ORGANOGERMANIUM COMPOUNDS

V*. CLEAVAGE OF SUBSTITUTED (PHENYLETHYNYL)TRIETHYLGERMANES BY AQUEOUS METHANOLIC PERCHLORIC ACID

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INTRODUCTION

Electrophilic substitutions at acetylenic carbon atoms have received little attention, and the only systematic study seems to have been that by Dessy and Kim, who examined the acid cleavage of di(phenylethynyl)mercury compounds[2]. We have now measured the rates of cleavage of a series of $X–C_6H_4–C{\equiv}C–GeEt_3$ compounds [see equation (1), in which Y = H or Me] by a mixture of methanol (5 vol.) and aqueous perchloric acid (2 vol.) at 20.05°.

$$X–C_6H_4–C{\equiv}C–GeEt_3 + YOH \xrightarrow{H^+} X–C_6H_4–C{\equiv}CH + Et_3GeOY \qquad (1)$$

RESULTS AND DISCUSSION

The results are shown in Table 1, which lists the values of the observed first-order rate constants, k_1, at the acid concentrations used, and the values of k_{rel}, the rates relative to that of the unsubstituted compound. (The relative rates were not all measured at the same acid concentration, but the values are probably not very sensitive to change in the concentration.)

It is reasonable to assume that the reaction involves the carbonium ion $Ar–C^+{=}C(H)GeEt_3$, (I), as an intermediate, analogous to the intermediate $RO–C^+{=}CH_2$ formed in the rate-determining step of the acid-catalysed hydration of ethynyl ethers[3]. It is likely that the C–Ge bond of the intermediate (I) is broken more readily than the corresponding C–H bond, or, in other words, that the energy barrier for reversion of the intermediate to the starting materials is higher than that for its decomposition to products, so that in this case, also, the protonation of the acetylene is the rate-determining step. Since the cleavage of the $Ar–C{\equiv}C–GeEt_3$ compounds at a given acid concentration is faster than the hydration of the corresponding $Ar–C{\equiv}CH$ compound, the carbonium ion (I) (and the transition state on the way to it) must be stabilized by the large inductive release of electrons of which trialkylgermyl groups

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[*] For Part IV see ref. 1.

TABLE 1

CLEAVAGE OF SUBSTITUTED C_6H_5–C≡C–$GeEt_3$ COMPOUNDS BY A MIXTURE OF METHANOL (5 VOL.) AND AQUEOUS PERCHLORIC ACID (2 VOL.) AT 29.05°

Substituent(s)	$[HClO_4]$ *(M)**	10^3k_1 *(min⁻¹)*	k_{rel}	*Substituent(s)*	$[HClO_4]$ *(M)**	10^3k_1 *(min⁻¹)*	k_{rel}
p-OMe	0.049	125	110	*p*-F	1.00	36.5	0.89
2,4,6-Me_3	0.049	45.7	—	*m*-OMe	2.20	113	0.67
	0.216	222	40	*o*-OMe	1.00	25.7	0.63
p-*tert*-Bu	1.00	222	5.4	*p*-I	2.20	49.8	0.29
p-Me	0.216	29.2	—	*p*-Cl	2.20	46.0	0.27
	1.00	216	5.3	*p*-Br	2.20	39.1	0.23
2,3-Me_2	1.00	207	5.05		4.50	239	—
o-Me	1.00	85.8	2.1	*m*-Cl	4.50	61.2	0.059
m-Me	1.00	69.6	1.7	*o*-Cl	4.50	61.4	0.059
H	1.00	40.9	1.00	*o*-Br	4.50	78.4	0.075
H	2.20	169	1.00	*m*-Br	4.50	59.1	0.057
				m-CF_3	4.50	23.0	0.022

* Concn. of aqueous acid before mixing.

are capable[4,*]. It also appears that the intermediate ion (I) loses a triethylgermyl group, presumably in nucleophilic attack by solvent on germanium, more readily than it abstracts a hydroxyl group from the medium.

The rate-determining transition state involves a structure in which a substantial excess of positive charge is present on the carbon adjacent to the aromatic ring. (This is so even if destruction, not formation, of the intermediate is rate-determining.) Thus the effects of *meta* and *para* substituents might be expected to correlate with the electrophilic substituent constants, σ^+, derived from the rate of solvolysis of α,α-dimethylbenzyl chlorides in 90 % aqueous acetone[5], but this is not the case. We have analysed the results in terms of the Yukawa-Tsuno equation[6], $\log k_{rel} = \rho[\sigma + r(\sigma^+ - \sigma)]$, where ρ is defined by the points for appropriate *meta*-substituted and unsubstituted compounds**, σ is the Hammett substituent constant given by ionization of benzoic acids in water[7], and r is zero for this ionization, and unity for the solvolysis of α,α-dimethylbenzyl chlorides. The values of r calculated for a ρ of -3.3 for the cleavage of X–C_6H_4–C≡C–$GeEt_3$ compounds are shown in the Table 2.

