BASE-CATALYSED HYDROGEN-EXCHANGE BETWEEN ORGANOGERMANIUM HYDRIDES AND METHANOL *

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Summary

First order rate constants have been determined for the loss of tritium from tritiated germanium hydrides in MeOH/MeONa at 20—40° C. The rate constant for Ph_3GeT (T = ^3H) is greater than that for exchange at the 9-position of fluorene under similar conditions. Values of k_{rel}, the rate relative to that for Ph_3-GeH, for $(XC_6H_4)_3GeT$ compounds at 30° C are: (X =) *m*-Cl, 380; *p*-Cl, 71; *m*-Me, 0.48; *p*-Me, 0.078; *o*-Me, 0.081; *p*-OMe, 0.025; *o*-Me, 0.018, and there is a good linear correlation between log k_{rel} and σ. For the compounds (XC_6H_4)-Ph_2GeT the values of k_{rel} are (X =) *p*-NO_2, 1280; *p*-CN, 680; *m*-Cl, 10; and *p*-F, 1.1, and a plot of log k_{rel} against σ^- constants is much better than that against σ constants. The results imply that there is substantial delocalization of charge from the anionic germanium centre into the aromatic rings, and thus an important degree of $(p—p)_\pi$ bonding between the germanium atom and these rings in the anion.

The rates of exchange fall on going from Ph_3GeT to Ph_2GeHT, to $PhGeH_2T$ (the values of k_{rel} being 1, 0.11, and ca. 0.015 respectively), implying an order of kinetic acidities opposite to the reported order of equilibrium acidities in liquid ammonia. Replacement of Ph by Et groups also leads to a fall in kinetic acidity, values of k_{rel} for $EtPh_2GeT$ and Et_3GeT being 6×10^{-2} and ca. 3×10^{-3}, respectively. Solvolysis, involving generation of hydrogen, is significant for $PhGeH_3$ under the reaction conditions, and important for Et_3GeH.

The value of the inverse solvent isotope effect, k_{MeOD}/k_{MeOH} is ca. 1.7 for both Ph_3GeT and $(m\text{-}ClC_6H_4)_3GeT$ at 20° C. This value, and the activation parameters determined for some of the $(XC_6H_4)_3GeT$ compounds are consistent with a transition state for the rate-determining step in which the hydrogen is roughly half transferred from germanium to methoxide ion, with partial liberation of the methanol molecules initially solvating the latter.
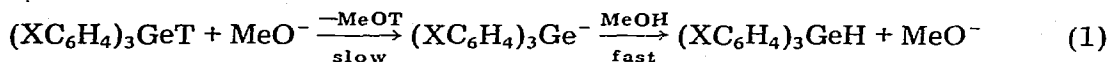
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* No reprints available.

Introduction

Whereas organo-silicon and -tin hydrides react with base in hydroxylic media with evolution of hydrogen, triphenylgermane undergoes exchange to give Ph_3-GeD when treated with MeOD/MeONa [1]. Germane itself was shown some years ago to undergo hydrogen-exchange with concentrated KOD/D_2O at $70°C$, but triphenylgermane could not be deuterated under such conditions [2].

We have now carried out a kinetic study of detritiation of some $(XC_6H_4)_3$-GeT and $(XC_6H_4)Ph_2GeT$ compounds (T = ^3H), and of Ph_2EtGeT, Ph_2HGeT, and PhH_2GeT by MeOH/MeONa. The results, reported below, provide information about the mechanism of the reaction and the relative stabilities of $(XC_6H_4)_3Ge^-$ anions, and throw light on the question of the extent of any delocalization of the lone pair of electrons into the aromatic rings by $(p \rightarrow p)_\pi$ interactions.

Results and discussion

The detritiations of the $(XC_6H_4)_3GeT$ compounds proceed at convenient rates in methanol containing 10^{-3} to 1.5 M MeONa at $20-40°C$, as shown in Table 1. The progress of the reaction was monitored by determining the proportion of tritiated hydride remaining, i.e. at various times samples of the reaction mixture were removed and added to a mixture of water with toluene containing a liquid scintillator, and the activity of the toluene extract was determined by scintillation counting. Good (pseudo) first-order kinetics were observed, and Table 1 lists the second-order, specific rate constants k_s, given by $k/[MeONa]$, where k is the observed rate constant at the base concentration used. Also shown are the values of k_{rel}, the rate relative to that of the parent Ph_3GeT. The values of k_s increase somewhat with the concentration of base, the effect being significally larger at 20 than at $30°C$, but the effects are not large enough to warrant applying corrections to k_s values determined at values of [MeONa] up to 0.5 M. A similar patterns of variation of the second-order rate constants with the base concentration has been noted previously in protio-detritiation of fluorene-9-t in MeOH at 20 and $45°C$, and can be associated with dependence of the H-acidity function of the medium on the base concentration [3]. Mass spectrometric examination of the gas above a sample of Ph_3-GeH kept under the conditions used for kinetic studies revealed no detectable evolution of hydrogen, and there was no detectable diminution of the $\nu(Ge-H)$ band in the IR and no appearance of a $\nu(Ge-OMe)$ band. Thus it can be concluded that the detritiation occurs exclusively by the process depicted in eq. 1, and that the rate measured is that of the triton abstraction from the $(XC_6H_4)_3$-GeT.

$$(XC_6H_4)_3GeT + MeO^- \xrightarrow[\text{slow}]{-MeOT} (XC_6H_4)_3Ge^- \xrightarrow[\text{fast}]{MeOH} (XC_6H_4)_3GeH + MeO^- \qquad (1)$$

The following features of the results for the $(XC_6H_4)_3GeT$ compounds are of interest.

