1006. *Aromatic Reactivity. Part XXI.*[1] *Effects of Strongly Deactivating Substituents in Protodetriethylgermylation.*

By C. Eaborn and K. C. Pande.

We have measured the rates of cleavage of some aryltriethylgermanes, $X\cdot C_6H_4\cdot GeEt_3$, in a mixture of acetic acid and aqueous sulphuric acid at 50·0°. The substituents, X, include halogen atoms, and carboxyl-, trifluoromethyl-, trimethylammonio-, and nitro-groups, all in *meta-* as well as *para*-positions. For some of the substituents the results provide the first quantitative measure of their effects in an electrophilic aromatic substitution.

The nitro-, trimethylammonio-, and trifluoromethyl groups deactivate little more from the *meta-* than from the *para*-position, in contrast with their behaviour in nitration. In the case of groups for which the necessary substituent constants are available, the results fit the Yukawa–Tsuno equation precisely.

We recently described the effects of some nuclear substituents on the rates of cleavage of triethylphenylgermanes by aqueous-methanolic perchloric acid.[2] The most deactivating substituent we could conveniently study in that medium was *m*-chloro, and to obtain information on the effects of groups which withdraw electrons more strongly we have measured the rates of cleavage of some substituted triethylphenylgermanes, $X\cdot C_6H_4\cdot GeEt_3$, in a mixture of acetic acid (containing 0·80% of water) and aqueous sulphuric acid at 50·0°, a medium previously used for cleavage of aryltrimethylsilanes.[3]

The results are shown in Table 1, which lists the concentration of sulphuric acid taken (1 volume of which was mixed with 2 volumes of acetic acid), the observed first-order rate constants, k, and the rates, $k_{rel.}$, relative to that of the unsubstituted compound, $C_6H_5\cdot GeEt_3$. The values of $k_{rel.}$ provide the first accurate measure of the effects of some of the substituents in an electrophilic aromatic substitution.

Table 1.

Cleavage of $X\cdot C_6H_4\cdot GeEt_3$ compounds in $CH_3\cdot CO_2H–H_2O–H_2SO_4$ at 50·0°.

X	H_2SO_4 (M)	10^3k (min.$^{-1}$)	$k_{rel.}$	X	H_2SO_4 (M)	10^3k (min.$^{-1}$)	$k_{rel.}$
p-OMe	0·295	55·4	392	*m*-Br	9·65	13·7	0·019
o-OMe	0·295	26·0	—	*m*-Cl	9·65	13·5	0·0191
	1·42	191	187·5		11·67	76·5	—
p-Me	1·42	12·7	—	*m*-CO_2H	11·67	71·0	0·0177
	3·62	79·4	12·4	*m*-CF_3	11·67	21·7	$5·4 \times 10^{-3}$
p-Ph	3·62	15·55	—		13·85	73·75	—
	5·55	69·3	2·43	*p*-CF_3	11·67	9·84	$2·46 \times 10^{-3}$
m-Me	5·55	50·8	1·78		13·85	36·1	$2·55 \times 10^{-3}$
H	5·55	28·5	1	*p*-CO_2H	11·67	20·65	$5·2 \times 10^{-3}$
	6·45	63·1	1		14·20	123·6	—
m-OMe	6·45	32·1	0·51	*m*-NMe_3^+	14·20	30·2	$12·6 \times 10^{-4}$
p-Cl	6·45	10·6	0·168	*p*-NMe_3^+	14·20	25·3	$10·6 \times 10^{-4}$
p-Br	6·45	8·40	0·133	*m*-NO_2	14·20	19·1	$8·0 \times 10^{-4}$
	9·65	94·3	—	*p*-NO_2	14·20	9·00	$3·76 \times 10^{-4}$
m-F	9·65	22·4	0·032				

The main features, and some comments, are as follows. (*a*) For substituents examined in both media (*viz.*, *p*-OMe, *o*-OMe, *p*-Me, *p*-Ph, *m*-Me, *m*-OMe, *p*-Cl, *p*-Br, and *p*-I), a plot of log $k_{rel.}$ for cleavages in $CH_3\cdot CO_2H–H_2O–H_2SO_4$ against log $k'_{rel.}$ for cleavages in $MeOH–H_2O–HClO_4$ is precisely linear (log $k_{rel.} = 0·95$ log $k'_{rel.}$). The slope of the line coincides, within experimental error, with that of the analogous plot[3] for aryltrimethylsilanes.