TABLE 2

X . . .	*p*-OMe	*p*-*tert*-Bu	*p*-Me	*p*-F	*p*-I	*p*-Cl	*p*-Br	(*m*-OMe)	(*m*-CF_3)
r . . .	0.69	0.42	0.35	0.35	0.42	0.49	0.48	(0.91)	(0.82)

It will be seen that this is a reaction to which neither σ nor σ^+ constants separately apply satisfactorily. In the Figure, a plot (circles) of $\log k_{rel}$ against $[\sigma + 0.64(\sigma^+ - \sigma)]$, (with $\rho = -3.3$), a value of r larger than the average has been used to reduce the deviation from the line of the point for the *p*-methoxy group.

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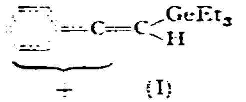
* It should be noted that if formation of the intermediate (I) were the fast step, then stabilization of the intermediate relative to stabilization of the ion Ar–C^+=CH_2 would have to be even greater than in the mechanism we have suggested.

** In finding ρ we use only those *meta*-substituents for which the σ-constants do not differ significantly from the σ^+-constants—in the present case, *m*-Cl, *m*-Br, and *m*-Me substituents. For *m*-OMe and *m*-CF_3 groups the values of $(\sigma^+ - \sigma)$ (+0.068 and +0.10, respectively) are quite large.

We think that a range of values of r is to be expected even for reactions in which a carbonium ion centre forms next to the aromatic ring[4,7], but it could be argued, that the intermediate (I) is an abnormal type of such a carbonium ion. In the ion, stabilization of the positive centre will be at a maximum when the plane of the ring is at right angles to the vacant $p\pi$ orbital of the positively charged α-carbon atom (that is, at right angles to the plane defined by the C–GeEt$_3$ and C–H bonds to the β-carbon atom), and there can then be no conjugation between the ring and the double bond. We think that overlap with the vacant p-orbital will be the more important, but if conjugation with the double bond dominated then an abnormal effect of nuclear substituents would result. Another possible origin of abnormality is that if there is, as we think, no conjugation between the ring and the double bond in the intermediate (I), there will for this reason be a loss of resonance stabilization on going from the initial state to the transition state, which will counteract the gain in resonance resulting from conjugation with the positive charge, and the magnitude of this loss will depend on the substituent present*.

It is of interest to compare the observed substituent effects with those in the acid-cleavage of phenyltriethylgermanes[8] under similar conditions, since the two reactions are closely analogous, one involving attachment (probably rate-determining) of a proton to an aromatic carbon atom bearing the germyl group to give an intermediate (II) in which the positive charge is delocalized over the ring, and the other involving attachment (again, probably rate-determining) of a proton to an acetylenic carbon atom bearing the same group, to give an intermediate, (I), in which delocalization is more extended. The Figure shows a plot (squares) of log k_{rel} for the cleavage of *meta*- and *para*-substituted phenylethynyl compounds against log k_{rel} for cleavage of the corresponding phenyl compounds; all the points lie close to the straight line defined by the *meta*-substituted and unsubstituted compounds. (This means that the value of r is effectively the same for the two reactions; it has been previously noted that a given r value tends to be associated with a smaller ρ value in side-chain than in nuclear reactions[6,9].) This excellent linear free energy relationship between the substituent effects in the two reactions confirms our suggestion that the absence of correlation of rates with σ^- values for the alkynyl compounds does not originate in the special features of the formed carbonium ion.


(I)


(II)

The slope, ρ, for the (phenylethynyl)germanes is lower than that, ρ', for the phenylgermanes, and $\rho/\rho' = 0.67$. This can be attributed primarily to the higher reactivity of the ethynyl compounds, which means that the transition state is less removed from the initial state than is the case with the phenyl compounds, and thus that the magnitude of the positive charge developed on carbon is smaller. (A secondary

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* It is possibly because of this loss of resonance energy that di(phenylethynyl)mercury is cleaved less readily than di(n-butylethynyl)mercury[2], in spite of the stabilizing effect of the phenyl group on the forming positive charge. With less reactive R–C≡C–M compounds, in which a larger degree of positive charge will be developed in the molecule in the transition state, the opposite order might be observed.

reason may be that neutralization of the formed charge by solvation is more effective for the side-chain process, leaving a smaller proportion to be stabilized by the conjugation with the aromatic ring.)

