4] have elucidated the mechanism of the acid catalysed solvolysis of allylic tin compounds. This paper deals with the kinetics and mechanism of alkali cleavage of allylic derivatives of group IVA elements in aqueous alcoholic media.

RESULTS AND DISCUSSION

A number of new allylic derivatives of silicon, germanium and tin have been synthesised for use in the work described in this paper. Table 1 lists these compounds

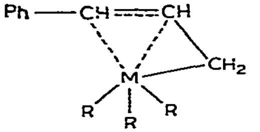
TABLE 1

SPECTROSCOPIC CHARACTERISTICS OF 3-PHENALLYL (R) DERIVATIVES OF SILICON, GERMANIUM AND TIN

Compound	λ^{a}_{max} (mμ)	log ε_{max}	ν(C=C) (cm^{-1})^{b}	γ(CH) (cm^{-1})^{b}
HR	250	4.184	1663	959
Me_3SiR	260	4.462	1644	959
Et_3SiR	260	4.247	1645	959
Et_3GeR	264	4.297	1641	959
Et_3SnR	275.5	4.346	1634	956
n-Bu_3SnR	267	4.036	1634	956
Ph_3SnR	273	4.249	1635	956

[a] Solutions in MeOH. [b] 1 % CCl_4 solutions.

together with their physical properties. 3-Phenallyl compounds have two main advantages over the parent allyl. Firstly, a distinction is possible between proton attack at C_3, yielding allyl benzene via an S'_E mechanism and attack at C_1, yielding β-methylstyrene by an S_E mechanism. Secondly, unlike alkyl substituted allylic derivatives, 3-phenallyl compounds absorb strongly at 260–280 mμ thus enabling reactions to be followed spectrophotometrically. *Trans*-β-methyistyrene has a λ_{max} of 250 mμ and the replacement of a β-methyl proton by Et_3Si, Et_3Ge and Et_3Sn produces bathochromic shifts of 10, 14, and 25.5 mμ, respectively. This represents a significant reduction in the π–π^* promotion energy and can be explained by increased delocalisation of the π electrons of the allylic double bond, caused by overlap with empty *d* orbitals of suitable symmetry on M, this effect being maximal in the conformation



(M = Si, Ge, Sn)
(R = Et)

In the case of the tin derivatives, a change of alkyl substituent from Et to n-Bu produces a hypsochromic shift of 8.5 mμ which may reflect steric inhibition to resonance caused by the bulky n-Bu groups forcing the molecule out of the optimum conformation for strong homoallylic interaction. Triphenyltin derivatives show a similar, but less marked trend reflecting the less bulky nature of phenyl groups.

An interesting parallel is apparent in the ν(C=C) frequencies in the infrared spectra of these compounds (Table 1). All the compounds synthesised show strong γ(CH) out-of-plane deformations at 956–959 cm^{-1} typical of *trans* olefins. The ν(C=C) frequencies themselves show a marked trend to lower frequencies for the series (M =) H, Si, Ge, Sn. This effect supports the concept of homoallylic interaction though it is rather ambiguous since the effect of increasing mass on the substituent on the double bond would produce a similar trend. The homoallylic interaction depicted above closely resembles the bonding in "mercurinium ions", which have been postulated as reaction intermediates by Kreevoy in his study of deoxymercuration[5] and acidolysis of allylmercuric iodide[6]. More recently, PMR studies of the reaction of ethylene and aqueous mercuric nitrate[7] have convincingly demonstrated the existence of the mercurinium ion. Work is in hand in these laboratories to obtain similar evidence for homoallylic interaction in the above compounds by examining their PMR spectra at low temperatures. Already preliminary results suggest the presence of a preferred conformation at −60°.