(a) The most striking aspect is the high kinetic acidity of Ph_3GeH, for which the second order rate constant, k_s, at $40°C$ is ca. 1.5×10^{-3} s^{-1} mol^{-1}. This is a

higher rate than that for protodetritiation of fluorene-9-t in MeOH/MeONa at 45°C, for which $k_s = 4.0 \times 10^{-4}$ s^{-1} mol^{-1} [3]. If the relationship between kinetic and equilibrium acidities observed for fluorene derivatives [3] applied also to the germanium hydrides, it would imply a pK_a of ca. 20.5 for Ph$_3$GeH, where the pK_a's refer to acidities in C$_6$H$_{11}$NH$_2$/C$_6$H$_{11}$NHCs with the value of the pK_a for 9-phenylfluorene being taken as 18.49 [4]. (The corresponding rough pK_a value for (m-ClC$_6$H$_4$)$_3$GeH would be ca. 15.5.) The pK_a of Ph$_3$GeH in Me$_2$SO is stated by Bordwell [5] to be ca. 25.5, based on a quoted value of 23.0 [6] revised to put it on the scale now used for this medium [7]. On this scale the pK_a of fluorene is 22.6, so the order of kinetic acidities of Ph$_3$GeH and fluorene in MeOH/MeONa is in marked contrast to that of the equilibrium acidities in Me$_2$SO.

(b) As expected, electron-withdrawing substituents, which should stabilize the germyl anion, markedly accelerate the reaction, while electron-releasing substituents retard it. The compound with X = m-Cl is about 380 times as reactive at 30°C as the parent compared with X = H.

(c) The rates for the *ortho*-substituted compounds are close to those for the *para*-isomers for X = Me and OMe. This implies that steric inhibition to coplanarity is not a major factor in the influence of the aryl groups in the triarylgermanes. It is noteworthy that the activating influence of the o-Cl group is markedly greater than that of p-Cl substituents, and indeed is slightly greater than that of m-Cl substituents. This can be attributed to the considerable inductive electron-withdrawing effect of the halogen, which will be of enhanced importance from the *ortho*-position. The o-Cl was found to be slightly more activating than the m-Cl substituent in the base cleavage of XC$_6$H$_4$CH$_2$SiMe$_3$ compounds [21], which is believed to involve rate-determining separation of the carbanion XC$_6$H$_4$CH$_2^-$ [16] and so to show a clear analogy to the hydrogen-exchange in the triarylgermanes.

(d) A plot of log k_{rel} against the σ constants [8] for the X groups is a satisfactory straight line, as shown in Fig. 1. The correlation coefficient of the best least squares line is 0.994, the slope 6.50, and the intercept on the log k_{rel} axis 0.16. (A plot against σ^0 constants [8], is less satisfactory on visual inspection, since a smooth line of marked curvature can be drawn through the points for X = H, m-Me, p-Me and p-OMe, but not much inferior upon statistical analysis-correlation coefficient, 0.991, slope 7.43, intercept −0.14.) The value of the observed slope, 6.5, must be divided by 3 to give the value of ρ per aryl group, viz. 2.2, to be compared with those in familiar systems, but this is still quite large, indicating a substantial dispersal of the negative charge from the forming anionic centre into the aromatic rings. These results alone do not tell us whether there is significant conjugative delocalization of the lone pair of the forming anion into the rings, since the inductive effects of the aryl groups must induce some relay of negative charge into the rings, and Streitwieser and his colleagues have estimated that approximately one-third of the stabilizing effect of an α-Ph substituent at a carbanionic centre is due to the inductive effect and two-thirds to the conjugative effect [9].

In order to throw light on the importance of any conjugative delocalization of the long pair on the forming germyl anion into the aromatic rings, the series of compounds (XC$_6$H$_4$)$_3$Ph$_2$GeT with X = H, m-Cl, p-NO$_2$ and p-CN was exam-

TABLE 1

KINETIC DATA FOR HYDROGEN-EXCHANGE BETWEEN TRITIATED ORGANOGERMANIUM HYDRIDES AND METHANOL CONTAINING SODIUM METHOXIDE

Compound	Temperature (°C)	10^3 [NaOMe] (M)	$10^6\ k_s$ (mol^{-1} l s^{-1})	k_{rel} [a]	E_{act} (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal K^{-1} mol^{-1})
$(C_6H_5)_3$GeT	20	50	138			
		101	138			
		421	148			
		830	168			
		(802) [b]	(280) [b]			
		1500	230			
	30	108	480			
		421	530	1.0	21	-4
		1500	600			
	40	108	1450			
		421	1520			
$(m\text{-}ClC_6H_4)_3$GeT	20	1.00	$7.6\ \times 10^4$			6
		(1.00) [b]	(12.8×10^4) [b]			
	30	1.00	2.08×10^5	380	17	-6
		5.80	$2.0\ \times 10^5$			
	40	5.80	$5.0\ \times 10^5$			
		1.00	$5.0\ \times 10^5$			
$(p\text{-}ClC_6H_4)_3$GeT	30	5.80	3.73×10^4	71		
		1.00	3.83×10^4			
$(o\text{-}ClC_6H_4)_3$GeT	30	5.80	2.24×10^5	425		
		1.08	2.27×10^5			
$(m\text{-}MeC_6H_4)_3$GeT	20	421	85			
	30	108	255	0.48	22	-4
	40	421	1.03×10^3			
$(p\text{-}MeC_6H_4)_3$GeT	20	421	14.2			
	30	108	41.5	0.078	22	-6
	40	421	161			
$(o\text{-}MeC_6H_4)_3$GeT	20	421	14.7			
	30	108	43.2	0.081	22	-7
	40	421	163			
$(p\text{-}MeOC_6H_4)_3$GeT	30	108	13.2	0.025		
$(o\text{-}MeOC_6H_4)_3$GeT	30	108	9.7	0.018		
$(p\text{-}PhC_6H_4)_3$GeT	20	101	144		22	-1

TABLE 1 (continued)

