# STUDIES IN IVth GROUP ORGANOMETALLIC CHEMISTRY

## XV*. BASE-CATALYZED HYDROLYSIS OF A SERIES OF IVth GROUP ORGANOMETALLIC ESTERS

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### INTRODUCTION

For some years disagreement has existed about the electronegativities of the IVB group elements[1-3]. One of the main controversial points is whether the electronegativities of the elements carbon, silicon, germanium, tin and lead decrease in a regular order, or whether the electronegativity values alternate, as proposed by Sanderson and by Allred and Rochow[3].

It was our aim to provide a contribution to this problem by determining the relative rates of hydrolysis for a series of analogous esters containing either silicon, germanium or tin. Some similar investigations have been reported in which aromatic nuclei or hetero-atoms with lone electron pairs are bonded to the metal atoms in question. Conclusions concerning the electronegativity of the metals in such cases always contain an element of uncertainty due to the influence of dative $\pi$-bonding (see e.g. ref. 4). We assumed, that complications of this nature might be avoided by studying compounds, in which the metal atom is bound to four saturated carbon atoms, since dative $\pi$-bonding or co-ordination in such compounds seems unlikely.

We set out to determine the rates of hydrolysis of a series of esters of the type $R_3M(CH_2)_nCOOEt$ (R = alkyl, M = Si, Ge or Sn, $n$ = 1, 2 or 3) in the expectation that these would reflect the inductive effects of the organometallic substituents $R_3M$. In each of the compounds studied, however, complications arose, the origins of which are quite clear for the lowest and the highest homologues. The compounds with $n = 2$ were hydrolyzed much faster than expected, and this is tentatively explained by postulating interaction in the transition state between the carbonyl oxygen and the metal atom.

### RESULTS

The rates of alkaline hydrolysis of the esters $Et_3M(CH_2)_nCOOEt$ (M = Si, Ge or Sn, $n$ = 1, 2 or 3) were determined by a procedure essentially identical to that described by Evans *et al.*[5] for aliphatic esters. Ethyl acetate, propionate and butyrate were

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included in the experiments for comparison. The results (averages of at least two independent experiments) are given in Table 1.

TABLE 1

RATE CONSTANTS OF THE ALKALINE HYDROLYSIS OF SOME ESTERS
($l \cdot mole^{-1} \cdot sec^{-1}$) 84.8 wt.% ethanol–water, 25° C

| *Compound* | $k \cdot 10^3$ | *Compound* | $k \cdot 10^3$ |
|---|---|---|---|
| $CH_3COOEt$ | 7.40 | $Me_3GeCH_2CH_2COOEt$ | 2.75 |
| $CH_3CH_2COOEt$ | 3.63 | $Et_3SiCH_2CH_2COOEt$ | 2.43 |
| $CH_3CH_2CH_2COOEt$ | 1.87 | $Et_3GeCH_2CH_2COOEt$ | 2.36 |
| | | $Et_3SnCH_2CH_2COOEt$ | 2.01 |
| $Et_3SiCH_2COOEt$ | – [a] | | |
| $Et_3GeCH_2COOEt$ | – [a] | $Et_3SiCH_2CH_2CH_2COOEt$ | 1.51 |
| $Et_3SnCH_2COOEt$ | – [a] | $Et_3GeCH_2CH_2CH_2COOEt$ | 1.56 |
| | | $Et_3SnCH_2CH_2CH_2COOEt$ | ~1.6[b] |

[a] Preferential hydrolysis of the metal–carbon bond occurred, resulting in the formation of $Et_3MOH$ and ethyl acetate.

[b] Owing to the small quantity available only one experiment could be made during which the rate of hydrolysis appeared to decrease slightly.

## DISCUSSION

The rates of hydrolysis found for ethyl propionate and butyrate are in good agreement with reported data[6,7]. For ethyl acetate slightly inconsistent values, obtained under comparable conditions, have been reported[6,7]. Smith and Levenson[7] supposed that the low value of Evans, Gordon and Watson[6] was due to loss of ethyl acetate by evaporation. Our results with this esters are in agreement with the findings of the former authors.

