THE ALKALI CLEAVAGE OF SOME (PHENYLETHYNYL)-SILANES AND -GERMANES

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(Received February 15th, 1965)

INTRODUCTION

There are several reports of the cleavage of ethynyl–silicon bonds[1,2,3], and a semi-quantitative study has been made of the relative ease of cleavage of phenylethynyl, 1-indenyl, 9-fluorenyl and other groups from silicon by potassium hydroxide in a homogeneous dioxane–water–methanol medium[4]. We recently discussed the acid-catalysed cleavage of a series of substituted (phenylethynyl)triethylgermanes[5], and we now describe a study of the alkali cleavage of these compounds together with other (phenylethynyl)-germanes and -silanes (eqn. 1, M = Si or Ge; Z = H or Me. In the subsequent discussion Z will be written as H for simplicity).

$$YC_6H_4C{\equiv}CMR_3 + HOZ \xrightarrow{OZ^-} YC_6H_4C{\equiv}CH + R_3MOZ \qquad (1)$$

RESULTS AND DISCUSSION

Exploratory studies showed that both (phenylethynyl)–silicon and –germanium bonds (in contrast to benzyl–germanium bonds[6]) were readily broken in aqueous–methanolic alkali, and that the rates of cleavage could be measured spectrophotometrically by techniques used for cleavage of benzyl–silicon and benzyl–tin bonds[6,7]. Some features of the results are discussed below.

Mechanism of the cleavage

In Table 1 are shown the wave-lengths, λ, used in the measurements, and values of the observed first-order rate constants, k_1, for a range of $PhC{\equiv}CMR_3$ compounds at the alkali concentrations specified. Also shown is the reactivity of each compound relative to that of the triethylsilyl compound, calculated by assuming that the rate is directly proportional to alkali concentration (*i.e.* that there is no salt-effect), as was found to be the case with the alkali cleavage of benzyl-silicon and related compounds[6,7]. The validity of this assumption is supported by the fact that the relative reactivities so calculated for the compounds $PhC{\equiv}CSiMe_3$ and $PhC{\equiv}CGeMe_3$ are constant for several alkali concentrations although derived from the rate for the $PhC{\equiv}CSiEt_3$ compound at one concentration.

(Phenylethynyl)trimethylsilane is cleaved *ca.* 2×10^7 times as readily as benzyltrimethylsilane[6,7]. A large difference was to be expected, in view of the much greater stability of the phenylethynyl than of the benzyl carbanion[6,8], and is in

TABLE 1

CLEAVAGE OF $PhC{\equiv}CMR_3$ COMPOUNDS BY AQUEOUS METHANOLIC ALKALI

MR_3	*λ (mμ)*	*[NaOH][a] (M)*	*10^3k_1 (min^{-1})*	*Rel. rate*
(A) At 29.4°. Aqueous Alkali (1 vol.) in Methanol (5 vol.)				
$SiEt_3$	273	1.88	25.0	1.00
$SiMeEt_2$	273	1.88	184	7.4
$SiMe_2Et$	273	0.0510	33.0	49
$SiPh_3$	265	0.964	152	11.8
$SiMe_3$	272	0.0510	188	277
	272	0.0260	95.8	277
	272	0.0117	43.2	277
$GeMe_3$	273	1.88	203	8.1
	273	0.964	105	8.2
	273	0.228	24.8	8.2
(B) At 50.0°. Aqueous Alkali (1 vol.) in Methanol (5 vol.)				
$GeMe_3$	273	0.228	157	7.0
$SiEt_3$	273	0.964	94.5	1.00
(C) At 50.0°. Aqueous Alkali (2 vol.) in Methanol (5 vol.)				
$GeMe_3$	273	0.0510	115	6.76
$GeEt_3$	273.5	1.88	44	0.070
$GePh_3$	265	1.88	3.82	0.0061
$SiPr\text{-}iso_3$	273	1.88	0.46	0.00074
$SiEt_3$	273	0.228	76	1.00

[a] Concn. of the aqueous NaOH.

accord with either the synchronous process (2) or the stepwise process (3)–(4) having reaction (4) as the rate-determining step*.

$$HO^- + R'MR_3 \longrightarrow [HO\text{-----}MR_3\text{-----}R']^- \longrightarrow HOMR_3 + R'^- \qquad (2)$$

$$HO^- + R'MR_3 \longrightarrow [HOMR_3R']^- \qquad (3)$$

$$[HOMR_3R']^- \longrightarrow [HO\text{—}MR_3\text{---}R']^- \longrightarrow HOMR_3 + R'^- \qquad (4)$$

A stepwise process, (3)–(4), with step (3) rate determining would not be consistent with the large influence of the nature of the organic group, R′ on the ease of cleavage of the $R'MR_3$ compounds.

We shall see below that when the results for the cleavage of $PhC{\equiv}CMR_3$ compounds are considered along with those for benzyltrimethylsilane and related compounds, the stepwise process affords conceptually simpler explanations of the observed results than does the synchronous process, but this is not an argument against the latter, which cannot be ruled out.