Compound	Tempera- ture (°C)	10^3 [NaOMe] (M)	$10^6 k_s$ (mol^{-1} l s^{-1})	k_{rel} [a]	E_{act} (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal K^{-1} mol^{-1})
	30	421	156			
		108	530			
		421	570	1.03		
	40	421	1.75×10^3			
$(p\text{-}O_2NC_6H_4)Ph_2GeT$	30	4.21	6.8×10^5	1.28×10^3		
$(p\text{-}NCC_6H_4)Ph_2GeT$	30	4.90	3.6×10^5	6.8×10^2		
$(m\text{-}ClC_6H_4)Ph_2GeT$	30	42.1	5.3×10^3	10		
$(p\text{-}FC_6H_4)Ph_2GeT$	30	420	600	1.13		
		830	630			
$EtPh_2GeT$	30	421	31.5	6×10^{-2}		
Ph_2HGeT	30	1500	65	0.11	(18)^c	(−19)^c
	40	1500	175			
PhH_2GeT	30	1500	7.7	1.5×10^{-2}		
	40	1500	1.87			
Et_3GeT	30	1500	3.1	$(6 \times 10^{-3})^d$	(16)^c	(−29)^c

^{a} The value of k_s for Ph$_3$GeT at 0.421 M NaOMe is used as the base. For other compounds, where values of k_s are available at more than one concentration of NaOMe an average is used, otherwise no allowance is made for any variation of k_s with [NaOMe]. ^{b} In MeOD/MeONa. ^{c} See text. ^{d} This value should be halved to make a rough correction for solvolysis.
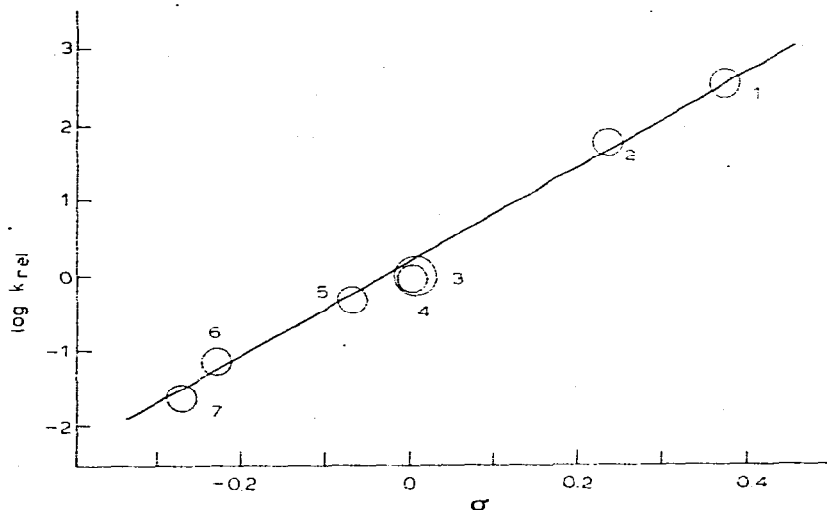
Fig. 1. Plot of log k_{rel} against σ for detritiation of $(XC_6H_4)_3GeT$. The numbering of the points is: (X =) 1, m-Cl; 2, p-Cl; 3, p-Ph; 4, H; 5, m-Me; 6, p-Me; 7, p-OMe.

ined, and the results are shown in Table 1. As expected, the 10-fold activating effect of the m-Cl substituent in $(m\text{-}ClC_6H_4)Ph_2GeT$, is rather greater than that of each of the 3 such substituents in $(m\text{-}ClC_6H_4)_3GeT$; if a factor of 10 applied additively for each of the substituents in the latter a value of k_{rel} of 1000 would be expected, compared with the observed value of 380. Although the number of points is very ïimited, it is clear that a plot of log k_{rel} against σ^- (values for p-F and $p\text{-}NO_2$ from ref. [8] and value for p-CN from ref. 10) is markedly better than that against σ (Fig. 2). The correlation coefficients are, respectively, 0.996 (slope 2.62, intercept 0.02) and 0.987 (slope 4.23, intercept —0.18). The value of the slope when σ^- constants are used is consistent with that for the plot against σ for the $(XC_6H_4)_3GeT$ compounds, whereas this is not the case when σ constants are used.

The need to use σ^- constants for the substituents, p-CN and $p\text{-}NO_2$, with powerful electron-withdrawing resonance effects is strong evidence for conjugative delocalization of charge into the aromatic rings from the germyl anion centre; this is illustrated in the resonance form I.
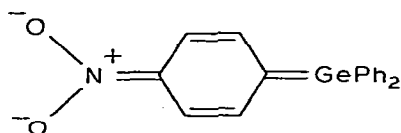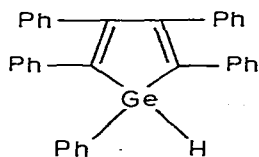
(I)   (II)

There is conflicting evidence in the literature on the existence of $(p \rightarrow p)_\pi$ bonding between germanium and carbon such as that implied by structure I. Thus Birchall and Jolly concluded from analyses of the ^1H NMR spectrum of the anion Ph_3Ge^- in $NH_3/NaNH_2$ that there was extensive charge delocalization into the aromatic rings [11], but Birchall and Drummond concluded from a
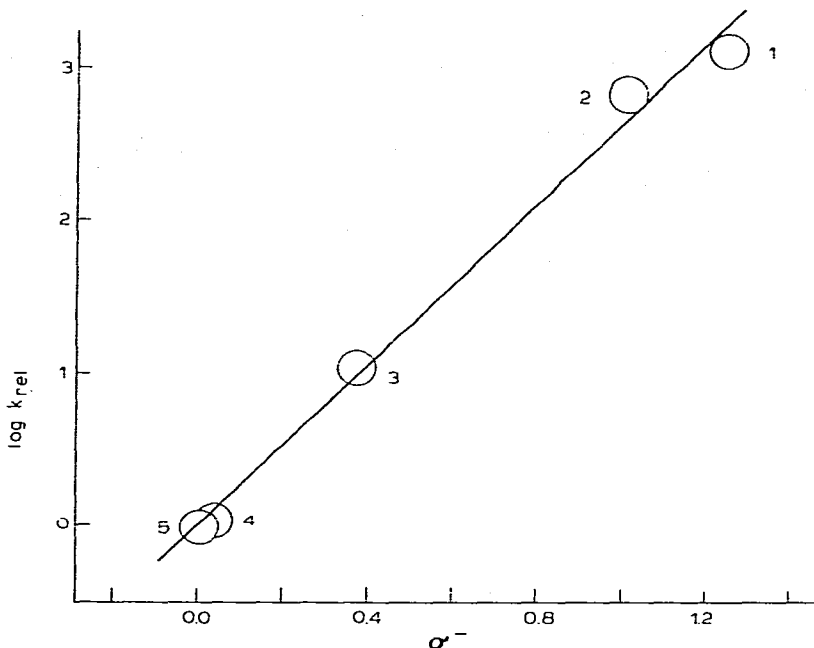
Fig. 2. Plot of log k_{rel} against σ^- for detritiation of $(XC_6H_4)Ph_2GeT$. The numbering of the points is as follows: (X =) 1, p-NO_2; 2, p-CN; 3, m-Cl; 4, p-F; 5, H.