Organometallic compounds of the first series, $Et_3MCH_2COOEt$, in which the carbethoxy group is separated from the metal atom by one methylene group, would be most ideally suited for the study of the effect of the triethylmetal group on the rate of saponification. However, the compounds of this type suffer metal–carbon bond cleavage under the alkaline conditions used in the rate determinations. Gold *et al.*[8], after shaking the ester $Me_3SiCH_2COOEt$ for 15 min with 5% aqueous sodium hydroxide at room temperature, observed 80% decomposition into $(Me_3Si)_2O$ and ethyl acetate. Cleavage of the carbon–tin bond in organotin esters having the ester group on the α-carbon atom has been reported and discussed by Van der Kerk and Noltes[9]. These authors observed complete conversion of the ester $Pr_3SnCH_2COOEt$ into tripropyltin hydroxide after three days at room temperature in a 0.1 *N* solution of sodium hydroxide in 75% ethanol. Lutsenko and Ponomarev[10] reported the immediate and analogous decomposition of the compound $Et_3SnCH_2COOMe$ upon contact with water.

We observed a similar instability with $Et_3SnCH_2COOEt$. Decomposition occurs even on contact with moist air. The silicon and germanium derivatives appear to be considerably more stable, but slow cleavage does occur under the conditions of the hydrolysis rate determination. In both cases the observed reaction rate increased

during the run, indicating the formation of a second compound which consumes alkali faster than the original ester. These findings can be explained by the reaction:

$$Et_3MCH_2COOEt \xrightarrow[(OH^-)]{H_2O} Et_3MOH + CH_3COOEt \quad (M=Si, Ge)$$

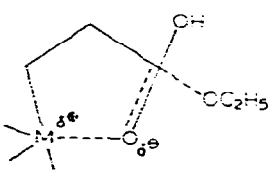
Evidence for this reaction was obtained by demonstrating the presence of ethyl acetate in distillates from the reaction mixtures by gas-chromatographic analysis.

With the next higher homologues, $R_3MCH_2CH_2COOEt$, no such complication was encountered, and the rate constants remained steady during a run.

Replacement of a trimethylgermyl group by the more electron-releasing triethylgermyl group, led to a lower rate of hydrolysis. This result accords with expectation, since base-catalyzed hydrolysis is retarded by electron-releasing substituents[11]. In the sequence M = Si, Ge, Sn (R = Et) the rate of hydrolysis has a tendency to decrease gradually, though the difference between the triethylsilyl and the triethylgermyl derivative is small, and only slightly larger than the experimental error, which is 2 ½% at most. The obvious interpretation is that the $Et_3Si$, $Et_3Ge$ and $Et_3Sn$ groups exert an increasing $+I$-effect in this order. Such a result would be consistent with a decreasing electronegativity in the order Si, Ge, Sn (but see below).

The rates of hydrolysis in the series $Et_3MCH_2CH_2CH_2COOEt$ (M = Si, Ge, Sn) do not differ significantly. Apparently, in these compounds the triethylmetal group is so remote from the ester group that the different inductive properties of the metals no longer influence the rate of hydrolysis. Thus the results within each group of compounds have a simple explanation. Comparison of the data between the types, however, shows a more complicated situation.

The decrease in rate constants in the sequence $CH_3CH_2COOEt$, $CH_3CH_2CH_2COOEt$, and $Et_3MCH_2CH_2CH_2COOEt$ ($k \cdot 10^3$ = 3.63, 1.87 and 1.5, respectively) is in accord with expectation. The esters $Et_3MCH_2CH_2COOEt$, however, are hydrolyzed faster ($k \cdot 10^3$ = 2.43–2.01) than both ethyl butyrate and the compounds $Et_3MCH_2CH_2CH_2COOEt$. This result is at variance with the fact that the $Et_3M$ group is more electron-releasing than a methyl group, and with the expectation that the inductive influence of the $Et_3M$ group upon the rate of hydrolysis should be more apparent in a position closer to the carbethoxy group. Thus, from either point of view, the hydrolysis of the $R_3M$-substituted propionic esters appears to be faster than can be explained by inductive effects alone. It is not clear how a steric effect could account for the results. As a tentative explanation, stabilization of the transition state by coordination of the carbonyl oxygen with the metal atom is proposed:




Such assistance seems to be effectively absent in the next higher homologues, $Et_3MCH_2CH_2CH_2COOEt$, in which a six-membered ring would be involved; such ring systems are frequently formed less easily than five membered rings.

This hypothesis cannot be supported by other facts, since as yet, no complexes

of the compounds $R_3M$ (M = Si, Ge or Sn) have been described. It must be borne in mind, however, that only a very small interaction is sufficient to account for the observed results.