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* In both cases the carbanion R'^- would subsequently rapidly extract a proton from the solvent. Possibly the carbanion is never wholly free, there being some interaction with the solvent in the transition-state as the M–R′ bond breaks[6,7,8].

Variation of R in $R_3SiC{\equiv}CPh$ compounds

In Table 2 are shown the rates of cleavage, k_{rel}, of $(XC_6H_4)_3SiC{\equiv}CPh$ compounds relative to that of the compound $(C_6H_5)_3SiC{\equiv}CPh$, and it will be seen that electron-withdrawal by the group X has a marked rate-enhancing effect. (Based on *meta*-substituents, $\rho = 2.2$, see below.) There is thus a substantial excess of negative charge on the silicon atom in the transition-state of the rate-determining step, and this is consistent with the stepwise mechanism (3)–(4) having step (4) slow. Because of the greater stability of the forming $PhC{\equiv}C^-$ carbanion compared with that of the $PhCH_2^-$ carbanion, it might be expected that the transition state for decomposition of the intermediate $H\bar{O}SiR_3C{\equiv}CPh$ would be closer in energy and structure to the intermediate than is the case for the decomposition of the intermediate $H\bar{O}SiR_3CH_2Ph$, and thus that rather more negative charge would be present on the silicon atom in the transition state of the former than of the latter decomposition. Unfortunately results are not available for cleavage of a series of $(XC_6H_4)_3SiCH_2Ph$ compounds, but a few results for $XC_6H_4SiMe_2CH_2Ph$ compounds[9] suggest that the effect of X is indeed rather smaller than in the phenylethynyl compounds, though the difference is less than might have been expected. (For example, with the $XC_6H_4SiMe_2CH_2Ph$ compounds, a *p*-Cl group accelerates the reaction three times; with $(XC_6H_4)_3SiC{\equiv}CPh$ compounds, the corresponding value for the average effect of one *p*-Cl group is 4.6). In terms of the synchronous process (2), the results would be explained by postulating a smaller degree of bond-breaking relative to bond-making for the phenylethynyl than for the benzyl compounds.

TABLE 2

CLEAVAGE OF $(XC_6H_4)_3SiC{\equiv}CPh$ COMPOUNDS BY AQUEOUS ALKALI (2 VOL.) IN METHANOL (10 VOL.) AT 30.0°

X	λ $(m\mu)$	$[NaOH]^a$ (M)	$10^3 k_1$ (min^{-1})	k_{rel}
p-OMe	267	1.88	74.7	0.24
	267	0.964	36.5	0.23
p-Me	272	1.88	81.6	0.26
	272	0.964	40.2	0.26
H	265	1.88	315	1.00
	265	0.964	156	1.00
m-Me	280	1.88	109	0.35
	280	0.964	54.2	0.35
p-F	275	0.0510	113	13.7
	275	0.0117	25.6	13.4
p-Cl	269.5	0.0228	361	98
	269.5	0.0117	186	98
m-Cl	268	0.0117	610	320

[a] Concn. of the aqueous NaOH.

The effects of the X groups do not correlate satisfactorily with their Hammett σ-constants (Fig. 1). A straight line can be drawn through the three points for unsubstituted and *meta*-substituted compounds*, but the points for the *para*-substituted compounds with X = Cl, F, Me, and OMe, all lie well away from the line in a direction

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* The line as shown (Fig. 1) has a slope of 6.6, but since there are three X groups present in each case the value of ρ is 2.2.

indicating that these compounds are all more reactive than expected from the σ-constants of the X groups; the effect is particularly large for the *p*-OMe group. Use of Schott and Harzdorf's σ_{Si}-constants[10] ($= \sigma_I + 0.75\,\sigma_M$) puts the points for X = *p*-Cl and *p*-F on the line for the *meta*-substituents and those for *p*-Me and *p*-OMe reasonably close to it, but this need not necessarily have any wider significance than that there is a fairly good linear free energy correlation between the effects of substituents on the alkaline solvolysis of $(XC_6H_4)_3SiH$ compounds, from which the σ_{Si}-constants were derived, and those on the alkaline cleavage of $(XC_6H_4)_3SiC{\equiv}CPh$ compounds.

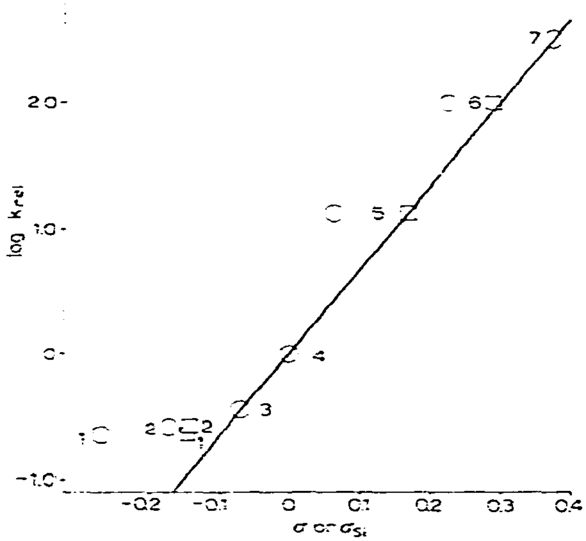

Fig. 1. Plot of log k_{rel} for the cleavage of $(XC_6H_4)_3SiC{\equiv}CPh$ compounds against σ (○) and against σ_{Si} (□). X: (1), *p*-OMe; (2), *p*-Me; (3), *m*-Me; (4), H; (5), *p*-F; (6), *p*-Cl; (7), *m*-Cl.