As has been pointed out before,[2,3] the composition of both types of medium varies

---

[1] Part XX, Baker and Eaborn, preceding paper.

[2] Eaborn and Pande, *J.*, 1961, 297.

[3] Deans and Eaborn, *J.*, 1959, 2299.

somewhat as the concentration of the added acid is changed, and values of $k_{rel.}$ are not necessarily exactly those which would be obtained if all the compounds were examined at one acid concentration, but the precision of the linear free-energy relation just noted confirms our view that no serious error in substituent effects is introduced by neglect of the medium change. It also indicates that the polar properties of the substituents concerned are not specifically affected by the change from $MeOH-H_2O-HClO_4$ to $CH_3{\cdot}CO_2H-H_2O-H_2SO_4$.

(*b*) Where analogous compounds, $X{\cdot}C_6H_4{\cdot}GeEt_3$ and $X{\cdot}C_6H_4{\cdot}SiMe_3$, have been studied in $CH_3{\cdot}CO_2H-H_2O-H_2SO_4$ (*viz.*, X = *o*-, *m*-, and *p*-OMe, *p*-Me, *p*-Ph, *m*- and *p*-Cl, *p*-CO_2H, *p*-NMe_3^+, and *p*-NO_2) a linear free-energy relation, $\log k^{Ge}_{rel.} = 0{\cdot}86 \log k^{Si}_{rel.}$, applies.

(*c*) As in protodetrimethylsilylation,[3] the nitro-group deactivates *meta*- and *para*-positions more than does the trimethylammonio-group. This means that withdrawal of electrons from the *meta*- and *para*-positions is stronger with the nitro-group, particularly when it is remembered that the rate of reaction of a positively charged ammonium compound with a positively charged electrophile is lowered by external electrostatic effects (which influence the entropy term and not the activation energy term in the rate equation [3,4]) below that which result from internally transmitted polar effects.[3] The effect of the nitro-group on the basicity of amines [5] and on the rate of *meta*-bromination of nitropolyalkylbenzenes is not much altered when steric effects force the group from the plane of the ring, and thus decrease the conjugation with the ring, and this is consistent with electron-withdrawal by the nitro-group's being almost wholly inductive, and originating in the positive charge on the nitrogen atom in the dipolar-ion group (cf. ref. 7). But if this were so, we should expect deactivation by the nitro-group, in which the effect of the positive charge on the nitrogen atom is partly neutralized by the negative charge distributed between the oxygen atoms, to be markedly smaller than that by the trimethylammonio-group, which has a unit positive charge on nitrogen; we conclude (as de la Mare and Ridd have done after considering the relative effects of a nitro-group on the *ortho*- and *para*-positions [7]) that the $-M$ effect of the nitro-group must also be important. The contribution of the $-M$ effect to deactivation of the *meta*-position presumably comes from secondary relay to the reaction centre of part of the excess of positive charge induced on positions *ortho* and *para* to it.