TABLE 2

OBSERVED FIRST ORDER (k_1, sec^{-1}) AND SECOND ORDER (k_s, l·mole^{-1}·sec^{-1}) RATE CONSTANTS FOR THE CLEAVAGE OF $Me_3SiCH_2CH{=}CHPh$ BY 0.64 *M* NaOH AND $Et_3SnCH_2CH{=}CHPh$ AND $n\text{-}Bu_3SnCH_2CH{=}CHPh$ BY 0.0458 *M* NaOH IN AQUEOUS ALCOHOLIC SOLUTIONS

$[R_3MCH_2CH{=}CHPh]$ (10^3 *M*)	10^4k_1	10^4k_s
$Me_3SiCH_2CH{=}CHPh$ in "60%" EtOH at 49.2°		
0.200	1.50	2.34
0.400	1.50	2.34
0.600	1.52	2.38
0.600	1.55	2.42
0.900	1.48	2.31
$Me_3SiCH_2CH{=}CHPh$ in "60%" MeOH at 40°		
0.600	0.91	1.42
0.600	0.92	1.44
$Et_3SnCH_2CH{=}CHPh$ in "60%" MeOH at 40°		
0.060	2.30	50
0.060	2.33	51
0.072	2.25	49
0.084	2.36	52
0.096	2.40	52
$n\text{-}Bu_3SnCH_2CH{=}CHPh$ in "60%" MeOH at 40°		
0.060	1.47	32
0.060	1.52	33

TABLE 3

VARIATION OF k_1 (sec^{-1}) WITH BASE CONCENTRATION FOR THE CLEAVAGE OF $Me_3SiCH_2CH{=}CHPh$ (6.00×10^{-4} *M*) AND $Et_3SnCH_2CH{=}CHPh$ (1.20×10^{-4} *M*)

$[OH^-]$ (10^2 *M*)	$[LiClO_4]$ (10^2 *M*)	10^4k_1	$10^4k_1/[OH^-]$[a]
$Me_3SiCH_2CH{=}CHPh$ in "60%" EtOH at 40°			
64	0	0.62	0.97
48	16	0.46	0.95
32	32	0.31	0.96
16	48	0.142	0.89
$Et_3SnCH_2CH{=}CHPh$ in "60%" MeOH at 40.0°			
4.58	0.00	2.33	51
3.66	0.92	1.63	45
2.75	1.83	1.28	47
1.83	2.75	0.82	45
0.92	3.66	0.41	45
4.58[b]	0.00	2.69	59

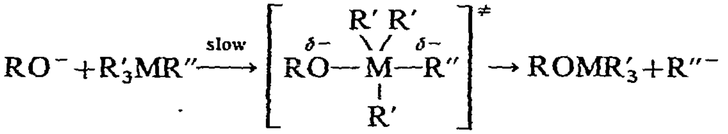
[a] k_s. [b] KOH used instead of NaOH.

Alkali cleavage of 3-phenallyl-silyl, -germyl and -tin derivatives in aqueous alcohol yield β-methylstyrene in 90% yield. This result clearly shows that proton attack has occurred at $C_1(S_E)$ rather than $C_3(S_{E'})$.

The kinetic data in Tables 2 and 3 show that the observed first order rate constant $k_1^{obs.}$, is independent of substrate concentration but varies linearly with base concentration (constant ionic strength being maintained by the addition of lithium perchlorate). The rate equation is therefore that of a simple bimolecular nucleophilic substitution

$$v = k_s \cdot [\text{substrate}] \cdot [OH^-] \qquad \text{where } k_s = k_1^{obs.}/[OH^-]$$

The anticipated dependence of $k_1^{obs.}$ on OH^- for strongly basic media could not be verified owing to the lack of data for aqueous alcoholic solutions of bases. However, the constancy of k_s, the specific rate constant, clearly demonstrates the participation of base in the transition state, and the mechanism is best regarded as a nucleophilic displacement of a carbanion by base, as indicated below



$$RO^- + R'_3MR'' \xrightarrow{\text{slow}} \left[\overset{\delta-}{RO} - \underset{R'}{\overset{R'\,R'}{M}} - \overset{\delta-}{R''} \right]^{\neq} \rightarrow ROMR'_3 + R''^- \qquad (1)$$

$$R''^- + H_2O \xrightarrow{\text{rapid}} R''H + OH^- \qquad (2)$$

It will be noted that base is not consumed during the reaction and consequently only first order rate laws are obeyed. Processes (1) and (2) may be concerted but discussion of this problem is deferred for the moment.