It must be pointed out that the influence on the rate of hydrolysis of such a stabilization of the transition state and that of the inductive effect of the $R_3M$ group cannot be evaluated separately. The contribution of each will vary to an unknown extent in passing from Si to Ge to Sn. Therefore a conclusion concerning the relative inductive effect of the $R_3M$ group and the relative electronegativity of the element M cannot be drawn with certainty from our data.

## EXPERIMENTAL

### *Determination of the rates of hydrolysis*

The method described by Evans *et al.*[5] was followed except for the following details. Potassium hydroxide was used instead of sodium hydroxide.

No attempt was made to use precisely equivalent amounts of ester and potassium hydroxide. The velocity coefficients, *k*, were calculated from the usual equations[12]. Furthermore some alcohol was added before titration in order to keep the solution clear.

The esters were freshly distilled before use.

### *Chromatographic analysis**

The gas-chromatographic analyses were carried out with an F & M Model 500 apparatus, fitted with a stainless steel column (1.8 m, outer diameter ¼ inch) packed with 20 % cross-linked polyester diethyleneglycol adipate (LAC 446) on Diatoport (60–80 Mesh). The helium flow rate was 60 ml/min, block temp. 265°, injection port temp. 265°, and column temp. 150°. Under these conditions decomposition did not occur as was shown by reinjection of an isolated pure fraction.

### *Preparation of the esters $Et_3MCH_2COOEt$ (M = Si, Ge, Sn)*

(1). *Ethyl (triethylsilyl)acetate.* Diazoacetic ethyl ester (4 g, 0.035 mole) was added slowly to 4.1 g (0.035 mole) of triethylsilane with copper powder (0.5 g) as a catalyst. Gas was evolved in an exothermic reaction. Fractionation yielded a fraction boiling 80–100°/14 mm, containing unsaturated impurities, not separable by distillation. These were eliminated by treatment with aqueous potassium permanganate solution and extraction with petroleum ether. Fractionation of the extract after drying over anhydrous magnesium sulphate yielded 2.8 g of a colourless liquid, boiling at 91–93°/16 mm, $n_D^{20}$ 1.4391, yield 40 %. (Found: C, 59.37, 59.52; H, 10.78, 10.96. $C_{11}H_{22}O_2Si$ calcd.: C, 59.34; H, 10.96 %.)

(2). *Ethyl (triethylgermyl)acetate.* Diazoacetic ethyl ester (17 g, 0.149 mole) and 16 g (0.1 mole) of triethylgermane reacted exothermally in the presence of 1 g of copper powder. Upon distillation a fraction contaminated with unsaturated impurities was obtained. These were eliminated by percolation over aluminium oxide (Wöhler,

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activity grade I) and elution with benzene*. The compound was distilled yielding a chromatographically pure fraction of 13.0 g, b.p. 99–99.5°/12 mm (lit.[13]: 125–126°/31 mm), $n_D^{20}$ 1.4536, yield 53 %. (Found: C, 48.25, 48.20; H, 8.80, 8.80. $C_{10}H_{22}O_2Ge$ calcd.: C, 48.65; H, 8.98 %.) Equivalent weight determined by saponification: 252 (calcd. 246.87).

(3). *Ethyl (triethylstannyl)acetate.* Triethyltin ethoxide (23.4 g, 0.093 mole) in 50 ml of ether was brought into reaction with ketene according to Lutsenko *et al.*[10]. Fractionation yielded 8.3 g (30 %) of product boiling at 88–90°/1 mm, $n_D^{20}$ 1.4796 (lit. 78–79°/2 mm, $n_D^{20}$ 1.4794), Sn content 40.72 % (calcd. 40.61 %).

*Preparation of the esters $R_3M(CH_2)_nCOOEt$ ($R$ = Et, $n$ = 2, 3, $M$ = Si, Ge, Sn and $R$ = Me, $n$ = 2, $M$ = Ge)*

The esters were prepared by addition of the appropriate silanes, germanes or stannanes to ethyl acrylate or ethyl vinylacetate, respectively. Addition of the $R_3M$-group in principle may occur at the terminal or at the adjacent unsaturated carbon atom. Usually, terminal addition takes place[1,13,15]. If, however, the unsaturated compound contains an electronegative substituent, conjugated to the unsaturated bond, as in ethyl acrylate, $CH_2{=}CH{-}COOC_2H_5$, complications occur in addition of silanes[16]. In this case addition of the organometallic group may take place at the non-terminal carbon atom as well. Moreover, products containing a third structure have been reported[17] when acrylic esters are involved:

$$R_3MH + H_2C{=}CH{-}COOR' \longrightarrow \begin{cases} R_3MCH_2CH_2COOR' & (I) \\ R_3MCHCOOR' \quad (CH_3 \text{ on CH}) & (II) \\ CH_3CH{=}C(OMR_3){-}OR' & (III) \end{cases}$$

Spectral and chemical evidence was obtained, indicating that the products isolated in our investigations are of type (I).

