

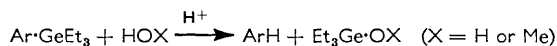
53. *Aromatic Reactivity. Part XII.*¹ *Cleavage of Aryltriethylgermanes by Aqueous-methanolic Perchloric Acid.*

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We have measured spectrophotometrically the rates of cleavage of a large number of aryltriethylgermanes in a mixture of aqueous perchloric acid and methanol. The results provide a detailed picture of substituent effects in an electrophilic aromatic substitution. These effects are discussed, and compared with those in other electrophilic aromatic substitutions.

There is a precise linear free-energy relationship between the rates of cleavage of aryltriethylgermanes and those of the analogous aryltrimethylsilanes.

WE have measured the rates of cleavage at 50.0° of a number of aryltriethylgermanes (mainly monosubstituted phenyltriethylgermanes) by a mixture of 2 volumes of aqueous perchloric acid and 5 volumes of methanol:



The reaction, aromatic protodetriethylgermylation (here referred to for brevity as degermylation—cf. ref. 2), is analogous to the cleavage of aryltrimethylsilanes (desilylation) previously described.^{2,3} Both reactions are electrophilic aromatic substitutions, and the influence of the constitution of the aryl group on the ease of cleavage provides additional information on substituent effects in such substitutions.

The near-ultraviolet absorption spectrum of an $\text{Ar}\cdot\text{GeEt}_3$ compound is shifted towards the visible region compared with that of the parent ArH compound (as with the corresponding $\text{Ar}\cdot\text{SiMe}_3$ compound); there is little difference in shapes of the spectra. By suitable choice of wavelength it is possible to measure the rate of cleavage of the aryltriethylgermanes in aqueous-methanolic perchloric acid by the spectrophotometric technique used for the aryltrimethylsilanes.^{2,3}

The results are shown in Table 1 as first-order rate constants, k_1 , observed at specified concentrations of acid, and also as rates, k_{rel} , relative to the rate of reaction of the parent compound, phenyltriethylgermane. It must be stressed that the spread of rates is such that all the compounds cannot accurately be studied at the same concentration of acid, and some values of k_{rel} are obtained by the overlap procedure used with silicon compounds.^{2,3} Since the medium employed consists of 4 volumes of aqueous perchloric acid mixed with 10 volumes of methanol, its water content changes somewhat as the concentration of the acid is varied, and the values of k_{rel} might be different if all the compounds

¹ Part XI, Eaborn and Taylor, *J.*, 1960, 3301.

² Eaborn, *J.*, 1956, 4858.

³ Deans and Eaborn, *J.*, 1959, 2299.

were examined in one medium, but we believe this effect to be small. It can be seen from Table 1 that where k_{rel} was determined for a compound at two acid concentrations the difference in the values was small, and was also random over the range of compounds so studied.

The results form the most detailed pattern of substituent effects yet obtained for an electrophilic aromatic substitution under one set of conditions. (More substituents have been studied in desilylation,^{2,3} but only by carrying out some of the measurements in acetic acid-sulphuric acid-water.) Qualitative examination of the results reveals the following features:

(i) Activation by *p*-alkyl groups is in the Baker-Nathan order $Me > Et > Pr^i > Bu^t$, and by *m*-alkyl groups is in the inductive order $Bu^t > Me$. The Baker-Nathan order has been observed so far for *para*-groups in all electrophilic aromatic substitutions except nitration in aqueous acetic acid⁴ and aromatic hydrogen exchange in some media;⁵ the

TABLE 1. Cleavage of substituted phenyltriethylgermanes by a mixture of aqueous perchloric acid (2 vol.) and methanol (5 vol.) at 50.0°.