Schott and Harzdorf suggested that the special σ_{Si}-constants were needed for the solvolysis of $(XC_6H_4)_3SiH$ compounds because of the importance of d_π–p_π bonding between the silicon atom and the ring[11], but it seems to us that the anomalies are in the wrong direction for this. In the alkaline solvolysis of both $(XC_6H_4)_3SiH$ and $(XC_6H_4)_3SiC{\equiv}CPh$ compounds, there is more negative charge on the silicon atom in the transition state than in the initial state, and, on the simplest reasoning, it seems likely that there will be less d_π–p_π bonding to the silicon atom in the transition state than in the initial state. This means that the initial state is stabilized more by this bonding than the transition state, and so the reactivity should be abnormally *low*, not high, for those substituents with large $+M$ effects, such as *p*-OMe, *p*-F, and *p*-Cl, which should preferentially enhance the extent of the d_π–p_π bonding.

The effects of varying the alkyl groups in $PhC{\equiv}CSiAlk_3$ compounds are shown in Table 1. The 280-fold difference between the reactivities of the Me_3Si and Et_3Si compounds seems too large to originate in the larger $+I$ effect of the ethyl group, though this must contribute. (For comparison, it may be noted that the corresponding factor is only 5.5 for cleavage of p-$R_3SiCH_2C_6H_4CO_2^-$ compounds[9].) We think that steric influences play a large role in the displacement of the phenylethynyl group.

One factor in this is that the Si–C bond is probably short in $\mathrm{Si{-}C{\equiv}CR}$ compounds (the effect of *sp*-hybridization of the ethynyl-carbon atom being reinforced by d_π–p_π bonding[11]) but more important, we suggest, is that stabilization of the forming carbanion $\mathrm{PhC{\equiv}C^-}$ by solvation must be very large compared with that of, say, the benzyl carbanion, since the centre of charge is so open to the solvent. A bulky $\mathrm{MR_3}$ group could interfere seriously with the solvation of the partly-formed carbanion in the transition state, and so lower the reactivity markedly.

With the $\mathrm{PhC{\equiv}CSiR_3}$ compounds, successive replacement of Me by Et groups brings about a fairly regular decrease in reactivity: reactivity ratios are, $\mathrm{SiMe_3/SiMe_2Et} = 5.7$; $\mathrm{SiMe_2Et/SiMeEt_2} = 6.6$; $\mathrm{SiEt_2Me/SiEt_3} = 7.4$. Similar replacement of the α-hydrogen atoms of the alkyl group by methyl groups involved in the change from $\mathrm{Et_3Si}$ to iso-$\mathrm{Pr_3Si}$ compounds does not bring about a very much bigger decrease in rate (the factor is 1350) than the replacement of the first three such atoms in the change from $\mathrm{Me_3Si}$ to $\mathrm{Et_3Si}$ compounds (factor, 280)[*]. This might at first sight seem to argue against the steric explanation of the effects, since steric hindrance usually increases rather steeply and irregularly with progressive regular increases in size, but this is probably less true for hindrance to a general orientation of solvent molecules about the reaction site than it is for the rather specific compressions within the molecules undergoing covalency change in the transition state complex which are involved in most examples of steric hindrance. Steric hindrance to solvation also provides an explanation of the fact that the compound $\mathrm{Ph_3SiC{\equiv}CPh}$ is markedly less reactive than the compound $\mathrm{Me_3SiC{\equiv}CPh}$, although electronic effects should make it more reactive; in contrast, the compound $\mathrm{Ph_3SiCH_2Ph}$ is cleaved more readily than $\mathrm{Me_3SiCH_2Ph}$[7].

Comparison of R_3SiR', R_3GeR' and R_3SnR' compounds

The germanium compounds $\mathrm{Me_3GeC{\equiv}CPh}$ and $\mathrm{Et_3GeC{\equiv}CPh}$ are less reactive than the corresponding silicon compounds (Table 1). Except possibly for displacement of alkoxy groups, nucleophilic displacements at germanium are normally slower than the corresponding reactions at silicon, although there is a small number of exceptions[6,12], some of which we think are to be attributed to smaller effects of steric hindrance in the germanium compounds[**]. Smaller steric hindrance to solvation with the $\mathrm{R_3GeC{\equiv}CPh}$ compounds than with the $\mathrm{R_3SiC{\equiv}CPh}$ compounds provides explanations of the facts that (*a*) the reactivity ratio $\mathrm{PhC{\equiv}CMMe_3/PhC{\equiv}CMEt_3}$ is smaller for the germanium compounds, and (*b*) the reactivity ratios $\mathrm{PhC{\equiv}CSiR_3/PhC{\equiv}CGeR_3}$ are fairly small (*cf.* ref. 6). We cannot at present offer explanations of the inversion of the relative reactivities of triphenyl and triethyl