Proton magnetic resonance spectra were determined** for the compounds $Me_3GeCH_2CH_2COOEt$ and $Et_3MCH_2CH_2COOEt$ (M = Si or Ge), *cf.* (4), (5) and (6) below. The spectra prove that the compounds in question have the structure $R_3MCH_2CH_2COOR'$.

The IR spectra of $Et_3MCH_2CH_2COOEt$ (M = Si, Ge and Sn) are very similar, indicating similar structures. The same applies to the spectra of the compounds $Et_3M(CH_2)_3COOEt$ (M = Si, Ge and Sn).

The former spectra rule out a structure of type (III), since a C=C absorption ($\sim$ 1600 $cm^{-1}$) and a strong absorption in the 1000–1100 $cm^{-1}$ region, which would be

* Probably treatment with potassium permanganate [this section, preparation (1)] is preferable.

** For the determination of the magnetic resonance spectra our thanks are due to Dr. M. VAN AMMERS, Agricultural University at Wageningen and to Dr. H. J. T. Bos of the University of Utrecht.

expected for the SiOC group, are absent. Furthermore a strong C=O absorption is present at 1740 $cm^{-1}$, as in all the other spectra.

Chemical evidence for these structures can be derived from the behaviour of the compounds towards alkali and bromine.

In IVth group organometallic chemistry, it is well known that an ester group on a carbon atom in an $\alpha$-position relative to the metal atom facilitates heterolytic cleavage of the bond between the metal and that carbon atom[9,18]. This bond is not weakened by an ester group in $\beta$-position or further removed from the metal atom. Therefore the behaviour of the esters in question both under hydrolytic conditions and towards bromine provides an indication as to their structure.

In determinations of the rates of hydrolysis, metal–carbon bond cleavage was not observed among the adducts of ethyl acrylate or ethyl vinylacetate, in contrast to the experiments with the compounds $Et_3MCH_2COOEt$. Furthermore, the adducts of triethylsilane and triethylgermane have been purified by hydrolysis and re-esterification. During this treatment no metal–carbon bond cleavage was observed.

The reactivity towards bromine has been investigated for silicon and germanium derivatives (*cf.* experimental part below). Here again, metal–carbon bond cleavage was observed only in the esters of (triethylsilyl)- and (triethylgermyl)acetic acid.

From the above-mentioned experiments and considerations it is concluded, that the esters obtained in our addition reactions with ethyl acrylate are indeed of the structural type (I):

$$Et_3MCH_2CH_2COOEt \quad (M=Si, Ge, Sn)$$

(*4*). *Ethyl 3-(triethylsilyl)propionate.* Triethylsilane (34.9 g, 0.3 mole) and approximately one half of 33 g (0.33 mole) of freshly distilled ethyl acrylate were refluxed in the presence of three drops of a 0.05 molar solution of chloroplatinic acid in isopropanol. After 1 hour the ethyl acrylate had vanished (IR spectral analysis showed the absence of an ethylenic bond). The remainder of the ethyl acrylate was added and refluxing continued for 2 hours. At that time IR spectral analysis demonstrated the absence of silane and acrylate. Fractionation with an efficient Vigreux column yielded the following fractions:

fr 1: 8.5 g, b.p. 85–103°/20 mm, $n_D^{20}$ 1.4375
fr 2: 6.2 g, b.p. 103–108°/20 mm, $n_D^{20}$ 1.4408
fr 3: 9.6 g, b.p. 108–109.5°/20 mm, $n_D^{20}$ 1.4419
fr 4: 16.3 g, b.p. 109.5°/20 mm, $n_D^{20}$ 1.4429

