THE JOURNAL OF Organic Chemistry®

VOLUME 36, NUMBER 23 | NOVEMBER 19, 1971

Carboxysilanes and -germanes. II.[1,2] Synthesis and Spectral Properties of Triorganosilane- and Triorganogermanecarboxylic Acid

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Received January 6, 1971

Procedures for the synthesis of carboxysilanes and -germanes of the type $Me_nPh_{3-n}MCO_2H$, where M = Si and Ge and n = 0–3, and $(XC_6H_4)_3GeCO_2H$, where X = *m*-CH_3, *p*-CH_3, *m*-OCH_3, *p*-OCH_3, *m*-F, *p*-F, and *p*-CF_3, by carbonation of the corresponding triorganosilyl- and triorganogermyllithium reagents are given. The spectral properties, uv, ir, and pmr, of a number of these acids and their carbon analogs are listed and discussed. The uv spectra of Me_3MCO_2H and $Me_3MCO_2^-$, $n \rightarrow \pi^*$ transition, are interpreted in terms of inductive release by the metalloid and π ($\pi^* \rightarrow$ d) bonding between the functional group and the metalloid.

In this and the following paper,[3] further studies are reported on the chemical and physical properties of triorganosilane- and triorganogermanecarboxylic acids. These studies were undertaken in order to obtain a better understanding of the bonding in and the properties of the structural unit, $\equiv MCO_2-$, where M = Si or Ge, which is novel in that the carboxyl group is bonded directly to the metalloid through carbon.

The chemical and physical properties of the carboxysilanes and -germanes and their derivatives differ markedly from their carbon analogs.[1-10] The differences in properties can be accounted for in terms of the inductive effect of the metalloid, the ability of the metalloid to form additional bonds, and π ($\pi \rightarrow$ d) bonding between the metalloid and the carboxy group.[11] In this paper, the spectral properties of carboxysilanes and -germanes are reported and interpreted in terms of inductive effects and π bonding between the carboxyl group and the vacant d orbitals of the metalloid, particularly in reference to the excited state. General methods for the preparation of carboxysilanes and -germanes are also discussed.

Experimental Section

Melting points were determined on a Fisher-Johns apparatus and are corrected. The spectra were obtained on the following instruments: ir, Beckman IR-8 and IR-20 spectrophotometers; uv, Cary 14 spectrophotometer; nmr, Varian A-60 spectrometer. The elemental analyses were performed by Alfred Bernhardt Microanalytical Laboratory, West Germany.

Preparation of the Triorganosilane- and Triorganogermanecarboxylic Acids.—Detailed descriptions of the synthetic procedures used are given below by citing typical examples. The yields, melting points, and analyses for the acids, intermediates, and by-products are given in Tables I and II.[12,13] For acids not included in Table I, *cf.* ref 1 and 2c.

A. **Procedure 1.**—Small pieces of lithium wire, 1.7 g (0.24 g-atom), were added to HMPA (80 ml), and the mixture was stirred until a permanent blue-black color was observed.[14] Trimethylbromogermane, bp 112–114° (lit.[15] bp 113.5°), 12.0 g (60 mmol), dissolved in HMPA (20 ml), was added to the above solution over a period of 2.5 hr. During the addition, the flask was cooled in an ice-water bath. After stirring for 3 hr, the reaction mixture remained colorless; therefore, the reaction was initiated by adding an aliquot of a solution prepared from lithium (0.5 g) and HMPA (20 ml). After stirring for 10 min, the reaction mixture was a light greenish brown. After stirring for 7 hr, the dark greenish-brown solution was filtered through glass wool and carbonated by pouring onto powdered Dry Ice. The Dry Ice slurry was poured directly into a 5% hydrochloric acid solution (150 ml). The aqueous solution was extracted several times with ether (750 ml) and the combined ethereal solution was dried (EtOH). Removal of the solvent under reduced pressure gave the crude trimethylgermanecarboxylic acid (1.7 g,

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[1] For preliminary reports on this work, *cf.* (a) O. W. Steward, J. E. Dziedzic, and J. O. Frohliger, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, INOR 118; (b) O. W. Steward, J. E. Dziedzic, and J. S. Johnson, Abstracts, Fourth International Conference on Organometallic Chemistry, Bristol, England, July 1969, D18; (c) O. W. Steward and J. E. Dziedzic, *J. Organometal. Chem.*, **16**, P5 (1969).

[2] Part I: O. W. Steward, H. W. Irwin, R. A. Gartska, and J. O. Frohliger, *J. Chem. Soc. A*, 3119 (1968).

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[13] J. H. Gardner and P. Borgstron, *J. Amer. Chem. Soc.*, **51**, 3375 (1929).

[14] A dry nitrogen atmosphere was maintained over all reactions involving lithium and organosilyl- and organogermyllithium reagents.