(*d*) As would be expected from their powerful *meta*-directing effects in nitration, the strongly electron-withdrawing nitro-, trimethylammonio-, and trifluoromethyl-groups deactivate the *para*- more than the *meta*-position,* but the most striking feature is that for each group the difference between its effect on the *meta*- and on the *para*-position is small. The smallness of the ratios $k^{m}_{rel.}/k^{p}_{rel.}$ for the three groups (*viz.*, NO_2, 2·1; CF_3, 2·2; NMe_3^+, 1·2) contrasts sharply with the $\frac{1}{2}m/p$ product ratio of 155 in nitration of nitrobenzene,[7] and the 100% *meta*-orientation in nitration of the phenyltrimethylammonium ion and of trifluoromethylbenzene.[8] Similarly small $k^{m}_{rel.}/k^{p}_{rel.}$ ratios for these substituents were found for solvolysis of substituted αα-dimethylbenzyl chlorides in 90% aqueous acetone at 25° (*viz.*, NO_2, 3·4; CF_3, 2·7; NMe_3^+, 1·7), and were held to be consistent with the groups' acting predominantly through inductive effects,[9,10] but the sharp discordance

---

* We find that in aqueous sulphuric acid, however, *m*- reacts more slowly than *p*-trimethylammoniophenyltriethylgermane. The effects of charged groups are known to be particularly sensitive to medium changes, but such a reversal of the relative deactivating influence of *m*- and *p*-trimethylammonio-substituents means their behaviour is more difficult to interpret than has been appreciated before.

[4] Frost and Pearson, "Kinetics and Mechanism," John Wiley and Sons Inc., New York, 2nd edn., 1961, pp. 142—145.

[5] Wepster, *Rec. Trav. chim.*, 1956, **75**, 1473.

[6] Illuminati, *Nature*, 1957, **179**, 780.

[7] de la Mare and Ridd, "Aromatic Substitution. Nitration and Halogenation," Butterworths Scientific Publications, London, 1959, pp. 82—83.

[8] Ref. 7, p. 8.

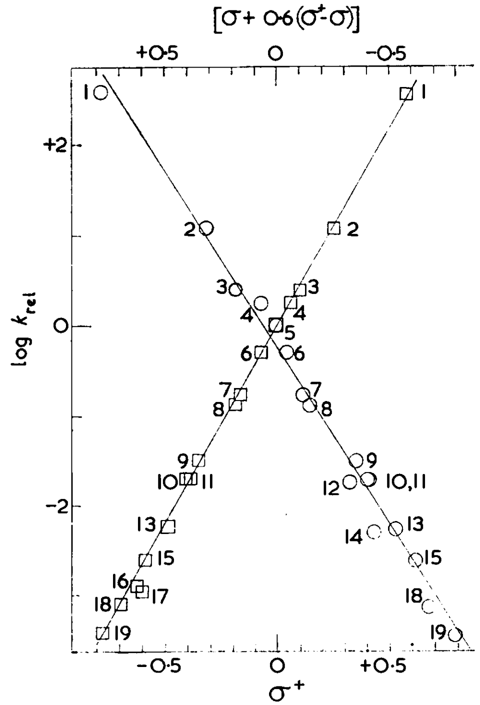
[9] Okamoto, Inukai, and Brown, *J. Amer. Chem. Soc.*, 1958, **80**, 4969.

[10] Okamoto and Brown, *J. Amer. Chem. Soc.*, 1958, **80**, 4976.

with the effects of the substituents in nitration remains unexplained; the picture is further complicated by indications from indirect measurements, that the nitro-group may deactivate the *meta*- more than the *para*-position towards molecular chlorination.[11]

The value of $k^m_{\text{rel.}}/k^p_{\text{rel.}}$ for the carboxyl group in the cleavage (*viz.*, 3·4) cannot be regarded as inconsistent with the $\frac{1}{2}m/p$ product ratio in nitration of benzoic acid (*viz.*, 31),[7] in view of the greater spread of rates usual in nitration (*e.g.*, the deactivating effect of the *m*-chloro-substituent is 20 times greater in nitration[12] than in the cleavage). The carboxyl group deactivates less than the trifluoromethyl group in both *meta*- and *para*-positions, and in the *meta*-position has an effect very similar to that of the chloro-substituent.