No.	Substituent	[HClO ₄] ^a (M)	10 ³ k ₁ (min. ⁻¹)	k _{rel}	No.	Substituent	[HClO ₄] ^a (M)	10 ³ k ₁ (min. ⁻¹)	k _{rel}
1	<i>p</i> -NMe ₂	0.00527	81.3	—	11	<i>p</i> -Pr ⁱ	6.21	78.8	12.0
		0.0527	99.5	—	12	<i>p</i> -Bu ^t	6.21	75.1	11.5
		0.229	100.4	—	13	<i>o</i> -Ph	7.34	33.4	3.22
				<i>ca.</i>	14	<i>p</i> -Ph	7.34	27.9	2.69
				3 × 10 ⁶	15	2,3-C ₄ H ₄ ^c	7.34	64.1	6.2
2	2,4,6-Me ₃ ^b	0.0527	37.3	—	16	3,4-C ₄ H ₄ ^d	9.15	49.3	1.79
		0.229	179	13,600	17	<i>m</i> -Bu ^t	7.34	35.2	3.2
3	<i>p</i> -OH	0.229	36.0	2,730			9.15	87.3	3.4
		0.495	88.0	—	18	<i>m</i> -Me	7.34	22.2	2.14
4	<i>p</i> -OMe	0.495	17.4	540			9.15	57.6	2.08
		0.970	45.2	—	19	H	4.01	1.54	1
		0.970	17.5	—			6.21	6.55	1
6	<i>p</i> -CH ₂ -SiMe ₃	2.80	129	207			7.34	10.36	1
		0.970	13.3	—			9.15	27.6	1
7	<i>p</i> -OPh	2.80	101.5	162	20	<i>p</i> -F	7.34	9.2	0.96
		2.80	24.5	39			9.15	26.4	0.89
8	<i>p</i> -Me	4.01	53.0	34.5	21	<i>m</i> -MeO	7.34	5.97	0.57
		2.80	8.8	—			9.15	16.1	0.58
		6.21	91.3	(13.9)	22	<i>p</i> -Cl	9.15	4.60	0.167
				14.1		11.91	21.2	—	
9	<i>o</i> -Me	2.80	7.69	12.3	23	<i>p</i> -Br	9.15	3.42	0.124
		4.01	19.2	12.5			11.91	16.5	0.130
		6.21	76.9	—	24	<i>p</i> -I	11.91	16.7	0.131
10	<i>p</i> -Et	6.21	85.1	13.0	25	<i>m</i> -Cl	11.91	2.09	0.0165

^a Concn. of the aqueous perchloric acid. ^b Denotes mesityltriethylgermane. Denotes 1-naphthyltriethylgermane. ^c Denotes 2-naphthyltriethylgermane.

inductive order has, as far as we are aware, been observed for *m*-Me and *m*-Bu^t groups in all the electrophilic aromatic substitutions studied.^{5,6}

(ii) *para*-Halogen is deactivating in the order $p-I \approx p-Br > p-Cl > p-F$, as in desilylation.^{2,3} The *p*-fluoro-group is deactivating (though very slightly) as it is in proto- and bromo-desilylation^{2,3,7} and in nitration,⁸ but contrary to its effect in molecular chlorination in acetic acid,⁹ and in detritiation.⁵ It seems that in reactions of high electron demand (as measured, for example, by the influence of a *p*-methyl group) the +*E* effect of the fluorine atom overpowers the -*I* effect. The anomaly remains, however, that the

⁴ Cohn, Hughes, Jones, and Peeling, *Nature*, 1952, **169**, 291.

⁵ Eaborn and Taylor, *Chem. and Ind.*, 1959, 949.

⁶ Stock and Brown, *J. Amer. Chem. Soc.*, 1959, **81**, 5621.

⁷ Eaborn and Webster, *J.*, 1957, 4449; *J.*, 1960, 179.