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TABLE I

PREPARATIONS OF R_3MCO_2H[a]

R_3M	Registry no.	Procedure	% yield[b]	Mp, °C[c]	% C		% H	
					Calcd	Found	Calcd	Found
Me_3Si	31593-12-1	2	42	38–40	40.64	40.74	8.53	8.67
Me_3Ge[d]	22776-20-1	1	17	36–37.5	29.52	29.69	6.20	6.19
$PhMe_2Ge$	31593-16-5	5	47	49–50.5	48.08	48.18	5.38	5.41
Ph_2MeGe[e]	31593-18-7	4	54	131.5–133 dec	58.60	58.49	4.93	4.88
$(p\text{-}MeC_6H_4)_3Ge$	2887-10-7	3	84	168–170 dec[f]	67.75	67.71	5.68	5.68
$(m\text{-}MeC_6H_4)_3Ge$	31593-21-2	3[g]	43	161–163 dec	67.75	67.63	5.68	5.65
$(p\text{-}MeOC_6H_4)_3Ge$	31593-22-3	5	35	132–134 dec	60.19	60.12	5.02	5.20
$(m\text{-}MeOC_6H_4)_3Ge$	31593-23-4	6	38	126.5–128 dec	60.19	60.16	5.02	4.93
$(p\text{-}FC_6H_4)_3Ge$	31593-24-5	5	17	153–155 dec	56.64	56.60	3.25	3.20
$(m\text{-}FC_6H_4)_3Ge$	31593-25-6	6[g]	13	180–183 dec	56.64	56.64	3.25	3.24
$(p\text{-}CF_3C_6H_4)_3Ge$	31593-26-7	5	14	163–165 dec	47.79	47.77	2.37	2.47

[a] For acids not in this table, *cf.* ref 1 and 2c. [b] Crude acid. [c] Corrected. [d] Reference 2c. [e] Nmr (CCl_4) 0.91 (s, 3, CH_3Ge), *ca.* 7.40 (10, C_6H_5Ge), 11.60 (s, 1, CO_2H). [f] Lit.[12] mp 141–143 dec. [g] Intermediate not isolated.

TABLE II

INTERMEDIATES AND BY-PRODUCTS

Compd	Registry no.	Procedure	% yield[a]	Mp or bp (mm), °C	% C		% H	
					Calcd	Found	Calcd	Found
$[(p\text{-}MeC_6H_4)_3Ge]_2$		3	30	345–347[b]				
$[(p\text{-}MeOC_6H_4)_3Ge]_2$	31593-81-4	3	40	371–373	64.01	64.04	5.37	5.40
$[(m\text{-}MeOC_6H_4)_3Ge]_2$	31593-82-5	3	36	189–191	64.01	63.84	5.37	5.45
$(p\text{-}MeOC_6H_4)_2$		5		172–173[c]				
$(p\text{-}CF_3C_6H_4)_2$	581-80-6	5		91–92	57.93	58.07	2.78	2.93
$(p\text{-}CF_3C_6H_4)_4Ge$	31593-84-7	5	14	173–174	51.50	51.63	2.47	2.58
$(m\text{-}CF_3C_6H_4)_2GeH_2$	31593-85-8	5	34	93–94 (0.6)[d]	46.09	46.07	2.76	2.83
$(m\text{-}CF_3C_6H_4)_3GeOH$[e]	31593-86-9	5	27	142–143	48.05	47.94	2.49	2.38
$(m\text{-}CH_3OC_6H_4)_3GeH$[f]	2816-29-7	6	91	83.5–85	63.84	63.71	5.61	5.62
$(C_6H_5)_2GeMe_2$	7301-42-0	4	45	80–81.5 (0.15)[g]	65.50	65.46	6.27	6.20

[a] Crude yield. [b] Lit.[12] mp 345°. [c] Lit.[13] mp 171–172°. [d] Bp; $n^{25}D$ 1.4873; ir (neat), GeH, 2092 cm^{-1}. [e] From decarbonylation of crude $(m\text{-}CF_3C_6H_4)_3GeCO_2H$. [f] Ir (Nujol), GeH, 2041 cm^{-1}. [g] Bp; $n^{25}D$ 1.5711; nmr (CCl_4) 0.53 (s, 3, CH_3Ge), *ca.* 7.30 (5, C_6H_5Ge).

11 mmol). Five successive crystallizations from pentane at −78° gave a sample of high purity.

B. **Procedure 2.**—Small pieces of lithium wire (12.5 g, 0.36 g-atom) were added to bis(trimethylsilyl)mercury[16] (17.1 g, 43 mmol) dissolved in THF (150 ml). After stirring for 6 hr, the black solution was filtered through glass wool, carbonated, and extracted as described in procedure 1. Removal of the ether under reduced pressure gave crude trimethylsilanecarboxylic acid (4.2 g, 23 mmol). Five successive crystallizations from pentane at −78° gave a sample of high purity.