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[*] Here and below we neglect the fact that some sets of relative reactivities which we compare were determined at different temperatures or in different media. These differences have relatively minor effects: for example, the ratio of reactivities $\mathrm{PhC{\equiv}CGeEt_3/PhC{\equiv}CSiEt_3}$ is 7.0 at 50° but 8.2 at 29.4° in $\mathrm{H_2O}$ (1 vol.)/MeOH (5 vol.), and 6.8 at 50° in $\mathrm{H_2O}$ (2 vol.)/MeOH (5 vol.).

[**] The germanium atom is larger, but only very slightly so than the silicon atom. Chipperfield and Prince have attributed the change in the ease of hydrolysis from the order $\mathrm{Ph_3SiCl} > \mathrm{Ph_3GeCl}$ to iso-$\mathrm{Pr_3GeCl}$ > iso-$\mathrm{Pr_3SiCl}$ to the d_π–p_π bonding in the aryl compounds, this being less important for the germanium compound[12]. We suggest, however, that in the penta-coordinate intermediate, or a transition state resembling it, d_π–p_π bonding will be less important, because of the excess of negative charge on the metal atom, than in the tetrahedral reactant. If this is so, the d_π–p_π bonding effects would tend to make silicon compounds *less* reactive than germanium compounds. It is relevant to note that in the cleavage of $\mathrm{R_3M}$-fluorenyl compounds the order of reactivity is $\mathrm{Me_3Si} > \mathrm{Me_3Ge}$ but $\mathrm{Et_3Ge} > \mathrm{Et_3Si}$[6], and it would be difficult to ascribe this to d_π–p_π bonding effects.

derivatives on going from silicon to germanium compounds, or, which is really the same problem, why the ratio of reactivities of the trimethyl to triphenyl derivatives is forty-six times larger for the germanium than for the silicon compounds*.

The (phenylethynyl)trialkylstannanes are cleaved very much more readily than the corresponding silicon compounds, and we have confirmed that they react[3] readily even with neutral aqueous methanol at room temperature; the cleavage is catalysed by base and thus probably involves nucleophilic attack at tin, rather than rate-determining ionization, even in the neutral solvolysis. It is also markedly accelerated by addition of water to the methanol solvent. The difference between the tin and silicon compounds is much greater than in cleavage of Me_3MCH_2Ph compounds[6], possibly because steric hindrance to solvation, which is smaller for the tin compounds, is more important with the phenylalkynyl compounds.

It is noteworthy that exchange of the acetylenic hydrogen atom of phenylacetylene occurs very much more rapidly than the cleavage of (phenylethynyl)-trimethylsilane in the same basic medium[13], whereas R'–$SiMe_3$ bonds, where R' is an organic group, are usually cleaved much more readily than the corresponding R'–H bonds by nucleophilic reagents[3]. (For example, base-catalysed cleavage of benzyltrimethylsilane is very much faster than base-catalysed hydrogen-exchange at the α-position of toluene[14].) This anomaly can be explained in terms of hindrance to solvation in the silicon compound, because the forming carbanion will be very exposed indeed to solvent molecules in attack of base on phenylacetylene and much less so in attack on (phenylethynyl)trimethylsilane.

Variation of Y in $YC_6H_4C{\equiv}CMR_3$ compounds

Tables 3 and 4 show that in cleavage of the compounds $YC_6H_4C{\equiv}CMR_3$, in which $MR_3 = GeEt_3$, $SiMe_3$, and $SiEt_3$, reaction is facilitated by electron-withdrawal and retarded by electron-release from the substituents, Y, as would be expected for a rate-determining separation of the carbanion $YC_6H_4C{\equiv}C^-$. For *meta*- and *para*-substituents, there is a good linear free-energy correlation between effects of the substituents in any two of the three series (Fig. 2). With the possible exception of *ortho*-substituted compounds, the substituent effects for $YC_6H_4C{\equiv}CSiEt_3$ compounds are slightly smaller in a more aqueous medium, presumably because the charge on the forming carbanion is more effectively dispersed by solvation and thus interacts less with the substituents.

The spread of rates for *meta*- and *para*-substituents in the three series falls in the order ($MR_3 =$) $Et_3Si > Me_3Si > Et_3Ge$. For the Et_3Si and Me_3Si compounds the order is a normal one, in that the smaller rate spread is associated with the more reactive series, in which the rate-determining transition state will not lie as far along the reaction coordinate in the direction of the separated carbanion. In this sense, it is abnormal that the smallest rate spread is associated with the least reactive series, *viz.* the Et_3Ge compounds. It is not difficult, in terms of the stepwise mechanism (3)–(4), to see how this could arise. It is reasonable to believe that the lower reactivity of the germanium compounds is to be associated with generally lower susceptibility of the

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* It is relevant to note that this difference would be consistent with Chipperfield and Prince's hypothesis[12] (on which we comment above) that d_π–p_π bonding, considered to be more important for silicon than for germanium, contributes more in the transition (penta-coordinate) state than in the initial (tetrahedral) state.