more detailed study of the ${}^1H$ NMR spectrum that there is no delocalization of charge into the phenyl group of the anion PhH_2Ge^- [12]. However, Curtis reasonably attributes the very high acidity of pentaphenyl-1-germacyclopentadiene (II), which is at least 6 pK_a units more acidic than Ph_3GeH in tetrahydrofuran, to delocalization involving $(p-p)_\pi$ interaction between the negative germyl centre and the attached unsaturated carbon centres [6]. Furthermore Sakurai and his colleagues recently concluded that there is definite delocalization of the free electron of the radical $Ph_3Ge^\cdot$, though this is markedly smaller than that in the corresponding carbon radical, $Ph_3C^\cdot$ [13]. .

In view of the compelling evidence for substantial delocalization of the lone pair of the triarylgermyl anion, the smallness of the activation by the p-Ph group in $(p\text{-}PhC_6H_4)_3GeH$ is of interest. In the base-cleavage of $XC_6H_4CH_2SiMe_3$ compounds, the p-Ph group causes a 12-fold activation, and in the light of the ρ factors for the two reactions a large activation might be expected in the hydrogen-exchange, whereas the observed k_{rel} value is only 1.03. However, the effect of a p-Ph group even in systems requiring use of σ^- constants is very variable (probably mainly depending on the degree of approach to coplanarity in the transition state of the p-Ph ring with the aromatic ring to which it is attached), and Exner has listed experimental σ^- values for this substituent ranging from 0.02 to 0.11 [22]; the lowest of these is consistent with our results, and it appears that the demand for delocalization of electrons from the reaction centre is not powerful enough to induce a large response from the p-Ph group.

Rate data for the compounds Ph_2HGeT, PhH_2GeT, Ph_2EtGeH and Et_3GeH are included in Table 1. The ratio of the observed rate constants for Ph_3GeT

and Ph_2HGeT at $30°C$ is ca. 9.1 (at 1.5 M base) and that for $Ph_2GeH/PhGeH_3$ is ca. 8.5 *. The last ratio must be lower than the true figure, since a little hydrogen was found to be evolved from $PhGeH_3$, indicating that some of the tritium was being lost by conversion of Ge—H into Ge—OMe bonds, but this probably represents less than 10% of the reaction, since there was no detectable diminution of the ν(GeH) bond or appearance of ν(GeOMe) bonds in the IR spectrum of material recovered after >95% loss of tritium. Thus we can take a factor of ca. 9 as applying to the effect of each additional Ph group on going from $PhGeH_3$ to Ph_2GeH_2 to Ph_3GeH. The influence of introducing an additional Ph group into Ph_2HGeT, to go to Ph_3GeT, would be expected to be somewhat smaller than that on going from $PhGeH_3$ to Ph_2GeH_2 because of the "saturation" effect, but this effect should be small in view of the fairly small range of reactivities involved. In the series $PhCH_3 \rightarrow Ph_2CH_2 \rightarrow Ph_3CH$, in which a much greater range of reactivity is covered, the influence of the third phenyl group is exceptionally low because of steric inhibition of coplanarity, but this is not expected to be an important factor when the groups are around the larger germanium atom. It is noteworthy that, because of the deactivating influence of the p-OMe groups, the triarylgermane (p-$MeOC_6H_4$)$_3$GeH is less than twice as reactive as the monoaryl $PhGeH_3$, and the $ortho$-substituted (o-$MeOC_6H_4$)$_3$GeH is even closer to the latter in reactivity.

If we assume that the change from PhH_2GeT to H_3GeT would be accompanied by a further factor of about 10, this would imply a k_s value of ca. 7 × 10^{-7} s^{-1} mol^{-1} for the exchange in H_3GeT at $30°C$, which would be very roughly comparable with that for exchange in a carbon acid with a pK_a ($C_6H_{11}NH_2$—$C_6H_{11}NHCs$) of 27—28 [3]. A pK_a of 25 in water has been estimated by Jolly for GeH_4 [14], but this rough agreement must be fortuitous since the pattern of the kinetic acidities of germanium hydrides seems to be very different from that of their equilibrium acidities. Thus Birchall and Jolly found Ph_3GeH to be a "much weaker" acid than GeH_4 in liquid ammonia [11] and Birchall and Drummond found $PhGeH_3$ to be a much stronger acid than Ph_3GeH in that medium, though still weaker than GeH_4 by 2—2.5 pK_a units [12]. We did not examine the exchange in the case of GeH_4, and it is conceivable, though rather unlikely, that there is a sudden sharp reversal of the trend observed for Ph_3GeH, Ph_2GeH_2 and $PhGeH_3$, but it is clear from our results that the kinetic acidity of Ph_3GeH is substantially greater than that of $PhGeH_3$, in contrast with the pattern of equilibrium acidities. The failure of Ph_3GeH to undergo exchange in D_2O/KOD at $70°C$, in which GeH_4 undergoes exchange fairly readily [2], might be taken to imply a lower kinetic acidity for Ph_3GeH than GeH_4, but the insolubility of the triarylgermane in water is almost certainly the major cause of its unreactivity in the aqueous system.