C. **Procedure 3.**—A THF solution (450 ml) of *p*-tolylmagnesium bromide (0.20 mol) was added over a period of 2 hr to germanium tetrachloride (12.5 g, 58 mmol) dissolved in THF (250 ml). Small pieces of lithium wire (2.5 g, 0.36 g-atom) were added and the mixture was stirred for 10 hr. The mixture was filtered through glass wool, poured onto powdered Dry Ice, and acidified with a 5% hydrochloric acid solution (300 ml). The insoluble white solid, crude hexa-*p*-tolyldigermane, 6.0 g (8.7 mmol, 30%), mp 350–360°, was separated by filtration. A sample was purified by sublimation. The remaining organic material was extracted with ether (500 ml), and the combined ethereal solution was extracted with two 100-ml portions of a 5% sodium hydroxide solution. After acidification and ether extraction (300 ml), the ethereal layer yielded crude *p*-toluic acid (2.8 g) on evaporation. A sample was purified by sublimation, mp 179–180.5° (lit.[17] mp 180°). Hexa-*p*-tolyldigermane (5.0 g, 7.2 mmol) and small pieces of lithium wire (0.69 g, 0.10 g-atom) were added to a mixture of THF (100 ml) and HMPA (30 ml). After the solution was stirred for 21 hr, the dark green solution was filtered through glass wool and poured onto powdered Dry Ice. The Dry Ice slurry was acidified with 5% hydrochloric acid (300 ml) and extracted several times with ether (300 ml). The combined ethereal solution was extracted with two 50-ml portions of 5% sodium hydroxide, and the combined aqueous solution was acidified and extracted with ether (400 ml). After drying (EtOH), removal of the ether under reduced pressure gave crude tri-*p*-tolylgermanecarboxylic acid (4.8 g, 12.2 mmol), mp 145–155° dec. Several successive crystallizations from ethanol gave a sample of high purity.

D. **Procedure 4.**—An ethereal solution (75 ml) of phenyllithium (0.12 mol) was added over a period of 40 min to dimethyldichlorogermane (10.0 g, Alfa Inorganics, Inc.) dissolved in THF (250 ml). (After this experiment was completed, it was found that the dimethyldichlorogermane employed was a mixture of 19 mol % methyltrichlorogermane and 81 mol % dimethyldichlorogermane by nmr analysis.) After the addition of phenyllithium was completed, small pieces of lithium wire (2.8 g, 0.405 g-atom) were added and the mixture was stirred for 11 hr. The reaction mixture was carbonated and the crude acid extracted as described for procedure 3. Crystallization of the syrupy material from a pentane solution (−15°) gave crude diphenylmethylgermanecarboxylic acid (2.0 g, 7.0 mmol), mp 110–120°, a 54% yield based on the methyltrichlorogermane added. Several successive crystallizations from pentane–ether gave a sample of high purity. Evaporation of the ethereal layer remaining after basic extraction gave a syrupy residue. Fractional distillation under reduced pressure gave crude biphenyl (0.40 g), mp 65–68°, and diphenyldimethylgermane (6.0 g, 23.5 mmol), bp 75–85° (0.15 mm), a 45% yield based on the dimethyldichlorogermane added. Sublimation yielded a sample of high purity of biphenyl, mp 67–68° (lit.[18] mp 68.5°). Fractional distillation under reduced pressure of crude diphenyldimethylgermane gave a sample of high purity.

E. **Procedure 5.**—A THF solution (450 ml) of *p*-anisylmagnesium bromide (0.21 mol) was added over a period of 3 hr to germanium tetrachloride (12.0 g, 56 mmol) dissolved in THF (250 ml). After the addition was completed, lithium aluminum hydride (1.3 g, 34 mmol) dissolved in ether was added, and the mixture was stirred for 18 hr. After the excess lithium aluminum hydride was decomposed with absolute ethanol, the reaction mixture was poured onto a mixture of cracked ice and dilute hydrochloric acid. The organic material was extracted with ether (500 ml) and, after drying (EtOH), the solvent was removed under reduced pressure. Distillation under reduced pressure

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[16] C. Eaborn, R. A. Jackson, and R. W. Walsingham, *J. Chem. Soc. C*, 2188 (1967).

[17] H. Fischli, *Chem. Ber.*, **12**, 615 (1879).

[18] H. Gilman and E. A. Zuech, *J. Org. Chem.*, **26**, 3035 (1961).

of the remaining material gave crude, *p,p'*-bianisole (1.2 g), mp 165–178°. A sample of high purity was obtained by sublimation. An ir spectrum (neat) of the syrupy residue remaining after removal of the *p,p'*-bianisole showed a strong Ge–H absorption band (2045 cm^{-1}), indicative of tri-*p*-anisylgermane. The syrupy residue was dissolved in THF (120 ml) and HMPA (60 ml), and small pieces of lithium wire (4.4 g, 0.63 g-atom) were added. After the solution was allowed to stir for 12 hr, the reaction mixture was carbonated and the crude acid extracted as described for procedure 3. Crystallization of the syrupy material from benzene–hexane (0–5°) gave crude tri-*p*-anisylgermanecarboxylic acid, (8.7 g, 19.8 mmol), mp 115–125° dec. Several successive crystallizations from benzene–hexane gave a sample of high purity.

