233. *Organogermanium Compounds. Part III.*[1] *Relative Inductive Effects of Trimethylsilyl and Trimethylgermyl Groups.*

By R. W. Bott, C. Eaborn, K. C. Pande, and T. W. Swaddle.

p-Trimethylgermyl- is slightly weaker than *p*-trimethylsilyl-methylbenzoic acid, and trimethyl-*p*-trimethylgermyl- is cleaved more easily than trimethyl-*p*-trimethylsilyl-methylphenylsilane by aqueous methanolic perchloric acid. Thus a trimethylgermyl group releases electrons to a saturated carbon atom slightly more strongly than does a trimethylsilyl group.

Trimethylgermyl- is stronger than trimethylsilyl-acetic acid, but probably because of steric effects.

The electronegativities of the Group IVB elements are in dispute (for reviews see refs. 2 and 3), and there is disagreement, for example, on whether silicon is more or less electronegative than germanium. On the original Pauling scale,[4] electronegativities of 2·5, 1·8, and 1·7, respectively, were assigned to carbon, silicon, and germanium, but Allred and Rochow derived values of 2·6, 1·90, and 2·0, respectively, from measurement of the proton shifts in Me_4M compounds, and amassed other evidence in favour of germanium's being more electronegative than silicon.[2] The deductions from the nuclear magnetic resonance studies have been criticized by Drago, who, from re-analysis of thermochemical data concludes that the electronegativities of the Group IVB elements are either essentially constant or decrease in the order Si > Ge > Sn > Pb.[3]

To throw light on this question we first compared the strengths of the acids *p*-$Me_3Si{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2H$ and *p*-$Me_3Ge{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2H$, by measuring their apparent dissociation constants, in 39 wt.-% methanol–water by a spectrophotometric method, and in 50 vol.-% ethanol–water by pH titration. The values obtained (with no corrections for use of alcoholic media), along with values for benzoic and *p*-toluic acid under the same conditions, are as follows:

X in *p*-$X{\cdot}C_6H_4{\cdot}CO_2H$	H	Me	$Me_3Si{\cdot}CH_2$	$Me_3Ge{\cdot}CH_2$
10^8k_a (39 wt.-% $MeOH–H_2O$ at 25°)	227	174	135	125
10^8k_a (50 vol.-% $EtOH–H_2O$ at 20°)	200[a]	132[a]	79·4[b]	75·7

[a] Values at 18° obtained by Eaborn and Parker.[5] [b] Cf. the value of 83·2 at 18° previously reported.[5]

The difference between the germanium- and silicon-containing acids is very small, but because of the consistency of the results from the two methods we believe it to be real, indicating that the Me_3Ge group has a slightly larger $+I$ effect than the Me_3Si group.

We obtained a more clear-cut result by measuring the rates of cleavage of *p*-$X{\cdot}C_6H_4{\cdot}SiMe_3$ compounds at 50° by a mixture of methanol (5 vol.) and aqueous perchloric acid (2 vol.), of the strength specified in the following Table, which lists the first-order rate constants, k_1:

X in *p*-$X{\cdot}C_6H_4{\cdot}SiMe_3$	Me	$Me_3Si{\cdot}CH_2$	$Me_3Ge{\cdot}CH_2$
10^3k_1 (7·34M-$HClO_4$)	12·7	190	315
10^3k_1 (6·21M-$HClO_4$)	—	117	202
10^3k_1 (3·06M-$HClO_4$)	—	5·4	9·15

These cleavages of aryl–silicon bonds are facilitated by electron-releasing substituents in the aryl group,[6] and it will be seen that the accelerating effect of the $Me_3Ge{\cdot}CH_2$ group

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[1] Part II, Eaborn, Leyshon, and Pande, *J.*, 1960, 3423.

[2] Allred and Rochow, *J. Inorg. Nuclear Chem.*, 1958, **5**, 269; Allred, *ibid.*, 1961, **17**, 215.

[3] Drago, *J. Inorg. Nuclear Chem.*, 1960, **15**, 237.

[4] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N.Y., 2nd edn., 1940, p. 64.

[5] Eaborn and Parker, *J.*, 1954, 939.