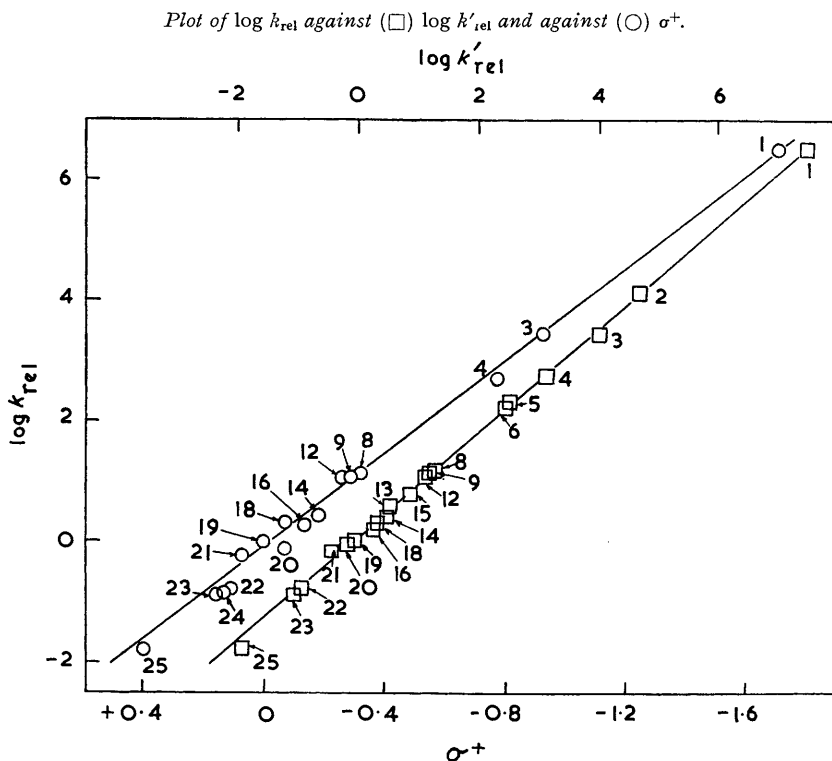
⁸ de la Mare and Ridd, "Aromatic Substitution, Nitration and Halogenation," Butterworths Scientific Publ., London, 1959, p. 85.

⁹ de la Mare, *J.*, 1954, 4450.

p-fluoro-group can deactivate in nucleophilic aromatic substitution,¹⁰ where the $+E$ effect cannot be called into operation.

(iii) The methoxy-group activates more from the *para*- than from the *ortho*-position, and deactivates from the *meta*-position. Deactivation by the *m*-methoxy-group appears to be the common result in electrophilic aromatic substitution, but the group is reported to be activating in molecular bromination in acetic acid.¹¹

(iv) The *p*-phenoxy-group activates much less effectively than the *p*-methoxy-group. This effect has been observed previously for molecular bromination in acetic acid,⁹ and almost certainly operates in nitration in acetic anhydride, in which the *p*-phenoxy-group activates only 234 times.¹² The smaller effect of the *p*-phenoxy-group presumably results partly from the $-I$ effect of the phenyl group, partly from increased steric interaction



between the group and the hydrogen atoms *ortho* to it, which prevents the phenoxy-group from getting into the plane of the ring and thus hinders $p_{\pi}-p_{\pi}$ overlap, and partly from conjugation of π -electrons of the oxygen atom with the phenyl group, which renders them less available to activate the ring in which substitution is occurring.

(v) The phenyl group activates the *ortho*- more than the *para*-position, as in proto-desilylation but not bromodesilylation.¹³ The 4-position of biphenyl is more reactive in degermylation than is the 2-position of naphthalene, as in other electrophilic substitutions except possibly nitration (cf. ref. 14).

¹⁰ Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons, Ltd., London, 1953, p. 805; Miller, *Austral. J. Chem.*, 1956, **9**, 61.

¹¹ de la Mare and Vernon, *J.*, 1951, 1764.

¹² Dewar and Urch, *J.*, 1958, 3079.

¹³ Deans, Eaborn, and Webster, *J.*, 1959, 3031.

¹⁴ Eaborn, Lasocki, and Webster, *J.*, 1959, 3034.

(vi) The effect of any substituent is smaller in protodegermylation than in protodesilylation. This is to be associated with the higher reactivity of the aryl-germanium bond than of the aryl-silicon bond, which means that there is less demand on the electrons of the aryl system on going from the ground state to the transition state.