F. Procedure 6.—A THF solution (450 ml) of *m*-anisylmagnesium bromide (0.21 mol) was added over a period of 3.5 hr to germanium tetrachloride (12.5 g, 58 mmol), dissolved in THF (250 ml). After the addition was completed, lithium aluminum hydride (1.8 g, 47 mmol) was added, and the procedure described for procedure 5 was followed. On removal of the solvent under reduced pressure, crude tri-*m*-anisylgermane (20.9 g, 53 mmol), mp 78–84°, was obtained. Two successive crystallizations from ethanol-benzene gave a sample of high purity. *n*-Butyllithium (10 ml, 1.6 *M* in hexane) was added over a period of 10 min to tri-*m*-anisylgermane (5.0 g (0.125 mol) dissolved in ether (30 ml). After the solution had been stirred for 10 min, the yellow-orange solution was carbonated and the crude acid extracted as described for procedure 3. Crude tri-*m*-anisylgermanecarboxylic acid (3.2 g, 4.8 mmol), mp 124–128°, gave a sample of high purity, after several successive crystallizations from benzene–petroleum ether (bp 30–60°).

Results and Discussion

Synthesis.—To date, the only known method of preparing triorganosilane- and triorganogermanecarboxylic acids is by carbonation of triorganosilyl- and triorganogermyl–alkali metal derivatives[19,20] and triarylgermylmagnesium compounds.[20]

In this paper the syntheses of Me_3SiCO_2H and Me_3GeCO_2H,[2c] by the carbonation of Me_3SiLi[21] and Me_3GeLi,[22] respectively, are reported. The alkylarylgermanecarboxylic acids, $Me_2PhGeCO_2H$ and $MePh_2GeCO_2H$, were synthesized by carbonation of the corresponding germyllithium derivatives.

A series of triarylgermanecarboxylic acids with substituent groups on the aromatic rings in the meta and para positions were synthesized for spectral studies and pK_a determinations. Previously, only the *p*-tolyl derivative had been reported.[23] The triarylgermyllithium reagents, which were carbonated to yield the carboxylic acids, were synthesized as indicated in eq 1–3. Method 1 was employed to prepare the *p*-CH_3

$$[(XC_6H_4)_3Ge]_2 \xrightarrow[\text{THF-HMPA}]{\text{Li}} 2(XC_6H_4)_3GeLi \qquad (1)$$

$$(XC_6H_4)_3GeH \xrightarrow[\text{THF-HMPA}]{\text{Li}} (XC_6H_4)_3GeLi \qquad (2)$$

$$(XC_6H_4)_3GeH \xrightarrow[\text{Et}_2\text{O}]{n\text{-BuLi}} (XC_6H_4)_3GeLi \qquad (3)$$

derivative; method 2, the *m*-CH_3, *p*-CH_3O, *p*-F, and *p*-CF_3 derivatives; and method 3, the *m*-CH_3O and *m*-F derivatives. In most cases, methods 1 and 2 were modified from the cited procedures[20] by adding hexamethylphosphoramide (HMPA) to the reaction mixture. Addition of HMPA to the reaction decreases the initiation time for germyllithium formation by partially dissolving the lithium metal[24] and generally enhances the yield of the carboxylic acid. Method 2 was found to be the most versatile of the methods employed and thus was used most frequently for the synthesis of the carboxylic acids. Method 1 would seem to be a good approach to synthesizing all of the triarylgermanecarboxylic acids, but difficulties were encountered in preparing the starting materials, $(XC_6H_4)_6Ge_2$. In two cases, hexa-*p*-anisyldigermane and hexa-*m*-anisyldigermane, cleavage of the Ge–Ge bond was not successful.

The stability of triorganosilane- and triorganogermanecarboxylic acids toward base-catalyzed decarbonylation has been discussed in several papers. Whereas Ph_3GeCO_2H and Et_3GeCO_2H are reported to be stable toward dilute alkali,[4,8,22] $Me_nPh_{3-n}SiCO_2H$, $n = 0\text{–}2$, are reported to undergo decarbonylation.[4,7] In connection with the studies reported in this and the following paper, we have observed that both silane- and germanecarboxylic acid undergo base-catalyzed decarbonylation, the silanecarboxylic acids decomposing more rapidly than the analogous germanecarboxylic acids and the rate of decarbonylation being facilitated by electron-withdrawing groups.

Both Me_3SiCO_2H and Me_3GeCO_2H are quite stable toward base, and the corresponding anions can be prepared in 76 wt % ethanol–water. The triarylgermanecarboxylic acids with electron-withdrawing substituent groups on the aromatic ring decarbonylate when the base, sodium 4-nitrophenoxide, is added to solutions of the acids in dimethyl sulfoxide. The triorganosilanecarboxylic acids decarbonylate on dissolving in dimethyl sulfoxide.