(*e*) Deactivation by *meta*-halogen is in the order Cl = Br > F. The smaller effect of a *m*-fluoro-compound compared with that of a *m*-chloro- or *m*-bromo-substituent has been noted previously in detritiation[13] (for which, however, only approximate results were obtained), and in molecular bromination of substituted polymethylbenzenes in nitromethane,[14] and it indicates that the $+T$ effect of fluorine is able to influence the *meta*-reaction site, presumably by secondary relay from positions *ortho* to this site.[15]



Plot of log $k_{\text{rel.}}$ for cleavage of $X{\cdot}C_6H_4{\cdot}GeEt_3$ compounds against σ^+ (circles) or $[\sigma + 0{\cdot}6(\sigma^+ - \sigma)]$ (squares).

1, *p*-OMe. 2, *p*-Me. 3, *p*-Ph. 4, *m*-Me. 5, H. 6, *m*-OMe. 7, *p*-Cl. 8, *p*-Br. 9, *m*-F. 10, *m*-Br. 11, *m*-Cl. 12, *m*-CO_2H. 13, *m*-CF_3. 14, *p*-CO_2H. 15, *p*-CF_3. 16, *m*-NMe_3^+. 17, *p*-NMe_3^+. 18, *m*-NO_2. 19, *p*-NO_2.

(*f*) A plot of log $k_{\text{rel.}}$ against the σ^+-constants[16] for the various substituents approximates to a straight line (see Figure), but from any line drawn through the origin there are real deviations for some points, including those for *p*-phenyl and *p*-chloro-substituents, whose behaviour is known not to be adequately interpretable in terms of their σ^+-constants.[17] The biggest deviation from the line drawn in the Figure involves

---

[11] Ref. 7, p. 146.
[12] Ref. 7, p. 85.
[13] Eaborn and Taylor. *J.*, 1961, 2388.
[14] Illuminati and Marino, *J. Amer. Chem. Soc.*, 1956, **78**, 4975.
[15] Brown, Okamoto, and Ham, *J. Amer. Chem. Soc.*, 1957, **79**, 1906.
[16] Brown and Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.
[17] Eaborn, *J.*, 1956, 4858; Eaborn and Taylor, *J.*, 1961, 1012; Kohnstam, *J.*, 1960, 2066.

the *p*-carboxyl group, and, as in cleavage of trimethylphenylsilanes,[3] a point nearer the line is obtained if the σ^+-constant for the *p*-methoxycarbonyl group (CO_2Me) is used.* Much bigger deviations occur with *m*- and *p*-trimethylammonio-groups, but we have omitted these from the plot because of the known difficulty of applying substituent constants to charged groups.

Application of the Yukawa–Tsuno equation,[19] $\log k_{\text{rel.}} = \rho[\sigma + r(\sigma^+ - \sigma)]$, leads to an excellent straight line (the values of ρ and r being 4·4 and 0·6, respectively), with all the substituents for which approriate σ- and σ^+-constants [16] are available. (It must be stressed that only σ-constants derived from ionization of substituted benzoic acids [20] must be used, not those deduced indirectly.) It is particularly significant that the results for the *meta*- and *para*-nitro- and -trifluoromethyl substituents, which cannot be reconciled with results in nitration, agree precisely with an equation which applies [19] to a wide range of electrophilic aromatic substitutions and side-chain reactions; it may mean that the results in nitration are not typical of those in electrophilic aromatic substitutions as a whole. (The same observation could have been based, of course, on the poorer but still reasonable fit of the points for the nitro and trifluoromethyl substituents to the $\log k_{\text{rel.}}$—σ^+ plot.) It is noteworthy, too, that even points for the *m*- and *p*-trimethylammonio-substituents are reasonably close to the line; this may be coincidental, but if the Yukawa–Tsuno equation proved capable of interpretating the effects of these groups, even semi-quantitatively, in a range of reactions it would be a considerable achievement.