TABLE 4

VARIATION OF k_1 (sec^{-1}) WITH SALT CONCENTRATION FOR ALKALI CLEAVAGE OF $Me_3SiCH_2CH{=}CHPh$ AND $Et_3SnCH_2CH{=}CHPh$

$[OH^-]$ $(10^2 M)$	Salt	[Salt] $(10^2 M)$	$10^4 k_1$	$10^4 k_s$
$Me_3SiCH_2CH{=}CHPh$ in "60%" EtOH at 40°				
64–16[a]	$LiClO_4$	0–48[a]		0.96
64	$NaClO_4$	64	0.41	0.64
64	NaI	64	0.43	0.67
$Et_3SnCH_2CH{=}CHPh$ in "60%" MeOH at 40°				
4.58–0.92[a]	$LiClO_4$	0.00–3.66[a]		46
2.29	$LiClO_4$	6	0.90	39
2.29	$NaClO_4$	6	0.99	43
2.29	NaI	6	1.02	45

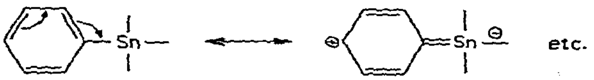
[a] At constant ionic strength, compare Table 3.

Added salt has a small retarding effect (Table 4) which is consistent with the transition state depicted above in which charge is dispersed relative to the initial state. The small negative salt effect is not appreciably affected by change in the cation of the salt used.

Table 2 indicates that steric effects play an important role in determining reaction rates. Both triethylsilyl and triethylgermyl derivatives reacted very slowly indicating a $k(\mathrm{Me})/k(\mathrm{Et})$ of at least 10^3 for the silanes. Though no comparison was possible between the silicon and germanium compounds in aqueous alcohol, recent results[8] for cleavage by OH^- in aqueous DMSO has confirmed the order of reactivity found by Bott, Eaborn and Swaddle, though the relative rates were markedly different

$$Et_3Sn \gg Et_3Si > Et_3Ge$$

Steric effects are noticeable in the 3-phenallyltin series in changing from triethyl to tri-n-butyl to triphenyl derivatives. In the latter, however, both steric and electronic effects inhibit reaction. Overlap of ring molecular orbitals with the empty *d* orbitals of tin result in negative charge being transferred to the metal thus inhibiting attack by base



It is interesting to compare the rates of cleavage of benzyl- and 3-phenallylsilanes. k_s for cleavage of trimethylbenzylsilane[3] in "83.4%" methanol at 50.0° has a value of 3.5×10^{-7} l·mole^{-1}·sec^{-1} compared with 0.63×10^{-4} l·mole^{-1}·sec^{-1} for the cleavage of the corresponding 3-phenallylsilane in methanol at 40°. The allylsilane reacts some 10^4 times as fast as the benzyl analogue. It is difficult to attribute this marked increase in reactivity of the 3-phenallylsilane to better stabilisation of the incipient carbanion in the transition state due to an extra conjugate link. An attractive alternative explanation is that bond fission is more important than bond formation and that neighbouring group participation by the allylic double bond electrons facilitates the departure of the carbanion. Thermodynamic data relating to the cleavage of silicon and tin compounds appears in Table 5.

TABLE 5

VARIATION OF k_s (l·mole^{-1}·sec^{-1}) WITH TEMPERATURE FOR THE CLEAVAGE OF $Me_3SiCH_2CH{=}CHPh$ BY 0.64 *M* NaOH IN "60%" EtOH AND $Et_3SnCH_2CH{=}CHPh$ BY 0.0458 *M* NaOH IN "60%" MeOH AND THERMODYNAMIC PARAMETERS, E_A AND log *A* DERIVED FROM THIS DATA

Temp. (°C)	10^4k_s Si	10^4k_s Sn
25	0.206	9.2
30	0.366	16.3
35	0.66	26.0
40	0.97	46.0
49.2	2.36	

Compound	E_A (kcal·mole^{-1})	log *A* (l·mole^{-1}·sec^{-1})
$Me_3SiCH_2CH{=}CHPh$	19.2	9.2
$Et_3SnCH_2CH{=}CHPh$	18.8	10.0