All of the arylgermanecarboxylic acids prepared were isolated from an ethereal solution of the reaction mixture by extraction with 5% aqueous sodium hydroxide. However, attempts to isolate $(m\text{-}CF_3C_6H_4)_3GeCO_2H$ by this method were not successful. The acid decomposed on extraction at 0° as was evident from the disappearance of the carbonyl stretching band (1667 cm^{-1}) which is characteristic of the germanecarboxylic acids (*cf.* ir section).

Ultraviolet Spectra.—The electronic spectral properties of triorganosilane- and triorganogermanecarboxylic acids and their conjugate base forms differ markedly from their carbon analogs. The spectra of the acids, R_3MCO_2H, and anions, $R_3MCO_2^-$, show an absorption band in the ultraviolet region, $\lambda_{\max}^{\text{EtOH}}$ 246–254 nm (ϵ <870), while aliphatic carboxylic acids absorb at a shorter wavelength, $\lambda_{\max}^{\text{EtOH}}$ 205–213 nm (ϵ <150) and aliphatic carboxylate ions show no absorption maximum above 200 nm;[25,26] *cf.* Figure 1. For the compounds studied to date, the absorption maximum of the silicon derivatives occurs at a slightly longer wavelength than for the corresponding germa-

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[19] H. Gilman and H. J. S. Winkler in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold, New York, N. Y., 1960, Chapter 6.

[20] F. Glockling, "The Chemistry of Germanium," Academic Press, London, 1969, pp 161–170.

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[25] A. E. Gillan and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold Ltd., London, 1958, Chapter 5.

[26] J. P. Philips, "Spectra-Structural Correlations," Academic Press, New York, N. Y., 1964, pp 80–84.

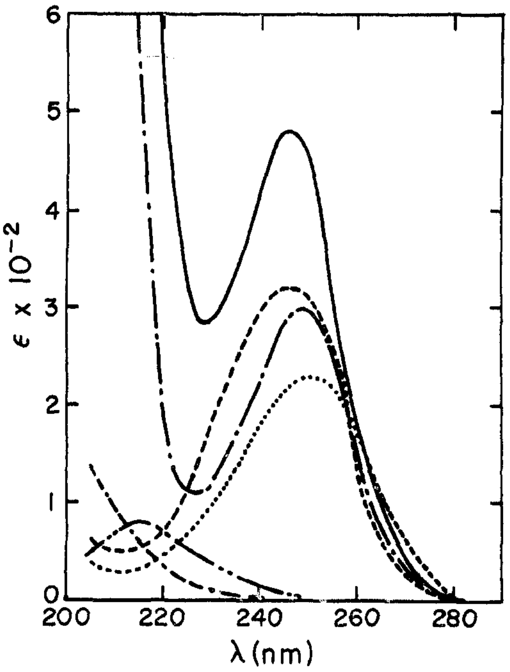

Figure 1.—The ultraviolet spectra of Me_3MCO_2H and $M_3MCO_2^-Na^+$ in absolute ethanol: acid, M = Ge (----), Si (·····), C (-·-··-·); anion, M = Ge (——), Si (·-··-·), C (--·--·).

nium derivatives (2–6 nm), while the extinction coefficient of the germanium derivatives is larger. The ultraviolet spectral data for the acids and anions are given in Table III along with some recently reported data on the corresponding methyl esters. The assignment of these bands as n → π* transition is based on their low intensity and on the bathochromic shift of the absorption maximum as the solvent is made more polar (cyclohexane to ethanol, $\Delta\lambda_{max}$ 5–6 nm), which is consistent with the data on aliphatic carboxylic acids.[27]

Table III

Ultraviolet Spectra Data for R_3MCO_2R' and $R_3MCO_2^-$

Compd	n → π* transition		
	λ_{max}, nm (ε)	eV	Solvent
Me_3CCO_2H[a]	205 (117)	6.05	C_6H_{12}
	213 (71)	5.82	EtOH
$Me_3CCO_2^-$[a]	<205		EtOH
Me_3SiCO_2H	243 (299)	5.10	C_6H_{12}
	249 (228)	4.98	EtOH
$Me_3SiCO_2^-$	248 (305)	5.00	EtOH
Me_3GeCO_2H[a]	241 (413)	5.14	C_6H_{12}
	246 (325)	5.04	EtOH
$Me_3GeCO_2^-$[a]	246 (480)	5.04	EtOH
$Me_2PhSiCO_2H$	~254 (<790)	4.94	EtOH
$Me_2PhGeCO_2H$	~248 (<870)	5.00	EtOH
$H_3GeCO_2^-$[b]	239 (<500)	5.19	H_2O
Me_3CCO_2Me[c]	212 (100)	5.85	C_6H_{12}
Me_3SiCO_2Me[c]	245 (330),	5.06,	C_6H_{12}
	250 (330)	4.96	
	245 (320)	4.96	95% EtOH

[a] Reference 2c. The values previously reported for the germanium acid and anion have been revised since the acid used for the spectral data contained small amounts of decarbonylation products. [b] Reference 9. [c] Reference 10.