Comparison of the rate constants for Ph_2EtGeT and Ph_2HGeT shows that replacement of a hydrogen atom by an ethyl group is associated with a 2-fold fall in rate. This at first sight seems a surprisingly small factor in view of the electron-releasing inductive effect of alkyl groups relative to hydrogen and some increased steric hindrance to solvation of the transition state, but is rea-

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* No statistical correction need be made for the additional Ge—H bonds in Ph_2GeH_2 and Ph_2GeH_3 since effectively only one of the protium atoms will be replaced by tritium in each active molecule. In tritiation, as distinct from detritiation, the statistical correction would be needed.

sonable when viewed against the rate increase by only a factor of 9 on introduction of a Ph group. The observed rate constant for tritium loss from Et_3GeT is, however, surprisingly high, since the rates for Et_3GeT, Et_2PhGeT and Ph_3-GeT imply that replacement of one Ph group of Ph_3GeT by an Et group causes an 18-fold rate decrease while introduction of two more Et groups causes only a further 11-fold decrease. Under the conditions used for the exchange, hydrogen is evolved from Et_3GeH and about half of the Ge—H bonds are converted into Ge—OMe bonds, but this would only account for half of the observed rate of tritium loss, still leaving a substantial anomaly.

We note that in all the exchanges of germanium hydrides in MeOH/MeONa, solvolysis, with generation of hydrogen [15], must be regarded as a competing process, but only when the rate of exchange is unusually low does this become significant.

Activation parameters and solvent isotope effects

Approximate activation energies and entropies were determined for six of the $(XC_6H_4)_3GeH$ compounds. For five of the compounds, viz. those with X = H, m-Me, p-Me, o-Me and p-Ph, which do not differ much in reactivity, the value of E_{act} is 21 or 22 kcal mol^{-1}, and the values of $\Delta S^{\neq}$, which are in the range —1 to —7 cal K^{-1} mol^{-1}, also show no significant variation. The value of E_{act} for the markedly more reactive $(m$-ClC$_6$H$_4)_3$GeH is significantly lower, viz. 17 kcal mol^{-1}, with the value of $\Delta S^{\neq}$ falling in the range observed for the other compounds.

The abnormal apparent activation parameters for the reactions of Ph_2HGeT and PhH_2GeT do not represent a real anomaly. They originate in the fact that a high base concentration (1.5 M) has to be used for these relatively unreactive compounds, and since, as we have noted, the increase in specific rate constant with the base concentration is greater the lower the temperature, misleading small temperature coefficients, and thus low E_{act} and $\Delta S^{\neq}$ values, are to be expected.

We have drawn attention above to the fact that the kinetic acidity of Ph_3GeT in methanol is rather similar to that of fluorene-9-t and the reactivities of the substituted tritiated triarylgermanes span a range similar to that for various fluorene derivatives [3]. It is thus significant that the values of E_{act} and $\Delta S^{\neq}$ are very similar in the two systems, e.g. the values of E_{act} and $\Delta S^{\neq}$ for fluorene-9-t are 23.3 kcal mol^{-1} and —1.2 cal K^{-1} mol^{-1}, compared with 21 kcal mol^{-1} and —4 cal K^{-1} mol^{-1}, respectively, for Ph_3GeT, while the corresponding value for $(m$-ClC$_6$H$_4)_3$GeT, 17 kcal mol^{-1} and —6 cal K^{-1}, are close to those, viz. 17.1 kcal mol^{-1} and —6 cal K^{-1} mol^{-1} for the comparably reactive 1,12-o-phenylene-7,12-dihydropleiadene [3]. As in the case of the fluorene derivatives [3], the near-zero values of $\Delta S^{\neq}$ can be attributed to liberation of solvating methanol from the methoxide ion as it moves to the transition state, which offsets the loss of freedom normally associated with the transition state of a bimolecular reaction. The proton transfer for the fluorene derivatives appears to be roughly half complete in the transition state [3] *, and this also seems to be the case for the germanium hydrides.

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* The high value of the kinetic isotope effect for the reverse reaction, that of the 9-fluorenyl anion with MeOH and MeOD, also indicates that proton transfer is roughly half complete in the transition state [16].

For Ph$_3$GeH and (*m*-ClC$_6$H$_4$)$_3$GeH the first order rate constants were determined for the exchange in MeOD, in each case at a sodium methoxide concentration very close to that used for the reaction in MeOH. The results, shown in Table 1, correspond to values of 1.7 ± 0.15 for both Ph$_3$GeH and (*m*-ClC$_6$H$_4$)$_3$-GeH, respectively, at 20°C for the inverse solvent isotope effect, i.e. k_s(MeOD)/k_s(MeOH). This value is within the normal range for reaction catalysed by sodium methoxide in methanol, but is significantly lower than the value of ca. 2.0—2.2 expected for complete liberation of the solvent molecules initially bound up in solvation of the methoxide ion [17]. (Ratios in the range 2.0—2.5 are commonly observed in cleavages of Me$_3$Si—R compounds in MeOH/MeONa, in which the methoxide ion is thought to be fully or almost fully attached to the silicon atom in the transition state of the rate-determining step [16,18]) This result is consistent with the proposal above of a transition state in which the proton is roughly half-transferred, and thus the solvating methanol molecules not completely liberated. Somewhat surprisingly, in view of the close analogies noted above, a rather higher value for the k_s(MeOD)/k_s(MeOH) ratio, viz. 2.2, which would be consistent with complete proton transfer in the transition state, was reported for detritiation of 9-methylfluorene-9-*t* at 45°C [3], but the rate constants at 45°C listed in ref. 3 for 9-phenylfluorene-9-*t* correspond with a ratio of ca. 1.7—1.8, in agreement with our result for the germanium hydrides, and a range of ratios between 2.0 and 2.6 can be derived for 9-methyl-fluorene-9-*t* by taking the extremes of the possible rate constants listed for 9-methylfluorene-9-*t*, suggesting that the experimental uncertainty is large and that there may not be a real difference between the solvent isotope effects for the germanium hydride and fluorene reactions. However, the proton transfer in the transition state may, indeed be somewhat more advanced in the transition state for the hydrocarbon reactions, with the solvent isotope effect a more sensitive indicator of the degree of proton transfer than the activation parameters or the kinetic acidities.