[6] Eaborn, *J.*, 1956, 4858; Eaborn, " Organosilicon Compounds," Butterworths Scientific Publ., London, 1960, pp. 146—152.

is 1·7 times as great as that of the $Me_3Si{\cdot}CH_2$ group. Thus we conclude that the Me_3Ge group releases electrons to the methylene group more strongly than does the Me_3Si group, which is consistent with germanium's being slightly less electronegative than silicon. Since trimethyl-*p*-tolylsilane is cleaved about 20 times faster than trimethylphenylsilane,[6] the *p*-$Me_3Si{\cdot}CH_2$ and *p*-$Me_3Ge{\cdot}CH_2$ substituents accelerate the cleavage 300 and 490 times, respectively, which compares with a 1500-fold acceleration by the *p*-OMe substituent.[6]

We also measured the apparent dissociation constants of the acids $Me_3Si{\cdot}CH_2{\cdot}CO_2H$ and $Me_3Ge{\cdot}CH_2{\cdot}CO_2H$ by pH titration in water at 20°. The results are shown in the following Table which, for comparison, includes some results obtained by Sommer, Gold, Goldberg, and Marans: [7]

X in $X{\cdot}CH_2{\cdot}CO_2H$	H	Me_3C	Me_3Si	Me_3Si	Me_3Ge
10^7k_a	175 [a]	100 [a]	60 [a]	60	105

[a] Values obtained by Sommer *et al.*[7]

In this case, the germanium-containing acid is stronger than the silicon-containing acid, but this does not conflict with the above conclusions since steric effects must be important here. Thus the weakness of the acid $Me_3C{\cdot}CH_2{\cdot}CO_2H$ cannot be accounted for by polar effects alone (electron release by the Me_3C group would have to be greater than that by the Me_3Ge group) but can be attributed to steric hindrance of solvation of the anion formed on dissociation.[8] The greater strength of the trimethylgermyl- than of trimethylsilyl-acetic acid can be attributed to smaller hindrance to such solvation in the former, arising from the greater length of the C–Ge than of the C–Si bonds. The difference between the atomic radii of germanium and silicon is small (0·05 Å), but it is sufficient, for example, to lead to a considerably smaller barrier to rotation of the methyl groups in tetramethylgermane (400 cal.) than in tetramethylsilane (1100—1500 cal.).[9]

Attempts to include the Me_3Sn group in our study were frustrated by (i) our failure to prepare the acid *p*-$Me_3Sn{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2H$, and (ii) the cleavage of the $Me_3Sn–CH_2Ar$ rather than of the $Me_3Si–Ar$ bond when the compound *p*-$Me_3Sn{\cdot}CH_2{\cdot}C_6H_4{\cdot}SiMe_3$ is treated with aqueous-methanolic perchloric acid. Our results for the Me_3Si and Me_3Ge groups, however, mean that Allred and Rochow's nuclear magnetic resonance measurements on Me_4M compounds [2] can no longer be taken to indicate that electron release of an Me_3M group to a saturated carbon atom decreases in the order (M =) $Si \approx Sn > Ge \gg Pb$. Eaborn and Pande's discussion of the relative ease of cleavage of Me_3M–aryl bonds,[10] in which the Allred and Rochow sequence was assumed, thus needs to be revised.

EXPERIMENTAL

p-*Trimethylgermylmethylbenzoic Acid.*—The organolithium reagent from *p*-chlorobenzyltrimethylgermane (10 g.) and lithium (2 g.) in ether (60 ml.) was added to solid carbon dioxide. When the mixture had warmed to room temperature, the excess of lithium was filtered off, and the ethereal solution was treated with dilute hydrochloric acid and extracted several times with 0·2M-sodium hydroxide, the extracts being added immediately to an excess of hydrochloric acid. The organic acid was re-extracted with ether, and the solvent was removed, to leave a solid which after recrystallization from 3 : 1 light petroleum–acetone gave p-*trimethylgermylmethylbenzoic acid* (4 g., 40%), m. p. 173—174° (Found: C, 52·5; H, 6·4. $C_{11}H_{16}GeO_2$ requires C, 52·25; H, 6·4%).

4-*Bromo- and* 4-*Chloro-benzyltrimethylstannane, and Attempted Preparation of* p-*Carboxybenzyltrimethylstannane.*—Bromotrimethylstannane (60 g.) was refluxed for 5 hr. with the Grignard reagent from 4-chlorobenzyl chloride (50 g.), magnesium (8 g.), and ether (300 ml.). Treatment with 5% aqueous ammonium chloride followed by separation, washing, drying (Na_2SO_4), and

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[7] Sommer, Gold, Goldberg, and Marans, *J. Amer. Chem. Soc.*, 1949, **71**, 1509.