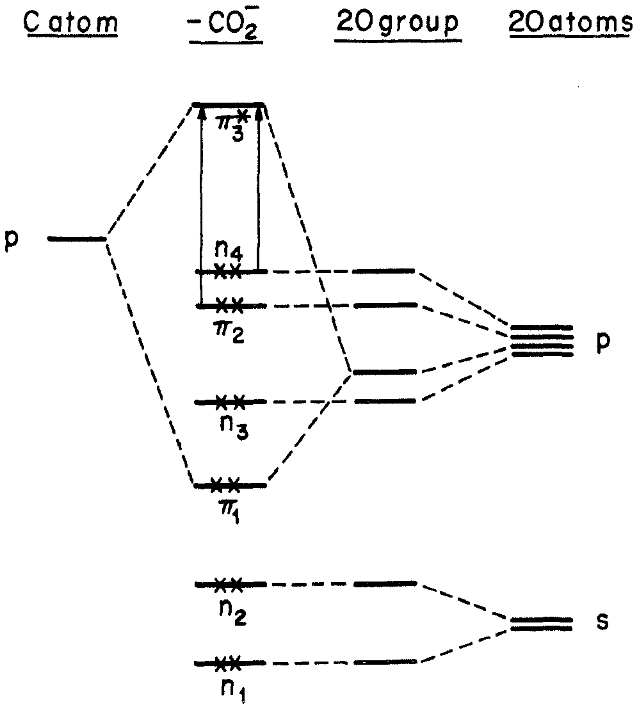

Figure 2.—A qualitative MO diagram for the $-CO_2^-$ ion.

For triorganosilane- and triorganogermanecarboxylic acids with substituent phenyl groups, the n → π* transition of the carboxyl group is masked by the phenyl π → π* transition with peaks in the region 247–272 nm. In all cases the molar extinction coefficients of the peaks in this region of the spectra are larger for the phenyl substituted silane- and germanecarboxylic acids than for their carbon analogs. The absorption maximum and molar extinction coefficient for the n → π* transition of $PhMe_2MCO_2H$ were estimated from the difference in the spectra of the acids and the corresponding compounds, $PhMMe_3$;[29] *cf.* Table III.

The relative positions of the energy levels for the n and π orbitals of the carboxylate ion, which is isoelectric with the nitro group,[28] are given in the qualitative molecular orbital diagram (Figure 2). The lowest energy transition is expected to be a forbidden transition, n → π*; a higher energy allowed transition, π → π*, is also expected. These electronic transitions are not observed above 200 nm for aliphatic carboxylate ions.[25,26] A similar ordering of transitions is expected for the carboxyl group when the change in electron repulsion on electronic excitation is considered.[30] In this case, the forbidden n → π* transition is observed, *ca.* 205–213 nm, just within the range of conventional spectrophotometric instruments.

The nature of the atom bonded to the carboxyl group or carboxylate ion through carbon will change the energy requirements for the electronic transitions. Substituting a metalloid, silicon or germanium, for carbon can significantly influence the energy of the n and π levels by inductive (+*I*) and π (π → d) bonding effects. The unfilled d orbitals on silicon (3d) and germanium (4d) can interact with the π system of the carboxyl group or carboxylate ion to lower the energy, of the π

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(27) The solvent shift is in the opposite direction for carbonyl derivatives which are not associated due to hydrogen bonding; see ref 25, 28.

(28) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, Chapter 9.

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levels, particularly the π^* level because of better matching of energy, while the greater electropositive nature of the metalloid than carbon would be expected to raise the energy of the n and π levels; *cf.* Figure 3.

The effect of metalloid substitution on the spectra of ketones, a simpler chromophore, has been reported.[31–33] The energy of the n $\rightarrow$ π^* transition of acylsilanes and -germanes is lower than for aliphatic ketones by about 1.0 eV resulting in absorption in the visible region.[34,35] Recent experimental measurements indicate that roughly one-fourth of the bathochromic shift of the n $\rightarrow$ π^* transition of acylsilanes is due to π ($\pi \rightarrow$ d) bonding with the remainder resulting from the inductive effect of silicon relative to carbon.[33]

Calculations based on ionization potentials[36] and electronic transition energies, n $\rightarrow$ π^*, of aliphatic carboxylic acids indicate that the n level is $\sim$0.8 eV lower and the π^* level is $\sim$0.8 eV higher than the corresponding levels in aliphatic ketones. MO calculations indicate that the d orbitals of silicon and germanium are higher in energy than the π^* level of aliphatic ketones.[37] Thus, there is a better matching of energy between the metalloid nd orbital and the π^* orbital of the silane- and germanecarboxylic acids than for the acylsilanes and -germanes, indicating that π ($\pi^* \rightarrow$ d) bonding should be more important in the former and thus result in a larger bathochromic shift of the n $\rightarrow$ π^* transition. However, smaller spectral shifts are observed for the silane- and germanecarboxylic acids, $\Delta\lambda_{\max}^{\mathrm{EtOH}} \sim 35$ nm. Since the energy of the n $\rightarrow$ π^* transition is the result of two energy states, the smaller shift for the carboxysilanes and -germanes could be the result of a much lower sensitivity of the n levels of the carboxyl chromophore to the inductive effect of the metalloid. There is no reason to expect that the inductive effect on the n levels of the carboxyl group would be the same as on the n level of the ketone group.