Change of solvent

As Table 6 shows, cleavage is faster in the more aqueous solvents. At first sight, this appears to be anomalous behaviour since charge dispersal in the transition state would predict a reduction in rate in going to more polar media. However, the nature of the attacking species has yet to be established. In aqueous alcoholic sodium hydroxide the following equilibrium is set up:

$$ROH + OH^- \overset{K}{\rightleftarrows} RO^- + H_2O$$

where K has values at 40° of 4.5 and 0.57 for methanolic and ethanolic solutions respectively[9]. Alkoxides are stronger bases than OH^-. Since, in the present work, we are concerned with OH^- attack on silicon, germanium, or tin, the same relative basicity is not necessarily maintained. Basicity and nucleophilicity are not interchangeable in the present circumstances. The latter displays a marked dependence on both electronic and steric effects. We have already demonstrated the importance of steric effects in these base catalysed cleavage reactions. The magnitude of these effects is not perhaps surprising since steric hindrance at the reaction centre is much more marked than in say tert-butyl chloride which is unreactive to an S_N2 attack by OH^-. It seems likely that OH^- will be a much more effective nucleophile than MeO^- or EtO^- due to size factors. This is supported by the fact that cleavage of Me_3SiCH_2CH:CHPh by ethoxide (0.64 M) in ethanol at 40° could not be detected before the base itself began to decompose (after 70 min). In these terms the dependence of rate on solvent composition is readily understood. As the water content increases the OH^- increases at the expense of RO^- and the reaction rate rises. It is perhaps significant that this effect is much more pronounced in the case of the triethyltin compound than for the trimethylsilyl derivative, again highlighting the importance of steric effects in these reactions. Steric factors however may not be the only ones in play. It is conceivable that on going to more aqueous media the transition state is less solvated, methanol being a stronger nucleophile than water. The rise in rate could then be explained by the gain entropy of activation more than outweighing the loss of enthalpy of activation.

TABLE 6

EFFECT OF CHANGE OF SOLVENT ON k_s ($l \cdot mole^{-1} \cdot sec^{-1}$) FOR CLEAVAGE OF $Me_3SiCH_2CH{=}CHPh$ IN AQUEOUS EtOH AND AQUEOUS MeOH AND FOR CLEAVAGE OF $Et_3SnCH_2CH{=}CHPh$ IN AQUEOUS MeOH AT 40°

[ROH]	10^4k_s		$k(H_2O)/k(D_2O)$	
(Mole %)	Si	Sn	Si	Sn
R = Et				
49.5	0.95			
31.9	1.08			
22.3	1.25			
13.2	1.85			
11.8	2.28			
R = Me				
64.2	0.63	9.6		
40.2	0.91	46	0.50	
26.9	1.86			0.76
23.0	8.1	124		0.76

Solvent isotope effects

Bunton and Shiner[10] have discussed the theoretical aspects of solvent isotope effects with reference to bimolecular nucleophilic substitution at carbon by hydroxide ion. Values of $k(H_2O)/k(D_2O)$ can be derived for model transition states by taking account of the hydrogen bonding present in the transition state relative to the initial state. The relation between the kinetic isotope effect $k(H_2O)/k(D_2O)$ and the relevant hydrogen stretching frequencies is

$$k(H_2O)/k(D_2O) = \text{antilog}\{[\Sigma\nu(H) - \Sigma\nu'(H)]/12.53\ T\}$$

where $\Sigma\nu(H)$ and $\Sigma\nu'(H)$ are the sum of hydrogen stretching frequencies in the initial and transition states respectively and T is the absolute temperature. The stretching frequencies (cm^{-1}) of the hydrogens of water donated to oxygen bases in aqueous solution can be estimated from the equation

$$\nu = 3040 + 22.9\text{p}K_b$$

and the hydrogen bonds donated by acids given by

$$\nu = 2937 + 28.8\text{p}K_a$$

This theory predicts that if, in a reaction, centres of high local acidity or basicity are developed, then there will be an increase in the strength of hydrogen bonds which exist between these centres and the solvent water molecules, *i.e.* there will be a decrease in the O–H stretching frequency relative to the initial state and $[\Sigma\nu(H) - \Sigma\nu'(H)]$ will be positive, giving rise to values of $k(H_2O)/k(D_2O)$ which are greater than unity. Conversely, if centres of acidity or basicity are destroyed in proceeding from the initial state to the transition state, $k(H_2O)/k(D_2O)$ will be less than unity. These concepts have been applied in nucleophilic attack by OH^- at a saturated carbon atom. For hydroxide ion to act as a nucleophile, one of the hydrogen bonds donated to it by water must be broken. This effectively strengthens the H–O bond in the water molecule concerned causing its O–H stretching frequency to increase. Thus $\Sigma\nu'(H) > \Sigma\nu(H)$ and, in the absence of any appreciable hydrogen bonding to the leaving group, $k(H_2O)/k(D_2O)$ will be less than unity. Four basic models were chosen for the S_N2 transition state (Table 7), reflecting the degree of covalent and electrostatic bonding in both incoming nucleophile and leaving group. Although the seat of substitution in the present system is silicon or tin, the same general arguments should be applicable.