TABLE 3

CLEAVAGE OF $YC_6H_4C{\equiv}CMR_3$ COMPOUNDS BY AQUEOUS ALKALI (2 vol.) IN METHANOL (5 vol.) AT 50.0°

Y	λ (mμ)	[NaOH][a] (M)	$10^3 k_1$ (min^{-1})	k_{rel}
$MR_3 = SiEt_3$				
m-Br	293.5	0.117	177	4.5
H	273	0.117	39.1	1.00
	273	0.228	76.4	—
p-Cl	281.5	0.117	100	2.56
o-Cl	292	0.117	70.6	1.81
p-Me	283	0.228	43.2	0.56
o-Me	290	0.228	31.6	0.41
$MR_3 = GeEt_3$				
m-CF_3	288.5	1.88	225	5.2
o-Br	293.5		64.0	1.49
m-Br	292.5		155	3.61
o-Cl	292.5		88.0	2.05
m-MeO	298.5		57.0	1.33
p-Cl	281.5		97	2.26
p-Br	287		102	2.38
p-F	276		59.7	1.39
p-I	292		93	2.17
H	273.5		42.9	1.00
m-Cl	283.5		157	3.66
m-Me	282		34.4	0.80
p-*tert*-Bu	272		26.7	0.62
o-Me	289		16.8	0.39
p-Me	283.5		27.0	0.63
p-OMe	296		21.0	0.49
2,4,6-Me_3[b]	276		3.63	0.085
2,3-Me_2[c]	292.5		12.9	0.30

[a] Concn. of the aqueous NaOH. [b] (Mesitylethynyl)triethylgermane. [c] (Xylylethynyl)triethylgermane.

germanium atom to nucleophilic attack, or in terms of the mechanism (3)–(4), with a relatively higher energy of the pentacoordinate intermediate for the Et_3Ge compounds than for the Et_3Si and Me_3Si compounds. However, because the Ge–C bond is weaker than the Si–C bond, the intermediate $HO\overset{-}{Ge}Et_3C{\equiv}CPh$ can be expected to lose a carbanion more readily than the $H\overset{-}{O}SiR_3C{\equiv}CPh$ intermediate, in other words, the rate constant for step (4) is faster for the germanium compounds. This means that in the transition state of step (4), the highest energy transition state for the overall reaction (though further removed in energy from the reactants) will be closer to the intermediate for the germanium compound. Thus there will be less charge on the forming carbanion, and so a smaller effect of substituents*.

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* In terms of the synchronous mechanism (2), the explanation would be that bond-breaking is less advanced in the transition state for germanium than for the silicon compounds. Because the Ge–C bond is weaker than the Si–C bond, the energy curve for dissociation of the M–C bond crosses the repulsion curve for the forming M–O bond at a point corresponding to a smaller degree of dissociation of the M–C bond when germanium is involved. On the other hand, because the curve for the forming M–O bond lies at higher energies for the Ge–O than for the Si–O bond, the crossing point can lie further along the repulsion curve, nearer the completed M–O bond, for the germanium compounds. In other words, bond-breaking will be less advanced for the germanium compounds in the transition state even though bond-making may be more advanced.

TABLE 4

CLEAVAGE OF $YC_6H_4C{\equiv}CSiR_3$ COMPOUNDS BY AQUEOUS METHANOLIC ALKALI AT 29.4°

Y	λ ($m\mu$)	$[NaOH]^a$ (M)	$10^3 k_1$ (min^{-1})	k_{rel}
(A) Aqueous Alkali (1 vol.) in methanol (5 vol.)				
R = Me				
m-Br	293.5	0.0117	192	4.4
H	272	0.0117	43.2	1.00
p-OMe	297	0.0510	80	0.425
o-Me	290	0.0510	109	0.58
p-Me	283	0.0510	113	0.60
R = Et				
m-Br	293.5	1.88	135	5.20
p-Cl	281.5	1.88	68.2	2.73
o-Cl	292	1.88	60.1	2.40
H	273	1.88	25.0	1.00
p-Me	283	1.88	13.7	0.55
o-Me	290	1.88	10.4	0.42
(B) Aqueous Alkali (2 vol.) in methanol (5 vol.)				
R = Et				
m-Br	293.5	0.964	211	4.86
p-Cl	281.5	0.964	113	2.60
o-Cl	292	0.964	109	2.51
H	273	0.964	43.4	1.00
p-Me	283	1.88	45.7	0.54
o-Me	290	1.88	34.3	0.41

[a] Concn. of the aqueous NaOH.