The π^* level of the carboxylate ion should be higher in energy than in the conjugate acid form due to greater electron delocalization in the ion. Thus, larger spectral shifts would be expected for $Me_3MCO_2^-$ than for the conjugate acid form due to better matching between the carboxylate ion π^* level and the metalloid nd level. The observed shift, $\Delta\lambda_{\max}^{\mathrm{EtOH}} > 42$ nm, is indeed larger; the $\lambda_{\max}^{\mathrm{EtOH}}$ for $Me_3CCO_2^-$ occurs below 205 nm. The larger extinction coefficient for $Me_3MCO_2^-$ than for the conjugate acid form, ratio of anion to acid form equals $\sim$1.4, is indicative of greater d-orbital participation in the anion form.

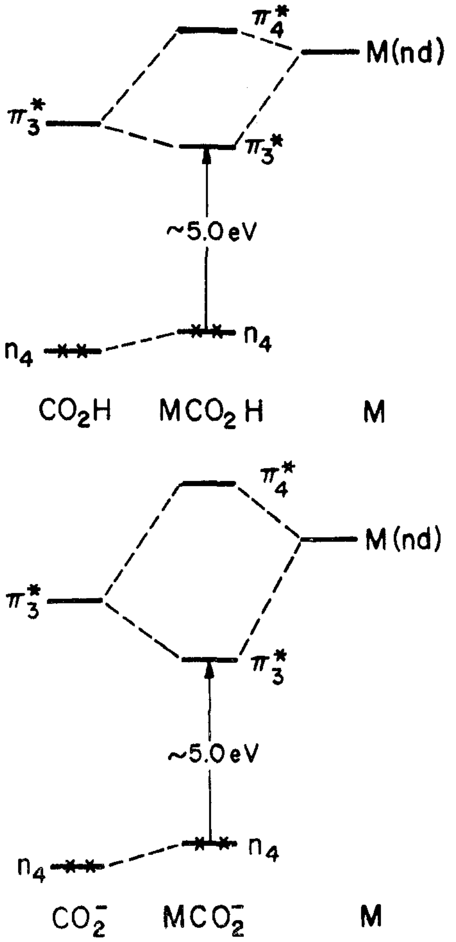

Figure 3.—Qualitative MO diagrams showing the effect of a metalloid and its d orbitals on the energy levels of the carboxyl group and the carboxylate ion.

Infrared Spectra.—Two of the most interesting features of the infrared spectra of the triorganosilane- and triorganogermanecarboxylic acids are the positions of the >C=O stretching frequency and the $\equiv MCO_2H$ stretching frequency. The carbonyl stretching absorption maximum for the acids, R_3MCO_2H (CCl_4 solution), is observed between 1645 and 1663 cm^{-1}, while this absorption occurs between 1693 and 1707 cm^{-1} for the carbon analogs. The positions of the absorption maximum for the acids in the solid state, KBr pellet, generally fall at lower energy. The shift of the carbonyl stretching absorption of the acids, R_3MCO_2H, from their carbon analogs, $\Delta\nu$ 28–53 cm^{-1}, is a good criterion for the structural unit, $\equiv MCO_2H$.[2c] For the series of triarylgermanecarboxylic acids with substituent groups on the aromatic rings, the position of the carbonyl stretching band parallels the inductive properties of the substituent group.

The stretching absorption for the $\equiv MCO_2H$ bond for the acids studied occurs between 572 and 600 cm^{-1} for R_3SiCO_2H and between 563 and 580 cm^{-1} for R_3GeCO_2H. The $\equiv MCH_3$ stretching absorption occurs at a shorter wavelength: $Me_nPh_{3-n}MCO_2H$, where n = 1–3; M = Si, ν 624–707 cm^{-1}; M = Ge, ν 584–607 cm^{-1}. The infrared spectral data are given in Tables IV and V.

Proton Magnetic Resonance Spectra.—The pmr spectra of the acids Me_3MCO_2H, where M = C, Si, and Ge, were determined in CCl_4; *cf.* Table VI. Each spectrum consists of two singlet resonance lines, $\equiv MCH_3{}^*$ and $\equiv MCO_2H^*$. The chemical shifts of the methyl proton are consistent with closely related C, Si, and Ge compounds.[11] The chemical shifts of the acidic proton are in accord with the electronegativities of the group IVb elements, C > Si $\approx$ Ge.