The close analogy between the results for the protodetritiation of the fluorene derivatives, for which there is strong evidence for generation of the carbanion in the rate determining step [3], and that of the germanium hydrides argues against the possibility that the latter may involve proton transfer from the solvent to the separating germanium atom as the Ge—T bond breaks, in a mechanism analogous to those believed to operate in cleavage of some benzyl-trimethylstannanes [18,19].

Experimental

Preparation of (XC$_6$H$_4$)$_4$Ge compounds

These were made from the reagents XC$_6$H$_4$Li (X = *o*-OMe, *p*-OMe, *p*-Me, *m*-Me, *o*-Me, *p*-Ph) or XC$_6$HgMgBr (X = *o*-Cl, *m*-Cl, *p*-Cl). Typical procedures were as follows:

(i) An organolithium compound was prepared from *p*-bromomethoxybenzene (0.50 mol) and lithium (1.07 g-atom) in ether (300 cm³) and the residual lithium was removed by filtration. A solution of tetrachlorogermane (0.03 mol) in ether (50 cm³) was added dropwise during 2 h with ice-cooling, and the mixture was stirred at room temperature for 2 h. The ether was then mainly

replaced by toluene, and the mixture was boiled under reflux for 4 h. Treatment with 0.5 M aqueous hydrochloric acid, followed by washing and drying (Na_2SO_4) and evaporation of the organic layer, left a solid, which was purified by chromatography on alumina. The yield of pure tetrakis(p-methoxyphenyl)-germane was 30%; m.p. 218—222°C.

For the preparation of (p-PhC$_6$H$_4$)$_4$Ge the organolithium reagent was made from p-bromodiphenyl and n-butyllithium.

(ii) A solution of tetrachlorogermane (0.040 mol) in ether (100 cm^3) was added dropwise during 1.5 h to the Grignard reagent prepared from m-bromo-chlorobenzene (0.44 mol) and magnesium (0.5 g-atom) in ether (200 cm^3). The solution was boiled under reflux for 8 h, then the ether was partly replaced by toluene, and refluxing was continued for an additional 8 h. Work-up as described under (i), but with purification by repeated recrystallization from toluene, gave tetrakis(m-chlorophenyl)germane (20%), m.p. 203—204°C.

The m.p.'s of the other (XC$_6$H$_4$)$_4$Ge compounds purified were: (X =) o-Me, 168—170°C; p-OMe, 218—222°C; p-Me, 228—229°C; m-Me, 148—149°C; o-Me, 175—177°C; p-Ph, 270—273°C; m-Cl, 203—204°C. For X = o- and p-Cl the products were used without final purification in the preparation of the (XC$_6$H$_4$)$_3$GeBr compounds.

Preparation of (XC$_6$H$_4$)$_3$GeBr compounds

These were made by treatment of the (XC$_6$H$_4$)$_4$Ge compounds with bromine. A typical procedure is as follows.

Bromine (0.0375 mol) in BrCH$_2$CH$_2$Br (30 cm^3) was added dropwise during 3 h to a solution of (p-MeC$_6$H$_4$)$_4$Ge (0.036 mol) in BrCH$_2$CH$_2$Br (100 cm^3) maintained at ca. 100°C. The mixture was kept at 100°C for an additional hour, then the volume was reduced to 60 ml. On cooling to 0°C a solid separated, and this was filtered off, washed with cold hexane, and recrystallized from n-hexane to give (p-MeC$_6$H$_4$)$_3$GeBr (80%), m.p. 128—129°C.

For X = o-Me, the reaction mixture was kept at 100°C for 4 h; for X = m-Me and p-Ph, 3 h at 100°C was followed by 1 h under reflux, while heating at the reflux temperature was used for o-, m-, and p-Cl (6 h).

The products had m.p.s as follows: (X =) o-Me, 106—108°C; m-Me, 118—120°C; p-OMe, 146—149°C; p-Ph, 240—242°C; m-Cl, 77—78°C; p-Cl, 132—135°C. The compound with X = o-Cl could not be obtained crystalline at room temperature, but no impurity could be detected by GLC, and the ^{1}H NMR spectrum was as expected.

Preparation of (XC$_6$H$_4$)$_3$GeH compounds

These were made by reduction of the corresponding bromides with lithium aluminium hydride in ether. A typical procedure is given below.

A solution of (p-MeC$_6$H$_4$)$_3$GeBr (0.025 mol) in ether (150 cm^3) was added dropwise during 2 h to LiAlH$_4$ (0.070 mol) in ether (150 cm^3). The mixture was boiled under reflux for 2 h, the ether was replaced by light petroleum (b.p. 60—80°C), and the solution was filtered, concentrated to small volume, and cooled. The precipitate was recrystallized from light petroleum (b.p. 60—80°) to give a solid (90%) of m.p. 87—88°C.