The transmission of substituent effects through the phenylethynyl system has been the subject of a number of recent publications, concerned with the pK_a values of phenylpropiolic acids[15–17], the reaction of these acids with diphenyldiazomethane[16,17] and with methanol in the presence of acid[15], the saponification of ethyl phenylpropiolates[16,18] and the chemical shifts in the NMR spectra of phenylacetylenes[19]. Plots (not shown) of log k_{rel} values for substituents in each reaction series $YC_6H_4C{\equiv}CMR_3$ (MR_3 = Me_3Si, Et_3Si, Et_3Ge) against pK_a values of phenylpropiolic acids, or against substituent parameters derived from the other reactions mentioned above, show considerable scatter. A better, but still not good straight-line plot (Fig. 3) is obtained for log k_{rel} *versus* σ-constants[20]*.

Similar, rather poor plots are obtained for log k_{rel} *versus* analogous log k_{rel} values for cleavage of $YC_6H_4CH_2SiMe_3$ and $YC_6H_4CH_2SnMe_3$ compounds, both of which correlate well with σ[6,7]. It is noteworthy that the *p*-fluoro substituent activates in the alkali cleavage of $YC_6H_4C{\equiv}CGeEt_3$ compounds, whereas it deactivates in the alkali cleavage of benzyl–tin and benzyl–silicon bonds[6].

The ρ values as given by the effects of *m*-halogen for the (phenylethynyl)-MR_3 cleavages, are small: *viz.* $GeEt_3$, 1.43; $SiEt_3$, 1.68 (compare the value of ρ, *viz* 4.9, in the cleavage of $YC_6H_4CH_2SiMe_3$ compounds[7]). This might to some extent be related

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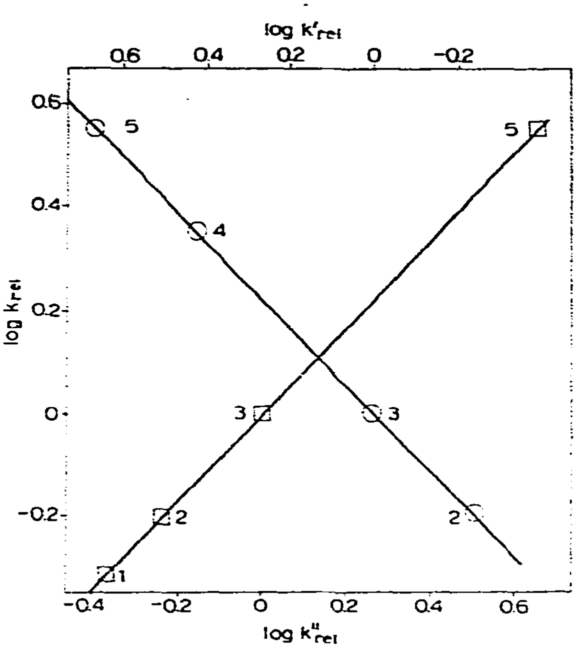
* The line shown is drawn through the points for X = H, *m*-Me, *m*-Cl, and *m*-Br; a rather better least-squares line could be drawn.



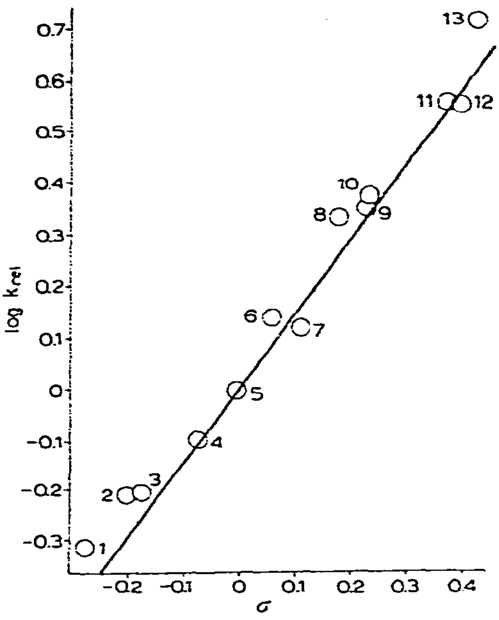


Fig. 2. Plot of log k_{rel} for the cleavage of $YC_6H_4C{\equiv}CGeEt_3$ compounds against log k'_{rel} for the cleavage of $YC_6H_4C{\equiv}CSiEt_3$ compounds (○) and against log k''_{rel} for the cleavage of $YC_6H_4C{\equiv}CSiMe_3$ compounds (□). Y: (1), *p*-OMe; (2), *p*-Me; (3), H; (4), *p*-Cl; (5), *m*-Br.

Fig. 3. Plot of log k_{rel} for the cleavage of $YC_6H_4C{\equiv}CGeEt_3$ compounds against σ. Y: (1), *p*-OMe; (2), *p*-*tert*-Bu; (3), *p*-Me; (4), *m*-Me; (5), H; (6), *p*-F; (7), *m*-OMe; (8), *p*-I; (9), *p*-Cl; (10), *p*-Br; (11), *m*-Cl; (12), *m*-Br; (13), *m*-CF_3.

to the insulating effect which the triple bond has been suggested to exert in the transmission of electronic effects[15–17,21*], but it must mainly be associated with the following factors: (*a*) the relatively small degree of separation of the carbanion in the transition state, (*b*) the tolerance of the electronegative *sp*-hybridized ethynyl carbon atom for negative charge, which renders charge-delocalization relatively unimportant**, and (*c*) the dispersal of the negative charge on the forming carbanion by the very effective solvation. These factors are, of course, inter-related.