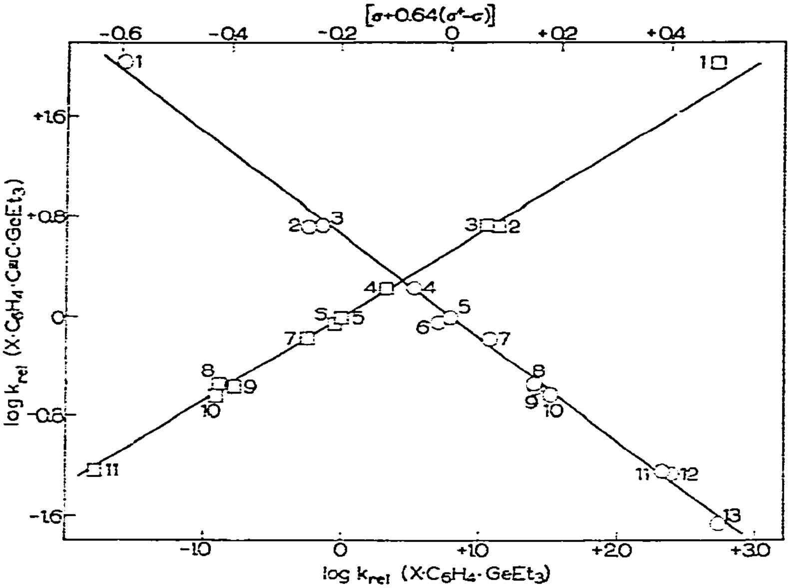

Fig. 1. Plot of log k_{rel} for the cleavage of (X-phenylethynyl)triethylgermanes against log k_{rel} for the cleavage of (X-phenyl)triethylgermanes (squares) and against $[\sigma + 0.64(\sigma^{+} - \sigma)]$ (circles). X is 1, *p*-OMe; 2, *p*-Me; 3, *p*-*tert*-Bu; 4, *m*-Me; 5, H; 6, p-F; 7, *m*-OMe; 8, *p*-I; 9, *p*-Cl; 10, *p*-Br; 11, *m*-Cl; 12, *m*-Br; 13, *m*-CF_3.

The corresponding ρ/ρ' ratio for acid cleavage of di(phenylethynyl)- and diphenylmercury compounds was reported by Dessy and Kim[2,10] to be 0.35, but the slopes they used were not those defined by the *meta*-substituted compounds but those given by the best line on a plot of log k_{rel} against $(\sigma + \sigma^{+})/2$. Such a plot would be equivalent to a Yukawa-Tsuno plot with $r = 0.5$ if *meta*-substituents were used to define a slope, but, in fact, for the phenylethynyl compounds the points for the *meta*- and unsubstituted compounds did not lie on a straight line; the value of ρ calculated from the k_{rel} value for the *m*-methyl compound at 32° is 1.8, while that calculated from the k_{rel} value for the *m*-chloro compound is 0.46. For the phenyl–mercury cleavage the value of ρ' calculated from the rate for the *m*-nitro compound[10] is 3.0. Dessy and Kim attributed the low value of ρ/ρ' to the insulating effect of a triple bond on transmission of substituent effects. While this insulating effect exists, as revealed by effects of substituents on reactions of phenylpropiolic acid and its derivatives[2,11,12], we think that in the carbon–metal cleavages the dominant effect of a substituent is on the partial positive charge formed next to the ring in the transition state, and the triple bond is not involved in the transmission of this effect.

There appears to be substantial steric hindrance by *ortho*-substituents in the cleavage of (phenylethynyl)triethylgermanes. This is shown most clearly in the deactivation by the *o*-methoxy group, which is a strongly electron-releasing group in electrophilic substitutions (see, for example, refs. 8 and 13), but the fact that the *ortho*-chloro deactivates as much as the *meta*-chloro group, and that the *ortho*-methyl activates little more than the *meta*-methyl group confirm the generality of the hindrance. (For each substituent studied in both positions, there is a similarity, no doubt fortuitous, between its effect from the *ortho* and from the *meta* position.) We suggest that the hindrance is to solvent orientation about the reaction centres, mainly involving the solvent molecules around the developing charge on the α-carbon atom, but also possibly those separating from the proton being transferred to the β-carbon atom. Some features of the reactivity of *ortho*-substituted derivatives of phenylpropiolic acid were attributed to direct field interactions between the substituents and the reaction centre[11], and such interactions might be expected in the reaction we have studied, since solvent molecules (which would raise the dielectric constant) are unlikely to intervene between the forming carbonium ion centre and the *ortho*-group. However, the partial negative charge on the *o*-chloro substituent, for example, would, by such interaction, *stabilize* the forming carbonium ion, to give an *ortho*- effect in the opposite direction to that observed.