More quantitative analysis of the results in Table I reveals the following features:

(vii) The plot of $\log k_{\text{rel}}$ against $\log k'_{\text{rel}}$, where k'_{rel} refers to acid cleavage of aryl-trimethylsilanes,^{2,3,14,15} is an excellent straight line over the whole range of substituents studied (see Figure). The excellence of the plot seems to confirm the accuracy of the experimental data in both desilylation and degermylation, and to justify the overlap procedure used in deducing relative rates. It also supports previous indications that the same mechanism operates in both reactions, with another mechanism possibly operating in destannylation and deplumbylation.¹⁵

(viii) The free-energy relationship noticed under (vii) holds exactly even for the *ortho*-substituted compounds, including the mesityl compounds, even though there is thought to be steric acceleration of the desilylation in this case.¹⁶ It appears that, coincidentally, the Et_3Ge group has exactly the same steric effect in degermylation as the Me_3Si group has in desilylation. (The size of the groups is not the only factor here: the extent to which the configuration at the central carbon approaches tetrahedral in the rate-determining transition state is also important.)

(ix) When the values of k_{rel} are expressed as rate factors f , the ratio $(\log f_p^{\text{Me}})/(\log f_m^{\text{Me}})$ has a value of 3.57. This compares with a value of 3.66 in desilylation, and falls in the middle of the range, 3.18—4.72, which covers a large number of electrophilic aromatic substitutions for which accurate data are available.¹⁷

The ratio $(\log f_p^{\text{Bu}^t})/(\log f_m^{\text{Bu}^t})$ has a value of 2.05. This compares with a value of 2.27 for protodesilylation in hydrogen chloride-acetic acid-water, and falls just outside the range of 2.27—3.82 which covers nine electrophilic aromatic substitutions for which data are available.⁶

The ratio $(\log f_p^{\text{Me}})/(\log f_p^{\text{Ph}})$ has a value of 2.73, which compares with a value of 2.82 for protodesilylation of aryltrimethylsilanes in acetic acid-sulphuric acid-water.¹³ This ratio shows considerable variation over the range of reactions for which it is accurately known, the $+E$ effect of the phenyl group being more effective in reactions of large electron demand (*i.e.*, with large values of f_p^{Me}).¹³

The ratio $(\log f_p^{\text{Me}})/(\log f_\beta^{\text{C}_6\text{H}_4})$ has a value of 4.54, compared with 3.96 in protodesilylation. This ratio varies considerably for the few reactions for which it can be calculated.¹⁴

(x) The substituent effects correlate well with the substituent constants σ^+ proposed by Brown and his co-workers for electrophilic aromatic substitutions, as shown by the straight-line plot (see Figure) of $\log k_{\text{rel}}$ against σ^+ . (The slope, ρ , is 3.9.) Those points which lie furthest from the line refer to substituents (*p*-Ph, *p*-halogens, and 3,4- C_4H_4) to which, it has been argued,^{2,13,14} single satisfactory σ^+ substituent constants cannot be assigned.

Since substituent effects in protodegermylation correlate so well with those in protodesilylation, it follows that other, more complex, approaches to the use of substituent constants which have been applied successfully to the desilylation¹⁹ would have the same success with degermylation.

Two features of the experimental work should be noted. First, the cleavage of the compound *p*- $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{GeEt}_3$ is much slower than would be expected from the value of

¹⁵ Eaborn and Pande, *J.*, 1960, 1566.

¹⁶ Eaborn and Moore, *J.*, 1959, 3640.

¹⁷ Stock and Brown, *J. Amer. Chem. Soc.*, 1959, 3323.

¹⁸ Brown and Okamoto, *J. Amer. Chem. Soc.*, 1958, 4979, and references therein.

¹⁹ Deno and Evans, *J. Amer. Chem. Soc.*, 1957, 79, 5804; Yukawa and Tsuno, *Bull. Chem. Soc. Japan*, 1959, 32, 971; McNulty and Pearson, *J. Amer. Chem. Soc.*, 1959, 81, 612; see also Bekhum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, 78, 815.