Gas-chromatographic analysis showed that fraction 1 consisted primarily of hexaethyldisiloxane and that fractions 2, 3, 4 each consisted mainly of one compound. None of these, however, was pure. The combined fractions 2, 3 and 4 were added to 300 ml of a 0.5 molar solution of sodium hydroxide in 75 % alcohol and kept at room temperature for two days. The alcohol was evaporated and the residue was dissolved in water. The solution was extracted three times with 50 ml of ether. Upon acidification of the aqueous layer with hydrochloric acid, two layers separated. The organic material was extracted with ether. After drying and evaporation of the ether 17.6 g of a colourless oil was obtained (67 % of the theoretical amount). A solution of 8.5 g of this oil and 0.35 ml of concentrated sulphuric acid in 14 g of 100 % ethanol

was kept at room temperature in the dark for two days. After neutralization with 5 g of sodium bicarbonate and filtration, fractionation yielded 5.2 g, boiling at 110–111°/20 mm, $n_D^{20}$ 1.4422. This fraction was gas-chromatographically pure. (Found: C, 60.87, 60.83; H, 11.57, 11.58; saponification 268 mg KOH/g. $C_{11}H_{24}O_2Si$ calcd.: C, 61.04; H, 11.18 %; saponification, 259 mg KOH/g.)

PROTON MAGNETIC RESONANCE SPECTRUM OF $(C_2H_5)_3SiCH_2CH_2COOCH_2CH_3$

| *Group* | *Chemical shift (ppm downfield from TMS)* | *Multiplicity* |
|---|---|---|
| $(C_2\underline{H}_5)_3SiC\underline{H}_2-$ | 0.2–1.2 | multiplet |
| $-CH_2C\underline{H}_3$ | 1.19 | triplet |
| $-C\underline{H}_2CH_3$ | 4.07 | quadruplet |
| $-C\underline{H}_2COO-$ | ~2.24 | distorted triplet* |

* Analysis gives $\nu_0\delta$ 84.1 $sec^{-1}$ at 60 Mc, $J_{AB}$ and $J'_{AB}$ 11.5 and 6.0 $sec^{-1}$ and $J_{AA}$-$J_{BB}$ = $\pm$ 1.0 $sec^{-1}$.

(5). *Ethyl 3-(trimethylgermyl)propionate.* Trimethylgermane (13.7 g, 0.116 mole), 3 drops of a chloroplatinic acid solution (*cf.* 4) and 15 g (0.15 mole) of ethyl acrylate were refluxed together. (The flask was equipped with a reflux condenser cooled with acetone and dry ice.) After two hours IR spectral analysis showed that neither germane (Ge–H stretching vibration at 2000 $cm^{-1}$) nor ethyl acrylate was left. Careful fractionation yielded 11.1 g of a colourless liquid (b.p. 74°/19 mm, $n_D^{20}$ 1.4365), which was not gas-chromatographically pure. When 8.9 g of this fraction was saponified and re-esterified as described in (4), 3.6 g of a colourless liquid was obtained, b.p. 74–75°/18 mm, $n_D^{20}$ 1.4355. This fraction was gas-chromatographically pure. (Found: C, 43.88, 44.02; H, 8.18, 8.33; saponification, 271.6 mg KOH/g. $C_8H_{18}GeO_2$ calcd.: C, 43.91; H, 8.29 %; saponification, 256.4 mg KOH/g.)

PROTON MAGNETIC RESONANCE SPECTRUM OF $(CH_3)_3GeCH_2CH_2COOCH_2CH_3$

| *Group* | *Chemical shift (ppm downfield from TMS)* | *Multiplicity* |
|---|---|---|
| $(C\underline{H}_3)_3Ge-$ | 0.12 | singlet |
| $-CH_2C\underline{H}_3$ | 1.20 | triplet |
| $-C\underline{H}_2CH_3$ | 4.08 | quadruplet |
| $-C\underline{H}_2COO-$ | 2.33 | distorted triplet* |
| $(CH_3)_3GeC\underline{H}_2-$ | 0.98 | distorted triplet* |

* These distorted triplets form an $A_2B_2$ spectrum. Analysis according to POPLE, SCHNEIDER AND BERNSTEIN, *High-Resolution Nuclear Magnetic Resonance*, gives $\nu_0\delta$ 79.6 $sec^{-1}$ at 60 Mc, $J_{AB}$ and $J'_{AB}$ 9.5 and 6.8 $sec^{-1}$ and $J_{AA}$-$J_{BB}$ = $\pm$ 2.4 $sec^{-1}$.