For the cleavage of the silane in "60%" MeOH a value of $k(H_2O)/k(D_2O)$ of 0.50 was obtained. This information enables us to reject the concerted mechanism

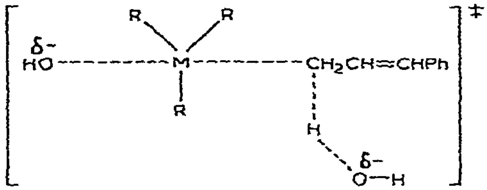
TABLE 7

CALCULATED ISOTOPE EFFECTS IN LIMITING TRANSITION STATES FOR REACTIONS OF HYDROXIDE ION[a]

Binding in transition state		$k(H_2O)/k(D_2O)$	Model
Incoming group	Leaving group		
Electrostatic	covalent	0.79	1
Covalent	covalent	0.54	2
Covalent	electrostatic	0.54	3[b]
Covalent	electrostatic	0.88	4[c]

[a] After Burton and Shiner[10]. [b] Leaving group equal or less basic than water. [c] Leaving group with same basicity as OH^- and possessing two hydrogen bonding acceptor sites.

since any gain in O–H stretching frequencies incurred by breaking hydrogen bonds to this base would be counterpoised by a loss in OH stretching frequency incurred by the formation of a new hydrogen bond to the incipient hydroxide ion in the transition state depicted below. This would result in a $k(H_2O)/k(D_2O)$ of unity. The observed $k(H_2O)/k(D_2O)$ of 0.50 is consistent with either model 2 or 3. The latter is improbable because the leaving group is a carbanion which is more basic than water. Hydrogen bonding would be expected to occur, increasing $k(H_2O)/k(D_2O)$.

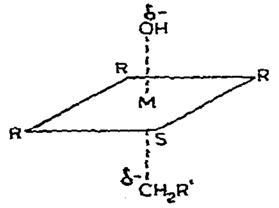


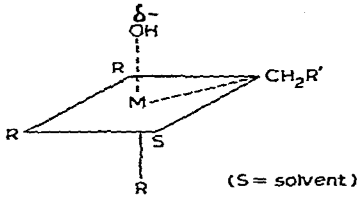
Thus bond making and bond breaking appear to be equally important in the transition state which approximates to model 2.

The small negative salt effect shown in Table 4 supports this hypothesis. $k(H_2O)/k(D_2O)$ for the tin compound in "60%" MeOH has a value of 0.77 and probably reflects the greater charge density on the incipient carbanion due to the increased electron-releasing property of tin relative to silicon. The increased carbanionic charge causes an increase of hydrogen bonding in the leaving group, thus raising $k(H_2O)/k(D_2O)$. No significant change in $k(H_2O)/k(D_2O)$ was observed on changing the solvent composition indicating that the mechanism was the same throughout the solvent range investigated.

Nature of the transition state

So far, we have considered the transition state for the cleavage reactions as being analogous to that of S_N2 substitutions at carbon. Owing to the availability of *d* orbitals, the structure of the transition state for S_N2 substitution at silicon, germanium or tin may be more complex. For example two types of octahedral transition states





can be visualised with a solvent molecule occupying the sixth coordination position, one with cis and the other with trans orientated incoming and leaving groups. In addition to transannular attack, edge displacement mechanisms may also operate.

EXPERIMENTAL

Preparation of trimethyl-3-phenallylsilane[11]

Oven dried magnesium turnings (7.5 g 0.31 mole), a small crystal of iodine, and dry ether (100 ml) were placed in a flask. A few drops of cinnamyl chloride were added and after reaction had commenced, cinnamyl chloride (3.5 g 0.025 mole) and trimethylchlorosilane (2.17 g 0.020 mole) in dry ether (50 ml) were added dropwise. The usual precautions for Grignard syntheses were taken. The mixture was stirred overnight. Distilled water (20 ml) was added dropwise with cooling and the ethereal layer separated off, dried and distilled under reduced pressure to yield 1.64 g (43 %) trimethyl-3-phenallylsilane, b.p. 89° 4 mm, n_D^{25} 1.5252. (Found: C, 75.81; H, 9.53. $C_{12}H_{18}Si$ calcd.: C, 75.75; H, 9.47 %.)