The physical properties of the hydrides are listed in Table 2. The IR and

TABLE 2

PHYSICAL CONSTANTS OF ORGANOGERMANIUM HYDRIDES PREPARED

Hydride	M.P. ($^{\circ}$C)	B.p./Press ($^{\circ}$C/mm Hg)	ν(GeH) (cm^{-1})	δ(GeH) (cm^{-1})	τ for GeH [a] (p.p.m.)
Ph$_3$GeH	41— 42		2037s	709s	4.34 [b]
(o-MeC$_6$H$_4$)$_3$GeH	102—105		2057m	697s	4.40 [b]
(m-MeC$_6$H$_4$)$_3$GeH		160—168/0.001	2037m	719s	4.43 [b]
(p-MeC$_6$H$_4$)$_3$GeH	87— 88		2032m	732s or 688s	4.48
(oMeOC$_6$H$_4$)$_3$GeH		160—180/0.001	2033m	694s	4.48
(p-MeOC$_6$H$_4$)$_3$GeH		170—180/0.001	2037m	731s or 689s	4.51
(o-ClC$_6$H$_4$)$_3$GeH		135—148/0.001	2058m	696s	4.49 [b]
(m-ClC$_6$H$_4$)$_3$GeH		160—168/0.002	2043m	715s or 687s	4.42 [b]
(p-ClC$_6$H$_4$)$_3$GeH		160—170/0.002	2042m	735s or 695s	4.39
(p-PhC$_6$H$_4$)$_3$GeH		190—208/0.001	2031s	709s or 685s	4.37
(m-ClC$_6$H$_4$)Ph$_2$GeH		145—155/0.001	2040ms	706s	4.39 [b]
(p-FC$_6$H$_4$)Ph$_2$GeH	<30		2034s	708s	4.41
(p-CNC$_6$H$_4$)Ph$_2$GeH	<30		2032s	710s	4.56
(p-NO$_2$C$_6$H$_4$)Ph$_2$GeH	96— 98		2038s	704s	4.32
Ph$_2$EtGeH [c]		97—103/0.5	2033ms	707s	5.15
Ph$_2$GeH$_2$		91— 94/1	2051s		5.10
Ph$_2$GeH$_3$ [d]		40— 43/20	2061s		4.48
Et$_3$GeH		120—122/760	2004s		5.30 [b]

[a] In CDCl$_3$ unless otherwise indicated. [b] In CCl$_4$. [c] n_D^{25} 1.5912. [d] n_D^{25} 1.5353.

NMR spectra were as expected. Less than 1% of impurity could be detected in the samples by thin layer chromatography.

Preparation of Ph$_2$EtGeH

A solution of bromine (0.02 mol) in BrCH$_2$CH$_2$Br (10 cm^3) was added during 3 h to a refluxing solution of Ph$_3$GeEt (0.02 mol) in BrCH$_2$CH$_2$Br (200 cm^3). The mixture was refluxed for 2 h, then concentrated under reduced pressure. Fractional distillation of the residue gave (bromo)ethyldiphenylgermane (71%), b.p. 130—131°C/0.2 mmHg. This was treated with an excess of LiAlH$_4$ in ether, and the usual work-up, culminating in fractional distillation, gave ethyl-diphenylgermane, (98%), with the properties listed in Table 2.

Preparation of (p-NO$_2$C$_6$H$_4$)Ph$_2$GeH

(a) A Grignard reagent was made from p-bromophenyltrimethylstannane (0.10 mol) in THF (tetrahydrofuran) at 40°C. Triphenylbromogermane (0.05 mol) was added, the mixture was refluxed for 4 h, the THF was replaced by toluene, and the mixture refluxed for a further 4 h. The usual work-up gave p-Me$_3$SnC$_6$H$_4$GePh$_3$, (4.1 g), which was taken up in CH$_2$Cl$_2$. The solution was cooled to —20°C and a solution of nitrosyl chloride (0.59 g, 0.009 mol) in CH$_2$-Cl$_2$ (50 cm^3) was added during 45°C, the temperature being maintained at —20°C [20]. The mixture was stirred at —20°C for 1 h, then allowed to warm to

room temperature. The solution was treated at 0°C with potassium permanganate (25 g) and 0.5 M sulphuric acid (100 ml) in the presence of ethyl acetate. The mixture was then stirred at 70°C for 1 h, and additional CH_2Cl_2 (100 ml) was added. The organic layer was separated, well washed with water, dried (Na_2SO_4), and evaporated, and the residue chromatographed on a silica gel column with toluene/hexane as eluent to give (p-nitrophenyl)triphenylgermane (1.7 g), m.p. 260—261°C. A sample (1.5 g) was treated with bromine in $BrCH_2CH_2Br$ in the usual way (8 h reflux, see above) to give bromo(p-nitrophenyl)diphenylgermane. This was reduced with an excess of sodium borohydride in THF at 10°C, and work-up, culminating in fractional distillation gave a little triphenylgermane followed by (p-nitrophenyl)diphenylgermane (see Table 2). Less than 1% of impurity could be detected by thin layer chromatography.

Preparation of (p-FC₆H₄)Ph₂GeH

The Grignard reagent from p-FC_6H_4Br in ether was treated with Ph_3GeBr, and after 2 h refluxing the ether was replaced by toluene and refluxing was continued for 4 h. The usual work-up gave p-fluorophenyltriphenylgermane, m.p. 214—217°C (after recrystallization from 4/1 C_6H_6/EtOH). Some of this product was treated with bromine in $BrCH_2CH_2Br$ at 120°C for 4 h, then the solvent was evaporated to leave a residue, which was washed with hexane. It was then reduced with $LiAlH_4$ in ether to give (p-fluorophenyl)diphenylgermane which was recrystallized from n-hexane to give a solid melting below 30°C (see Table 2). Less than 1% of impurity could be detected by thin layer chromatography.

Preparation of (p-CNC₆H₄)Ph₂GeH

Bromotriphenylgermane (0.030 mol) in ether (100 cm³) was added to the Grignard reagent made from p-dibromobenzene (0.05 mol) in ether (100 ml), and the mixture was refluxed for 6 h. The usual work-up followed by recrystallization from toluene and chromatography through silica gel with toluene/hexane (60/40) as eluent gave (p-bromophenyl)triphenylgermane (3.6 g), m.p. 224—226°C.