(6). *Ethyl 3-(triethylgermyl)propionate.* A mixture of 23 g (0.143 mole) of triethylgermane, 3 drops of chloroplatinic acid solution (*cf.* 4) and 16.8 g (0.168 mole) of freshly distilled ethyl acrylate was heated at 90° for ½ h and then at 125° for 1½ h*. The reaction mixture was saponified and re-esterified as described in (4). Repeated fractionation yielded 11.5 g of a colourless liquid, b.p. 118–118.5°/19 mm, $n_D^{20}$ 1.4538,

* In a parallel experiment, heat was generated when a temperature of 110° was reached.

$d_{20}^{4}$ 1.072, which was gas-chromatographically pure. (Found: C, 50.54, 50.60; H, 9.22, 9.36; saponification, 214.7 mg KOH/g. $C_{11}H_{24}GeO_2$ calcd.: C, 50.64; H, 9.27 %; saponification, 214.9 mg KOH/g.)

PROTON MAGNETIC RESONANCE SPECTRUM OF $(C_2H_5)_3GeCH_2CH_2COOCH_2CH_3$

| *Group* | *Chemical shift (ppm downfield from TMS)* | *Multiplicity* |
|---|---|---|
| $(C_2\underline{H}_5)_3GeC\underline{H}_2-$ | 0.4–1.4 | multiplet |
| $-CH_2C\underline{H}_3$ | 1.19 | triplet |
| $-C\underline{H}_2CH_3$ | 4.05 | quadruplet |
| $-C\underline{H}_2COO-$ | ~2.31 | distorted triplet* |

* Similar to the analogous band in $(CH_3)_3GeCH_2CH_2COOCH_2CH_3$.

(7). *Ethyl 3-(triethylstannyl)propionate.* Under an atmosphere of nitrogen 20.6 g (0.10 mole) of triethylstannane, 11 g (0.11 mole) of ethyl acrylate and 100 mg of hydroquinone were heated on a steam bath for 4 h. By that time only a trace of triethylstannane was left in the reaction mixture according to the IR spectrum (Sn–H absorption at 1820 $cm^{-1}$). Repeated fractionation yielded 17 g of a colourless liquid, b.p. 58–59.5°/0.17 mm, $n_D^{20}$ 1.4762, $d_{20}^{4}$ 1.231, yield 55 %. (Found: C, 42.99; H, 8.05; Sn, 38.80. $C_{11}H_{24}O_2Sn$ calcd.: C, 43.03; H, 7.88; Sn, 38.66 %.) Equivalent weight determined by saponification: 306 (calcd. 307.00).

(8). *Ethyl 4-(triethylsilyl)butyrate.* Triethylsilane (20 g, 0.17 mole) and 24.1 g (0.195 mole) of vinylacetic ethyl ester were heated for 10 hours at 100° in the presence of 0.1 g of hydroquinone and chloroplatinic acid [*cf.* this section, preparation (4)]. The IR spectrum showed the presence of a trace of triethylsilane and some vinylacetic ester. Repeated fractionation yielded a fraction of 12.3 g, boiling at 125°/11 mm, $n_D^{20}$ 1.4433, yield 54 %. (Found: C, 63.19; H, 11.55. $C_{12}H_{26}O_2Si$ calcd.: C, 62.55; H, 11.37 %.) Equivalent weight determined by saponification: 228 (calcd. 230.43).

(9). *Ethyl 4-(triethylgermyl)butyrate.* Approximately one quarter of a mixture consisting of 14.6 g (0.091 mole) of triethylgermane and 11.4 g (0.092 mole) of vinylacetic ethyl ester was heated in the presence of 0.1 g of hydroquinone and of chloroplatinic acid [*cf.* this section, preparation (4)]. At 70° an exothermal reaction occurred. The remainder of the mixture was added slowly at 80° and the reaction mixture kept for 2 hours at that temperature. The IR spectrum showed that triethylgermane was absent. Some vinylacetic ester was still present. Fractionation yielded 23.3 g of a colourless liquid, b.p. 128–131°/13 mm, $n_D^{20}$ 1.4546, $d_{20}^{4}$ 1.054, yield 93 %. (Found: C, 52.75, 52.29; H, 9.57, 9.44. $C_{12}H_{26}GeO_2$ calcd.: C, 52.43; H, 9.53 %.) Equivalent weight determined by saponification: 281 (calcd. 274.93).