[8] Hammond, " Steric Effects in Organic Chemistry," ed. Newman, John Wiley and Sons, New York, 1956, Chapter 9; Hammond and Hogle, *J. Amer. Chem. Soc.*, 1955, **77**, 338.

[9] French and Rasmussen, *J. Chem. Phys.*, 1946, **14**, 389.

[10] Eaborn and Pande, *J.*, 1960, 1566.

fractionation of the ethereal layer gave p-*chlorobenzyltrimethylstannane* (61 g., 81%), b. p. 124°/9 mm. (Found: C, 41·9; H, 5·4. $C_{10}H_{15}ClSn$ requires C, 41·6; H, 5·2%).

4-*Bromobenzyltrimethylstannane*, b. p. 126°/6 mm., was prepared analogously in 37% yield from 4-bromobenzyl bromide (Found: C, 36·4; H, 4·4. $C_{10}H_{15}BrSn$ requires C, 36·0; H, 4·5%).

Attempts were made to prepare *p*-carboxybenzyltrimethylstannane from 4-bromo- and 4-chloro-benzyltrimethylstannane by the method described above for *p*-trimethylgermylmethylbenzoic acid. Organic acids were produced, but as viscous semi-solids, smelling of trimethyltin hydroxide, from which pure material could not be isolated. Probably cleavage of the tin–benzyl bond had occurred.

p-*Trimethylsilylmethylbenzoic Acid*.—This acid, m. p. 179°, was prepared as previously described.[5]

Trimethylsilylacetic Acid.—This acid, m. p. 40°, was prepared by carbonation of the Grignard reagent from bromomethyltrimethylsilane (cf. ref. 7).

Trimethylgermylacetic Acid.—The Grignard reagent from chloromethyltrimethylgermane (11·7 g.), and magnesium (2·7 g.) in ether (100 ml.) was added to solid carbon dioxide. When the mixture had warmed to room temperature it was acidified with hydrochloric acid, more ether was added, and the ethereal layer was separated, washed, dried (Na_2SO_4), and evaporated. The residue was recrystallized to constant m. p. from heptane at low temperature, giving *trimethylgermylacetic acid* (5·9 g., 48%), m. p. 43·5° (Found: C, 33·9; H, 6·7%; acid equiv., 176·0. $C_5H_{12}GeO_2$ requires C, 34·0; H, 6·85%; equiv., 176·7).

4-*Chlorobenzyltrimethylgermane*.—A mixture of bromotrimethylgermane (40 g.) with the Grignard reagent from 4-chlorobenzyl chloride (80 g.) and magnesium (12 g.) in ether (500 ml.) was refluxed for 8 hr. Treatment with dilute hydrochloric acid followed by separation, washing, drying (Na_2SO_4), and fractionation of the ethereal layer gave 4-*chlorobenzyltrimethylgermane* (40 g., 80%), b. p. 112°/14 mm., n_D^{20} 1·5288 (Found: C, 49·3; H, 6·3. $C_{10}H_{15}ClGe$ requires C, 49·4; H, 6·2%).

Trimethyl-4-*trimethylsilylbenzylgermane*.—Dropwise addition of a mixture of 4-chlorobenzyltrimethylgermane (15 g.) and chlorotrimethylsilane (8 g.) to a refluxing mixture of sodium (3 g.) and toluene (80 ml.), followed by 1 hour's refluxing, filtration, and fractionation, gave *trimethyl*-4-*trimethylsilylbenzylgermane* (80%), b. p. 108°/5 mm., n_D^{20} 1·5067 (Found: C, 55·5; H, 8·7. $C_{13}H_{24}GeSi$ requires C, 55·6; H, 8·6%).

Trimethyl-4-*trimethylsilylbenzylstannane*.—By the method described in the preceding paragraph, but with refluxing for 2 hr., this *stannane*, b. p. 133—135°/7—8 mm., n_D^{20} 1·5251, was prepared in 32% yield from chlorotrimethylsilane, 4-chlorobenzyltrimethylstannane, and sodium in toluene (Found: C, 47·7; H, 7·5. $C_{13}H_{24}SiSn$ requires C, 47·7; H, 7·4%).