Some comment is required on the experimental procedure adopted. It was found that if the chlorosilane was added to the fully formed cinnamylmagnesium chloride appreciable quantities of bicinnamyl and other high boiling polymeric products were formed. The above procedure enabled the chlorosilane to react with the Grignard reagent as soon as it was formed thus preventing the formation of coupling products. The PMR spectrum was run on a Varian A-60A spectrometer and gave four principal resonances (ppm): 2.64 (Ph), 3.66 (CH=CH), 8.23 (CH_2) and 9.81 (CH_3), which gave proton ratios of 5.02 : 2 : 2 : 9.04 in accordance with the calculated values.

Preparation of other 3-phenallyl derivatives of silicon, germanium and tin

Adopting a similar preparative method the following new 3-phenallyl (R) derivatives were synthesised.

Et_3SiR (15 %), b.p. 110–114°/0.6 mm, n_D^{20} 1.5233. (Found: C, 76.6; H, 10.6. $C_{15}H_{24}Si$ calcd.: C, 77.5; H, 10.3 %.)

Et_3GeR (35 %), b.p. 105–108°/0.6 mm, n_D^{20} 1.5453. (Found: C, 64.8; H, 8.64. $C_{15}H_{24}Ge$ calcd.: C, 65.0; H, 8.66 %.)

Et_3SnR (20 %), b.p. 108°/0.5 mm, n_D^{20} 1.5645. (Found: C, 55.3; H, 7.2. $C_{15}H_{24}Sn$ calcd.: C, 55.8; H, 7.4 %.)

n-Bu_3SnR (10 %), b.p. 138–142°/0.5 mm, n_d^{20} 1.5185. (Found: C, 62.5; H, 8.75. $C_{21}H_{36}Sn$ calcd.: C, 62.1; H, 8.85 %.)

Ph_3SnR (44 %), m.p. 69.5°. (Found: C, 69.3; H, 5.15. $C_{27}H_{24}Sn$ calcd.: C, 69.5; 5.15 %.)

The low yields obtained are due to extensive coupling of the cinnamyl Grignard.

Other reagents

Ethanol and methanol were purified by standard procedures. Monodeuteromethanol (uvisol grade) and sodium deuteroxide were supplied by E. Merck, A. G. Darmstadt and were used without further purification. Boiled out de-ionised water was used throughout. 4 *N* carbonate free sodium hydroxide was used as a stock solution of base. Lithium perchlorate of reagent grade quality was used after drying at 110° for 6 h under 1 mm.

Kinetic technique

All reactions were performed in silica cells in a thermostatted compartment of an SP500 spectrophotometer. A stock solution of substrate was maintained at the reaction temperature in a thermostat. A freshly prepared solution of base was made up at the same temperature. (Fresh solutions of alkali were made up daily due to the appreciable decomposition of alcoholic alkaline solutions after two days). Appropriate volumes of substrate solution were placed in the cell, base added and timing commenced. The reaction cell was blanked against aqueous alcoholic alkali of identical concentration to that used in the reaction. Readings were taken at 301 mμ. The reaction was followed for eight half lives, after which readings became constant. The usual first order plot of log $(D_0-D_\infty)/(D_t-D_\infty)$ against time was obeyed for upwards of three half lives and the pseudo first order rate constant k_1 was evaluated graphically and was reproduceable to within 2%.

After the reaction was complete, the reaction solution was diluted tenfold with ethanol and the spectrum of the product was found to be identical with that of β-methylstyrene (λ_{max} 251 mμ) which had been formed in 90% yield as calculated from the absorption at 251 mμ.

Gas–liquid phase chromatograms of a reaction solution containing Et_3SnCH_2-CH=CHPh (0.0535 *M*) and sodium hydroxide (1.6 *M*) in "60%" aqueous methanol showed that β-methylstyrene had been formed in quantitative yields.

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