(10). *Ethyl 4-(triethylstannyl)butyrate.* Triethylstannane (10.35 g, 0.05 mole), 11.4 g (0.1 mole) of ethyl vinylacetate and 1 g of azobisisobutyronitrile (0.005 mole) were heated at 50–55° (*cf.* ref. 14). Triethylstannane was still present, after 10 h but not after 14 h. The excess of ethyl vinylacetate was evaporated, leaving some crystals (probably triethyltin cyanide) and a colourless liquid. The residue was filtered, washed with 8 ml of 2 *N* hydrochloric acid, dried and distilled using an efficient Vigreux column. The main fraction, b.p. 138–140°/14 mm, $n_D^{20}$ 1.4761, yield 64 %.

still contained approximately 5% impurity (gas-chromatographic analysis); Sn content 37.27%, calcd. 36.97%.

In a parallel experiment the reaction mixture, after removal of the excess of ethyl vinylacetate, was saponified with a 0.25 *N* solution of sodium hydroxide in 75% alcohol, extracted, and re-esterified as described in section (*4*). Repeated fractionation of the neutralized solution yielded a less pure fraction than the above mentioned product (b.p. 141–142°/13 mm, $n_D^{20}$ 1.4739, Sn content 36.21, 36.08%; yield 23%).

From this fraction 1.25 g of pure product was obtained by preparative gas-chromatography*; $n_D^{20}$ 1.4742. (Found: C, 45.00, 45.04; H, 8.10, 8.23; Sn, 36.91. $C_{12}H_{26}O_2Sn$ calcd.: C, 44.90; H, 8.16; Sn, 36.97%.)

*Reactivity towards bromine*

Equimolar amounts of bromine (1.87 *N* solution in chloroform) were added to the esters under investigation; the reaction conditions are indicated below. The reaction products were examined gas-chromatographically. The following results were obtained:

*$Et_3GeCH_2COOEt$.* After addition of $^1/_3$ of the amount of bromine an exothermic reaction occurred after which the mixture was completely colourless. The remainder of the bromine was added. Bromine uptake proceeded slower and after ½ h at 30° a slightly yellow solution was obtained. Reaction had occurred completely according to the equation:

$$Et_3GeCH_2COOEt + Br_2 \xrightarrow{\text{chloroform}} Et_3GeBr + BrCH_2COOEt$$

*$Et_3GeCH_2CH_2COOEt$ and $Et_3Ge(CH_2)_3COOEt$.* Neither of the compounds had reacted after ½ h and 20 min reflux, respectively.

*$Et_3SiCH_2COOEt$.* Upon addition of bromine in chloroform there was no spontaneous reaction such as that which occurred with the analogous germanium derivative. After ¼ h of reflux approximately half the amount of ester and after 1 h of reflux approximately 80% of the ester had been converted according to the equation:

$$Et_3SiCH_2COOEt + Br_2 \xrightarrow{\text{chloroform}} Et_3SiBr + BrCH_2COOEt$$

The carbon–metal bond of the functional substituent is less reactive than that of the germanium analogue.

*$Et_3SiCH_2CH_2COOEt$ and $Et_3SiCH_2CH_2CH_2COOEt$.* Neither of the two compounds had reacted after 10 and 20 min reflux, respectively.

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* A stainless steel column was employed of 1.8 m length, 0.25 inch outer diameter, packed with 20% cross-linked silicon rubber gum SE 30 on Diatoport 60–80 mesh, nitrogen flow 250 ml/min, column temperature 200°. Other conditions were similar to those used in chromatographic analysis.

experimental assistance in the preparation of the compounds and in the performance of the hydrolysis measurements.

## SUMMARY

The esters $R_3M(CH_2)_nCOOEt$ (R = Et, M = Si, Ge or Sn, $n$ = 1, 2 or 3, and R = Me, M = Ge, $n$ = 2) were prepared. The rates of alkaline hydrolysis were determined, except for the compounds with $n$ = 1, for which metal–carbon bond cleavage occurs.

The rates of hydrolysis of the substituted propionates ($n$ = 2) were found to be relatively high. A possible explanation, involving interaction in the transition state between the carbonyl oxygen and the metal atom, is proposed.

In the hydrolysis of the substituted butyrates ($n$ = 3), differences between the effects of the metal atoms were not apparent.

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