EXPERIMENTAL

Materials.—The preparations of the organogermanium compounds have been described,[21] except for those of the trimethylammonio-compounds which were made as follows.

A mixture of *m*- or *p*-dimethylaminophenyltriethylgermane and methyl iodide was kept at 40° for 0·5 hr., and the resulting *methiodide* recrystallized from ethanol–acetone to give the *m*-, m. p. 148—150° (with bubbling) (Found: C, 42·9; H, 6·9; N, 3·4. $C_{15}H_{28}GeIN$ requires C, 42·7; H, 6·7; N, 3·3%), or *p*-isomer, m. p. 203—205° (with bubbling) (Found: C, 42·7; H, 6·7; N, 3·3%). The iodides were hydrolysed to the hydroxides (which were used in the rate studies) by boiling them with an aqueous suspension of silver oxide, and after filtration water was evaporated at low pressure to leave a material which was taken up in methanol. The solution was filtered, and the residue was dissolved in anhydrous ethanol. Addition of ether gave the crystalline *hydroxides* [Found: N, 4·7 (*m*-isomer) and 4·5 (*p*-isomer). $C_{15}H_{29}GeNO$ requires N, 4·5%].

The acetic acid, purified as previously described,[3] contained 0·80% of water.

TABLE 2.

X	10^3 Concn. (M)	λ (mμ)	X	10^3 Concn. (M)	λ (mμ)
p-OMe	1·7	283	*m*-Cl	9	279
o-OMe	1·2	283, 286	*m*-Br	8·5	281
p-Me	10	274, 275	*m*-CO_2H	0·7	289, 290
p-Ph	1	292	*p*-CO_2H	0·7	285, 286
H	9	267, 268	*m*-CF_3	6	274
m-OMe	1·7	286	*p*-CF_3	6	274
p-Cl	8	278	*m*-$NMe_3^+OH^-$	10	269
p-Br	8	276	*p*-$NMe_3^+OH^-$	5	269
m-F	8	277	*m*-NO_2	6·5	370
			p-NO_2	9	370

Rate Measurements.—Techniques were as previously described.[3] A solution (2 vol., of concentration shown in Table 2) of the organogermane in acetic acid was mixed with aqueous

---

* Deans and Eaborn suggested that the σ^+-constants for the carboxyl groups might be in error, but there are now indications [18] that there is interaction between the groups and the cleavage medium possibly involving protonation of the group. This is being studied.

[18] Greasley, unpublished work.

[19] Yukawa and Tsuno, *Bull. Chem. Soc. Japan*, 1959, **32**, 971.

[20] McDaniel and Brown, *J. Org. Chem.*, 1958, **23**, 420.

[21] Eaborn and Pande, *J.*, 1960, 3200; Eaborn, Leyshon, and Pande, *J.*, 1960, 3423.

sulphuric acid (1 vol.) of the strength shown in Table 1. Optical densities at the wavelengths, λ, noted in Table 2 were recorded at suitable times. The temperature of the cells was controlled at 50·0° ± 0·03°.

Rate constants from duplicate runs normally agreed within 3%, usually within 1·5%. For the *m*-nitro- and *m*-bromo-compounds, however, the optical density changes available were too small for accuracy, and in these cases the rate constants could be in error by ±10%.

Measurements of the optical densities at 269 mμ of solutions of the *m*- and *p*-triethylgermylphenyltrimethylammonium hydroxides in 7·6M-aqueous sulphuric acid (*ca.* 0·01 g. in 10 ml.) at 50·0° led to first-order rate constants of 0·064 and 0·084 min.$^{-1}$, respectively.

This work was supported in part by the U.S. Department of Army through its European Office. We thank the Royal Society for the loan of apparatus, and the General Electric Co., Ltd., for a gift of germanium dioxide.

The University, Leicester.

[*Received, July* 11*th*, 1961.]