Some of the p-bromophenyltriphenylgermane (3.3 g) in DMF (20 cm³) was added dropwise with stirring to copper(I) cyanide (0.88 g) in DMF (20 cm²) at 120°C. The mixture was refluxed for 8 h then added to water. A solution of hydrated ferric chloride (4 g) in 1 M hydrochloric acid (200 cm³) was added. The mixture was kept at 70°C for 1 h, then toluene (200 cm³) was added, and the organic layer was separated, washed repeatedly with dilute hydrochloric acid, and then with 10% aqueous sodium hydroxide. The dried solution was evaporated and the residue was recrystallized from toluene to give (p-cyanophenyl)triphenylgermane (1.2 g), m.p. 221—227°C, ν(CN) 2210m and 2150w cm^{-1}. This product was treated with bromine in $BrCH_2CH_2Br$ for 6 h at 110°C, and the isolated bromide was reduced with sodium borohydride in THF/H_2O; column chromatography (silica gel with toluene/hexane as eluent) gave three fractions, one of which was identified as p-cyanophenyldiphenylgermane (0.2 g) (see Table 2), (the other fractions showed amine bands in the IR spectrum).

Tritiation procedure

(1) The triarylsilanes $(XC_6H_4)_3GeH$ with X = H, Me, Cl, *p*-OMe and *p*-Ph, and also $(p\text{-}FC_6H_4)Ph_2GeH$, were tritiated by conversion into the corresponding germyllithium compound followed by treatment of the latter with tritiated water.

A typical procedure was as follows. n-Butyllithium (0.01 mol) in ether (7 cm³) was added during 0.5 h to a stirred solution of tri-*p*-tolylgermane (0.01 mol) in ether (15 cm³) cooled in ice. The mixture was subsequently stirred at room temperature for 1 h, and then ether (30 cm³) containing tritiated water (0.1 cm³, 50 mCi). The mixture was stirred for 0.5 h then treated with an excess of water. The ethereal layer was separated, washed six times with water, and dried (Na_2SO_4). The solvent was evaporated and the residual solid recrystallized from light petroleum to give a sample of m.p. 87—88°C.

The non-solid tritiated hydrides were distilled at low pressure.

(2) The compounds Et_3GeH, Ph_2EtGeH, Ph_2GeH_2, $PhGeH_3$, $(p\text{-}NCC_6H_4)Ph_2$-GeH, and $(p\text{-}O_2NC_6H_4)Ph_2GeH$ were tritiated by base-catalysed exchange, as in the following typical procedure.

Ethyldiphenylgermane (0.5 g) was dissolved in methanol (20 cm³) containing 3 *M* sodium methoxide, and dimethylsulphoxide (6 cm³) was added. The mixture was warmed, and tritiated water (1 cm³, 500 mCi) was added. The mixture was heated under reflux, and from time to time a sample (1 cm³) was removed and added to toluene (10 cm³), and the mixture was neutralized with hydrochloric acid. The toluene solution was repeatedly washed with water, then dried ($MgSO_4$), and its activity then determined (see below). After 20 h a suitable level of activity had been introduced and the tritiated germanium hydride was recovered. (It is possible that some of the recovered hydrides contained a little of the corresponding methoxide or hydroxide, but these would not interfere in the kinetic studies.)

Rate measurements

An appropriate amount of the hydride was dissolved in anhydrous methanol (20 cm³) containing sodium methoxide of known molarity and pre-warmed to the appropriate temperature; to aid dissolution, solid hydrides were sometimes added as concentrated toluene solutions (ca. 0.1 cm³). The mixture was well shaken, then placed in a thermostat bath. After 10 min a 1 cm³ sample was removed, and other such samples were removed at appropriate intervals. Each sample was immediately added to toluene (20 cm³) containing BBOT * (4 g/l), and aqueous hydrochloric acid (containing enough acid to neutralize the base) was added. The mixture was shaken well, and the toluene layer was washed several times with water, and then dried (Na_2SO_4). Counting was then carried out with a Nuclear Enterprise Model 6500 scintillation counter. If C_0 is the initial count (on the sample removed after 10 minutes, taken as zero time for the run), C_t the count after time t, and C_∞ the count after 10 half-lives, the first order constant is given by the slope of the plot of $\log (C_0 - C_\infty)/(C_t - C_\infty)$ against time. The "infinity" counts were acceptably low, and the plots were satisfactorily linear to more than 80% of reaction.

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* 2,5-bis(5'-t-butyl-2-benzoxazotyl)thiophene.

Investigation of side reactions

(i) A solution of triphenylgermane in 1.5 M methanolic sodium methoxide was kept at 30°C for 1 day. After this time the gases above the liquid contained no dihydrogen detectable by mass spectrometry, and the IR spectrum of the recovered hydride showed no detectable decrease in the intensity of the ν(GeH) band compared with the intensities of the bands from the aryl groups.

A similar result was obtained with several other triarylsilanes.

(ii) When a similar experiment was carried on for 4 weeks, the recovered sample did show a small decrease in the intensity of the ν(GeH) band and the appearance of new bands of low intensity in the neighbourhood of the aryl bands.

(iii) After a solution of phenylgermane in 1.5 M methanolic sodium methoxide had been kept at either 40°C for 1 day or 30°C for 3 days, the gases above the liquid contained a very small amount of dihydrogen (detectable by mass spectrometry). The IR spectrum of the recovered material was not significantly changed, however.

(iv) A solution of triethylgermane (1 g) in 20 cm³ of 2 M methanolic sodium methoxide was kept at 40°C for 4 days. The gases above the liquid after this time contained a substantial amount of dihydrogen, and in the IR spectrum of the recovered material there was roughly a 35% decrease in the intensity of the ν(GeH) band relative to the alkyl bands, and corresponding new peaks appeared in the region expected for GeOMe groups.

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