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TABLE IV

INFRARED SPECTRAL DATA FOR $(CH_3)_n(C_6H_5)_{3-n}MCO_2H$

Compd	ν, C=O, cm^{-1} CCl$_4$	ν, C=O, cm^{-1} KBr	ν, MCO$_2$H, cm^{-1} (CCl$_4$)	ν, MCH$_3$, cm^{-1} (CCl$_4$)
Me_3CCO_2H	1693	1686		
Me_2PhCCO_2H	1693	1670		
$MePh_2CCO_2H$	1696	1675		
Ph_3CCO_2H	1706	1670		
Me_3SiCO_2H	1654	1646	572	707, 624
$Me_2PhSiCO_2H$	1645	1636	588	649, 631 sh
$MePh_2SiCO_2H$	1647	1636	593	661
Ph_3SiCO_2H	1654	1633	600	
Me_3GeCO_2H	1648	1650	563 sh	614, 575
$Me_2PhGeCO_2H$	1646	1640	566 sh	607, 584
$MePh_2GeCO_2H$	1654	1647	570	595
Ph_3GeCO_2H	1663	1642	575	

TABLE V

INFRARED SPECTRAL DATA FOR $(XC_6H_4)_3GeCO_2H$

X	ν, C=O, cm^{-1} CCl$_4$	ν, C=O, cm^{-1} KBr	ν, MCO$_2$H, cm^{-1} (CCl$_4$)
H	1663	1642	575
p-CH$_3$	1652	1647	563
m-CH$_3$	1654	1642	575
p-CH$_3$O	1655	1654	573
m-CH$_3$O	1659	1645	580
p-F	1656	1650	573
m-F	1662	1650	580
p-CF$_3$	1663	1661	572
n-CF$_3$	1667[a]		

[a] Not isolated.

TABLE VI

PROTON MAGNETIC RESONANCE DATA FOR $(CH_3)_3MCO_2H$

M	δ, ppm[a] CH$_3$	δ, ppm[a] OH[b]	Peak area ratio
C	1.22	12.53	1:8
Si	0.26	12.01	1:8.6
Ge	0.46	11.96	1:9.2

[a] Spectra determined in CCl$_4$, 22–35 w/v %, using TMS as an internal standard at 60 MHz. [b] Position slightly affected by concentration.

Both the position of the carbonyl stretching frequency and the chemical shift of the acidic proton of the acids, Me_3MCO_2H, in relation to their carbon analog suggest that there is little π ($\pi \rightarrow$ d) bonding in the ground state of the acid form and the observed order is mainly the result of the inductive properties of the group IVb elements.

Registry No.—$Me_3SiCO_2^-$, 31593-89-2; $Me_2PhSiCO_2H$, 17878-13-6; $MePh_2SiCO_2H$, 18414-58-9; Ph_3SiCO_2H, 18670-88-7; Ph_3GeCO_2H, 22718-99-6.

Acknowledgments.—The authors gratefully acknowledge the financial support of the Dow Corning Corp., Midland, Mich., and a grant from the National Science Foundation for the Cary Model 14 spectrophotometer. One of us (J. E. D.) is grateful to NASA for a traineeship, 1967–1969.

Carboxysilanes and -germanes. III.[1,2] Ionization Constants of Triorganosilane- and Triorganogermanecarboxylic Acids in Ethanol–Water and Dimethyl Sulfoxide Media

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Received January 6, 1971

Ionization constants of the following carboxylic acids have been determined by a spectrophotometric method: $Me_nPh_{3-n}MCO_2H$, where M = C, Si and Ge, n = 0–3, in ethanol–water media and where M = C and Ge, in dimethyl sulfoxide; $(XC_6H_4)_3GeCO_2H$, where X = H, *p*-Me, *m*-Me, *p*-OMe, *m*-OMe, *p*-F, *m*-F, and *p*-CF$_3$, in ethanol–water media and X = H, *p*-Me, *m*-Me, *p*-OMe, in dimethyl sulfoxide. The relative order of acidity, $R_3SiCO_2H \approx R_3GeCO_2H > R_3CCO_2H$, is explained in terms of π ($\pi \rightarrow$ d) bonding between the π orbitals of the CO_2^- group and the vacant nd orbitals of the metalloid with steric hindrance to anion solvation playing a smaller role. The transmission of substituent effects through the phenyl group and germanium also are discussed.

In a previous paper,[3] we reported the ionization constants of a number of acids of the type, R_3MCO_2H, where R = Me and/or Ph and M = C, Si, and Ge, in ethanol–water media. Since the triorganosilanecarboxylic acids are susceptible to base-catalyzed decarbonylation,[4] a new potentiometric method was developed for the determination of the ionization constants in acidic media.[5] In all cases studied, the silane- and germanecarboxylic acids were found to be more acidic than their carbon analogs. It was suggested that the observed order of acidity is the result of stabilization of the silane- and germanecarboxylate ions relative to their carbon analog by π ($\pi \rightarrow$ d) bonding between the CO_2^- group and the metalloid which overcomes the inductive effect ($+I$) of the metalloid. Also it was suggested that π ($\pi \rightarrow$ d) bonding becomes an important factor in anion stability since there is a full negative charge on which to operate; *i.e.*, in the anion form there is a demand for charge delocalization by π ($\pi \rightarrow$ d) bonding.

In this study we have determined the ionization con-

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