k_{rel} given in Table 1, because the compound is almost all converted into the unreactive salt, $p\text{-HMe}_2\text{N}^+\text{C}_6\text{H}_4\cdot\text{GeEt}_3$, in the media used. The rate of cleavage is fairly insensitive to the acid concentration, except for very low concentrations, as with the analogous trimethylsilyl compound.² The value of k_{rel} for the free base is derived, as in desilylation,² in the following way: p -dimethylaminophenyltriethylgermane reacts at an 0.00527M(added)-acid concentration 2.2 times as fast as the mesityl compound does in 0.0527M(added)-acid, and so about 22 times as fast as the mesityl compound would react in the weaker acid. In the reaction involving 0.00527M(added)-acid, 11.0% of NN -dimethylaniline is found spectrophotometrically to be present as free base, and, since the p -triethylgermyl derivative probably has a rather similar base strength, about 11% of it will remain as free amine. Thus p -dimethylaminophenyltriethylgermane is about 22×9 times as reactive as the mesityl compound, and thus about 3×10^6 times as reactive as phenyltriethylgermane.

Secondly, the phenol $p\text{-HO}\cdot\text{C}_6\text{H}_4\cdot\text{GeEt}_3$ could not be obtained satisfactorily pure: consequently the compound $p\text{-Me}_3\text{Si}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{GeEt}_3$ was used, since it was known that this would solvolyse very rapidly in the cleavage medium to give the phenol, the cleavage of which could then be studied. In confirmation, cleavage was found to proceed at an identical rate for the compounds $p\text{-Me}_3\text{Si}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{SiMe}_3$ and $p\text{-HO}\cdot\text{C}_6\text{H}_4\cdot\text{SiMe}_3$.

EXPERIMENTAL

Materials.—The preparation and properties of the aryltriethylgermanes have been described.²⁰

TABLE 2.

X	Concn. (M)	λ (m μ)	X	Concn. (M)	λ (m μ)
H	6×10^{-3}	266	<i>o</i> -Ph	5.5×10^{-4}	280
<i>o</i> -Me	5.5×10^{-3}	276	<i>p</i> -Ph	6×10^{-5}	275
<i>m</i> -Me	6×10^{-3}	275, 276	<i>o</i> -OMe	5.5×10^{-4}	283, 287
<i>p</i> -Me	5.5×10^{-3}	273	<i>m</i> -OMe	11×10^{-4}	286
<i>p</i> -Et	6×10^{-3}	276	<i>p</i> -OMe	10.5×10^{-4}	281, 283
<i>p</i> -Pr ^t	4×10^{-3}	236, 270	<i>p</i> -OPh	4×10^{-4}	251
<i>m</i> -Bu ^t	6.5×10^{-3}	270	<i>p</i> -O·SiMe ₃	1.5×10^{-3}	240
<i>p</i> -Bu ^t	4.5×10^{-3}	238, 270	<i>p</i> -CH ₂ ·SiMe ₃	2×10^{-3}	247
<i>p</i> -F	8×10^{-3}	276	<i>p</i> -NMe ₂	8×10^{-3}	275 ^a
<i>m</i> -Cl	6×10^{-3}	279	"	8×10^{-4}	275 ^b
<i>p</i> -Cl	5×10^{-3}	277	2,3-C ₄ H ₄	6.4×10^{-4}	299
<i>p</i> -Br	5×10^{-3}	274	3,4-C ₄ H ₄	6.4×10^{-4}	294
<i>p</i> -I	6×10^{-3}	288	2,4,6-Me ₃ ^c	2.5×10^{-3}	242

^a [HClO₄] = 0.00527. ^b [HClO₄] = 0.0527. ^c Refers to mesityltriethylgermane.

Medium.—The medium was the same as that used in protodesilylation.^{2,14} Four vol. of aqueous perchloric acid, of concentration shown in Table 1, were mixed with 10 vol. of a methanolic solution of the organogermane, X·C₆H₄·GeEt₃, of concentration shown in Table 2.

Kinetic Methods.—The methods described for protodesilylation were used.^{2,14,15} The change in absorption in 1 cm. cells held at 50.0° ± 0.04° was recorded at the wave lengths, λ , shown in Table 2. In the case of the *m*-Cl compound, sealed tubes were used for the reaction samples (for the *p*-Cl and *p*-Br compounds it was shown that runs in cells and sealed tubes gave rate constants agreeing within ±1%). In all cases rate constants of duplicates agreed within 2%.

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²⁰ Eaborn and Pande, *J.*, 1960, 3200.