A puzzling effect, apparently steric in origin, occurs in the [mesityl- and (2,3-dimethylphenyl)ethynyl] compounds. If the effects of *o*-, *m*- and *p*-substituents are assumed to be additive, the value of k_{rel} for the mesityl compound would be 23 (2.1 × 2.1 × 5.3), whereas the observed value is 40, so that the ratio of observed to calculated rate is 1.7. A ratio of 1.4 applies with the 2,3-dimethyl compound. Effects in the same direction were observed in the acid cleavage of mesityltriethylgermane[8] and -trimethylsilane[14] (the ratios of observed to calculated rates were 6.3 and 6.9, respectively) and of (2,3-dimethylphenyl)trimethylsilane[14] (for which the ratio was 1.6). In the aryl–MR_3 cleavages the effect was attributed to steric acceleration[14,15], arising from release of strain as the MR_3 group moves during reaction from the plane of the aryl–methyl bonds, but no such effect could be envisaged for the (phenylethynyl) compounds, since the molecule is linear, and the aryl group is as far away from the triethylgermyl group in the initial state as it can be.

We have not compared quantitatively the variation in the ease of cleavage of $Ph-C{\equiv}C-MR_3$ compounds as M is changed from Si to Ge to Sn, but we observed that the trimethylsilyl compound required markedly more concentrated acid than the triethylgermyl compounds for a convenient rate of cleavage (indeed, at the acid concentration necessary for cleavage of the silicon compound, hydration of the phenylacetylene occurred, which prevented rate measurements), while the trimethylstannyl compound was cleaved even by neutral aqueous methanol. The order of ease of cleavage is thus (M =) Si < Ge ≪ Sn, as in acid cleavage of $ArMR_3$ compounds[16], and differs from that in alkali cleavage of $ArCH_2MR_3$ compounds[17].

EXPERIMENTAL

Materials

The preparations of the (arylethynyl)triethylgermanes are described elsewhere[18].

Rate measurements

The spectrophotometric method used[13,16] for studying aryl–metal cleavages was employed. Aqueous perchloric acid (2 ml) was mixed with a cold methanolic solution of the organogermane (5 ml) of concn., *C*, listed in Table 3. The mixture was transferred to a quartz cell contained in a thermostatted cell holder of the spectrophotometer, where it was kept at 29.05° ± 0.03°. Optical density readings, at the wave-length, λ, specified in Table 3, were begun after a few minutes had been allowed for the solution to reach the steady temperature, and the "infinity" value was measured after 10 half-lives.

TABLE 3

Substituent(s)	λ $(m\mu)$	10^4C (M)	*Substituent(s)*	λ $(m\mu)$	10^4C (M)	*Substituent(s)*	λ $(m\mu)$	10^4C (M)
p-OMe	296	9	H	273.5	11	*m*-Br	292.5	18
2,4,6-Me_3	276	5	*p*-F	276	8	*o*-Cl	292.5	14
2,3,-Me_2	292.5	19	*p*-Cl	281.5	7	*o*-Br	293.5	17
p-Me	283.5	19	*p*-Br	287	14	*o*-OMe	304	6
p-*tert*-Bu	272	7	*p*-I	292	5	*m*-OMe	298.5	4
o-Me	289	8	*m*-Cl	283.5	4	*m*-CF_3	288.5	14
m-Me	282	9						

For all the compounds listed in Table 1 a wave-length was found at which the absorption of the $X{-}C_6H_4{-}C{\equiv}C{-}GeEt_3$ compound differed sufficiently from the parent acetylene $X{-}C_6H_4{-}C{\equiv}CH$; in general the spectrum of the germanium compound was similar to that of the acetylene but shifted a few mμ towards the visible.

Rate constants in duplicate runs agreed to within 1 %.

Products

The spectra of the reaction mixtures at the end of the reactions were those expected for solutions of the parent acetylenes.

In a larger scale study, triethyl(phenylethynyl)germane (7.4 g) in methanol (100 ml) was mixed with perchloric acid (40 ml, 1.0 *M*), and the mixture was kept at 25°, with occasional shaking, for 1.5 h. It was then poured into water (500 ml), and ether extraction, followed by washing, drying (Na_2SO_4), and fractionation of the ethereal layer gave phenylacetylene (2.5 g, 84 %), b.p. 144°, n_D^{25} 1.5472.

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SUMMARY

We have measured the rates of cleavage of some $X{-}C_6H_4{-}C{\equiv}C{-}GeEt_3$ compounds by aqueous methanolic perchloric acid at 29.05°.

The effects of substituents, which bear a linear free energy relationship to those in acid cleavage of aryltriethylgermanes, are discussed in the light of the probable mechanism of the reaction.

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