The scatter of the *ρ*–*σ* plots for the $YC_6H_4C{\equiv}CMR_3$ compounds is in contrast to the good linear plots found for the base-catalyzed ethynyl–hydrogen exchange of phenylacetylenes $YC_6H_4C{\equiv}CH$[13]. It is noteworthy that with the $YC_6H_4C{\equiv}CMR_3$ compounds the deviations for *para*-substituents are in the same direction as those noted above for the series of $(XC_6H_4)_3SiC{\equiv}CPh$ compounds, though considerably smaller. It is tempting once more to associate the deviations with d_π–p_π bonding in the reactants, $R_3MC{\equiv}CPh$, but the deviations are again in the wrong direction; for example, the greatest degree of stabilization by d_π–p_π bonding would be expected for the *p*-OMe compounds, whereas these compounds are more, not less, reactive than

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* But see ref. 18.

** This is not, we believe, equivalent to a general "insulating effect" of the triple bond on electron transmission, since the tolerance of charge is towards negative charge only, whereas the insulating effect would operate equally towards negative or positive charge.

expected from a ρ–σ correlation. Furthermore, if d_π–p_π bonding were the cause of the deviations, we should not expect such a good linear free energy correlation between substituent effects in $YC_6H_4C{\equiv}CGeEt_3$ compounds and those in $YC_6H_4C{\equiv}CSiEt_3$ compounds (Fig. 2) since d_π–p_π bonding is thought to be less important with germanium than with silicon[22].

For the $2,3\text{-}Me_2C_6H_3C{\equiv}CGeEt_3$ and $2,4,6\text{-}Me_3C_6H_2C{\equiv}CGeEt_3$ compounds the values of k_{rel} are not significantly different from those calculated by assuming additivity of substituent effects.

EXPERIMENTAL

Preparations involving organolithium reagents

(Phenylethynyl)triphenylsilane. To (phenylethynyl)lithium (0.04 mole), prepared by cross-metallating phenylacetylene with *n*-butyllithium in hexane/ether, was added fluorotriphenylsilane (0.026 mole) in ether (20 ml). Dry benzene (120 ml) was added and the ether was distilled from the reaction mixture, which was then refluxed for 2 h, set aside for 12 h, and hydrolysed with saturated aqueous ammonium chloride. The organic layer was separated, dried, and evaporated, finally (to remove excess phenylacetylene) under reduced pressure. The residue was recrystallised from methanol/light petroleum to give (phenylethynyl)triphenylsilane (5.1 g), m.p. 102° (lit.[23] m.p. 100–101°).

TABLE 5

$(XC_6H_4)_3SiC{\equiv}CPh$ COMPOUNDS MADE FROM ORGANOLITHIUM REAGENTS

X	*M.p.*	*Found %*		*Calcd. %*		*X*	*M.p.*	*Found %*		*Calcd. %*	
		C	*H*	*C*	*H*			*C*	*H*	*C*	*H*
o-Me	179–180°	86.4	6.5	86.5	6.5	*m*-Cl	90– 91	67.4	3.8	67.3	3.7
m-Me	80– 81	86.4	6.5	86.5	6.5	*p*-Cl	117–118	67.5	3.8	67.3	3.7
p-Me	127–128	86.7	6.5	86.5	6.5	*p*-F	127	75.3	4.2	75.3	4.1
						p-OMe	125–126	77.4	5.7	77.3	5.8

$(XC_6H_4)_3SiC{\equiv}CPh$ compounds. By the same method, but from the triarylbromosilanes, were prepared the new compounds listed in Table 5. The triarylbromosilanes were prepared from the triarylsilanes and bromine, or, in the case of tris(-*p*-methoxyphenyl)silane, *N*-bromosuccinimide[24], in carbon tetrachloride.

(Phenylethynyl)triphenylgermane. By the same method, from bromotriphenylgermane and phenylethynyllithium was prepared (phenylethynyl)triphenylgermane, m.p. 92.5–93° (lit.[25] m.p. 89°).

(Phenylethynyl)-tri-o-tolyl- and -triisopropyl-silane. By the same method, but with toluene in place of benzene, were prepared (from fluorotri-*o*-tolylsilane) (phenylethynyl)tri-*o*-tolylsilane (Table 5) and (from bromotriisopropylsilane) (phenylethynyl)triisopropylsilane, b.p. 135°/2.8 mm, n_D^{25} 1.5210. (Found: C, 78.9; H, 10.1. $C_{17}H_{26}Si$ calcd.: C, 79.0; H, 10.2 %.)