Comparisons of Acid Strengths.—(a) *Spectrophotometric*. Ten ml. of a solution of the organic acid (1—8 × 10^{-4}M) in 39 wt.-% methanol–water were mixed with 10 ml. of the same solvent containing sodium hydroxide (0·15M), sulphuric acid (0·075M), or a sodium acetate–acetic acid buffer, and the optical densities of the mixtures were recorded at every 2 mμ over a suitable wavelength range. The pH of the buffer solution was 5·85 (measured with a glass electrode in conjunction with a D-303-C Muirhead pH meter), but 5·90 on dilution with an equal volume of solvent; at this pH the acids are about half-dissociated. If the optical densities in acid, alkali, and buffer solution, respectively, are D_{Ac}, D_{Al}, and D_B, then the proportion, R, of acid present as the anion is given by $R = (D_{Al} - D_B)/(D_B - D_{Ac})$, and the p$K_a$ by pK_a = 5·90 + log R. The results were as follows:

Acid	λ (mμ)	R[a]	pK_a
$C_6H_5\cdot CO_2H$	240—248	0·55 ± 0·01	5·64
p-$Me\cdot C_6H_4\cdot CO_2H$	258—266	0·72 ± 0·01	5·76
p-$Me_3Si\cdot CH_2\cdot C_6H_4\cdot CO_2H$	272—284	0·93 ± 0·01	5·87
p-$Me_3Ge\cdot CH_2\cdot C_6H_4\cdot CO_2H$	270—288	1·01 ± 0·01	5·90

[a] The limits shown are those of maximum variation for measurements at the several wavelengths and in several separate determinations.

(*b*) *By* pH *titration*. The pH at half-neutralization was determined by use of a glass electrode in conjunction with a Pye 11086 pH meter, no corrections for use of alcoholic solvents being applied.

The substituted acetic acids were examined at several concentrations in water at 20°, 0·01N-sodium hydroxide being used for the titrations; apparent pK_a values of 5·22 ± 0·01 and 4·98 ± 0·01 were obtained for trimethylsilyl- and trimethylgermyl-acetic acid, respectively. The limits quoted are those of maximum variation over several independent measurements.

The substituted benzoic acids were examined in almost saturated solution in a mixture of equal volumes of ethanol and water at 20°, 0·04N-sodium hydroxide in the same medium being used for titration; uncorrected, apparent pK_a values of 6·095 ± 0·005 and 6·12 ± 0·01, respectively, were obtained for *p*-trimethylsilyl- and *p*-trimethylgermyl-methylbenzoic acid (the significance of the limits being that indicated in the preceding paragraph). Eaborn and Parker,[5] using a different meter and glass electrode, obtained pK_a 6·08 for the silicon-containing acid at 18°.

Rates of Cleavage of Aryl–Silicon Compounds.—Rates of cleavage of *p*-X·C_6H_4·$SiMe_3$ compounds in a mixture of methanol (5 vol.) and aqueous perchloric acid (2 vol) at 50·0° were measured spectrophotometrically by the method previously described.[6] The concentration of the organosilane was 1—2 × 10^{-3}M; wavelengths of 247 and 249 mμ (X = $Me_3Si{\cdot}CH_2$), 250 and 265 mμ (X = $Me_3Ge{\cdot}CH_2$), and 270 mμ (X = *p*-Me) were used.

*Cleavage of Trimethyl-*p*-trimethylstannylmethylphenylsilane.*—With this organosilane, the spectrophotometric method gave results which suggested that the Me_3Sn group was being removed, and preferential removal of this group by acid was shown in the following way, hydrochloric acid being used instead of perchloric acid to avoid the possibility of isolation of an organometallic perchlorate.

A mixture of 3N-aqueous hydrochloric acid (10 ml.) and a solution of trimethyl-*p*-trimethylstannylmethylphenylsilane (6 g.) in methanol (100 ml.) was kept at 50° for 3 hr. and then added to water. Ether-extraction, followed by separation, washing, drying (Na_2SO_4), and fractionation of the ethereal layer, gave trimethyl-*p*-tolylsilane (2·2 g., 73%), b. p. 190°, n_D^{20} 1·4935.

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THE UNIVERSITY, LEICESTER.

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