Preparations involving Grignard reagents

(Arylethynyl)trialkyl-germanes and -silanes were prepared from the appropriate

TABLE 6

$YC_6H_4C{\equiv}CMR_3$ COMPOUNDS MADE FROM GRIGNARD REAGENTS

Y	*MR$_3$*	*B.p.°/mm*	n_D^{25}	*Found %*		*Calcd. %*	
				C	*H*	*C*	*H*
H	GeMe$_3$	70/1.5	1.5429	60.5	6.4	60.4	6.5
H	SiMe$_2$Et	70/0.4	1.5251	76.7	8.6	76.7	8.6
H	SiMeEt$_2$	92/1.7	1.5243	77.1	8.9	77.1	9.0
H	SiEt$_3$	124/4.5	1.5245	77.7	9.3	77.7	9.3
m-Br	SiEt$_3$	132/1.7	1.5480	57.0	6.4	56.9	6.5
p-Cl	SiEt$_3$	121/1.8	1.5360	67.0	7.7	67.0	7.7
o-Cl	SiEt$_3$	133/3.0	1.5340	67.1	7.6	67.0	7.7
p-Me	SiEt$_3$	128/3.5	1.5245	78.1	9.6	78.2	9.6
o-Me	SiEt$_3$	108/1.4	1.5232	78.1	9.5	78.2	9.6

(arylethynyl)magnesium bromide and trialkylhalo-germane or -silane in tetrahydrofuran as previously described[26]. The properties of these new compounds are listed in Table 6.

Kinetic measurements

Rates of cleavage of ethynyl–silicon and –germanium bonds were determined spectrophotometrically by the methods used previously for alkali cleavage studies of benzylsilicon and related compounds[6,7]. A solution of the organometallic compound in methanol (5 vol. or 10 vol.) and aqueous sodium hydroxide (2 vol.) were mixed. A sample was transferred to a thermostatted 1 cm stoppered cell and the change in optical density (*D*) was measured at a suitable wave-length (*λ*) (shown in Tables 1–4). Infinity readings were measured after 10 half-lives on the cell sample except for runs of half-life greater than 1 h, for which infinity readings were made on samples kept in sealed tubes. For the compound PhC≡CSi-Pr-iso$_3$, which was cleaved slowly, sealed tubes were used throughout the runs[6]. Rate constants, which could be duplicated to within 1 %, were normally determined graphically, but values calculated throughout the reaction are given for the following runs.

(i) [PhC≡CSiEt$_3$]^a 8.8 × 10^{-4} *M*; [NaOH]^b 1.88 *M*; λ = 273 mμ; 29.4°

Time (min)	0	4	14	22	30	34	40	∞
10^3 D	574	541	468	424	385	369	348	216
10^4 k_1 (min^{-1})	—	242	252	247	250	250	249	—

(ii) [*p*-ClC$_6$H$_4$C≡CGeEt$_3$]^a 9.4 × 10^{-4} *M*; [NaOH]^b 1.88 *M*; λ = 281.5 mμ; 50.0°

Time (min)	0	2	4	6	8	10	12	∞
10^3 *D*	584	521	467	421	386	356	330	217
10^4 k_1 (min^{-1})	—	944	960	979	970	971	980	—

^{a} Concn. of the stock methanol solution of the organometallic compound. ^{b} Concn. of the aqueous NaOH.

ACKNOWLEDGEMENTS

This work was supported by the Office of Aerospace Research, United States Air Force, through its European Office. We thank Dr. L. SPIALTER, of the Chemistry

Research Laboratory, Aerospace Research Laboratories, Wright Patterson Air Force Base, for his interest and encouragement, and the Royal Society for the loan of apparatus.

SUMMARY

We have measured spectrophotometrically the rates of cleavage by aqueous methanolic alkali of some $(XC_6H_4)_3SiC{\equiv}CPh$ compounds, and also of some $YC_6H_4C{\equiv}CMR_3$ compounds in which $M = Si$ or Ge.

(Phenylethynyl)trimethylsilane undergoes cleavage *ca.* 10^7 times as fast as benzyltrimethylsilane. Reaction is facilitated by electron-withdrawal and retarded by electron-release in the substituents X or Y. The effects of the substituents Y, but not of the substituents X, can be correlated approximately with their Hammett σ-constants.

Solvation of the forming carbanion $YC_6H_4C{\equiv}C^-$ is thought to be of considerable importance, and steric hindrance to such solvation (which is smaller for GeR_3 than for SiR_3 compounds) may be the major cause of the following effects: (*a*) The (phenylethynyl)–$SiMe_3$ bond is broken by alkali much less readily than the (phenylethynyl)–H bond, (*b*) the silicon compound $PhC{\equiv}CSiMe_3$ is only 34 times as reactive as the corresponding germanium compound $PhC{\equiv}CGeMe_3$, (*c*) the trimethyl compound $PhC{\equiv}CSiMe_3$ is 280 times as reactive as the corresponding triethyl compound, which is *ca.* 1350 times as reactive as the corresponding triisopropyl compound.

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