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# Synthesis of $\alpha$ -germyl and $\alpha$ -silylcarboxylic acids and selected electrochemical oxidations

# Anna Rakovshik, Alex V. Shtelman, James Y. Becker\*

Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva 84105, Israel

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## ABSTRACT

New  $\alpha$ -germylcarboxylic acids,  $\alpha$ -silyl- $\alpha$ -halocarboxylic and  $\alpha$ -silyl- $\alpha$ -alkylcarboxylic acids including some known  $\alpha$ -silyl(cycloalkyl)carboxylic acids have been prepared by different synthetic methods. The anodic oxidation in basic methanol of selected examples of these acids has been investigated under various experimental conditions to afford mainly oxidative degermylation/desilylation and decarboxylation products. Based on the emerged products, various mechanisms are suggested and discussed.

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#### 1. Introduction

 $\alpha$ -Silylacetic acids ( $R_3$ SiCH<sub>2</sub>COOH) are widely used to synthesize  $\alpha$ , $\beta$ -unsaturated carboxylic acids and butyrolactons [1], as well as labeled diethyl malonate and  $\alpha$ -silylthioesters for biological purposes [2,3]. Recently we have shown that they could also be useful precursors for the synthesis of 1,2-disilylethanes in good yields by their electrochemical oxidation [4,5].

An efficient synthesis of  $\alpha$ -silylacetic acids with various substituents attached to the silicon atom (*R'R''R'''*SiCH<sub>2</sub>COOH), as well as of  $\alpha$ -silylcarboxylic acids with various alkyl groups at the  $\alpha$ -position [*R'R''R'''*SiCH(*R*)COOH] has been described previously [6,7].

The first and best known anodic electro-synthesis reaction is the Kolbe electrolysis [8] which leads to oxidative decarboxylation of carboxylate anions to generate radical intermediates that undergo C–C coupling to provide Kolbe 'dimers' (Scheme 1). However, under certain conditions, the radical intermediate could be further oxidized to the corresponding carbenium ion to afford the so-called "non-Kolbe" products, as illustrated in Scheme 1.

The selectivity of the Kolbe reaction depends on structural parameters of the carboxylic acid and electrochemical conditions [8,9]. For instance, the Kolbe 'dimers' are favored when a platinum anode is used and the radical intermediate is either primary or

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substituted by electron-withdrawing group(s) whereas the non-Kolbe products are favorable at C anodes, under basic solutions and at low current densities.

The present work extends the synthesis of this type of acids to  $\alpha$ -germylcarboxylic acids and to other unknown derivatives of  $\alpha$ -silylcarboxylic acids, and describes the outcome of the anodic oxidation of selected examples.

# 2. Materials and methods

### 2.1. General

All reagents and solvents were purchased from commercial suppliers and used without further purification. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance (DPX) 200 and Bruker (AMX) 500 Spectrophotometers (CDCl<sub>3</sub> as solvent). Chemical shifts for <sup>1</sup>H NMR spectra are reported as  $\delta$  in units of parts per million (ppm) relative to the signal of chloroform-d ( $\delta$ , 7.26, singlet). The number of protons (*n*) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. <sup>13</sup>C NMR spectra is reported as  $\delta$  in ppm relative to the signal of chloroform-d ( $\delta$ , 7.703, triplet). <sup>29</sup>Si NMR spectra are reported as  $\delta$  in ppm. Mass Spectra (MALDI-TOF) were obtained using Bruker Daltonics (Reflex IV). Mass spectral data were reported in units of mass to charge (*m/z*). IR spectra were recorded using Impact 410 spectrometer. Kolbe electrolyses were performed by using a Princeton Applied Research Potentiostat/Galvanostat Model 273A.



<sup>\*</sup> Corresponding author. Tel.: +972 8 6461197; fax: +972 8 6472943. *E-mail address*: becker@bgu.ac.il (J.Y. Becker).



#### 2.2. Synthetic procedures of $\alpha$ -germyl and $\alpha$ -silylcarboxylic acids

Me<sub>3</sub>GeCH<sub>2</sub>COOH [2-(trimethylgermyl)acetic acid, (I)] was prepared according to the procedure previously described for the synthesis of  $\alpha$ -silylcarboxylic acids [6,7]. In a typical example for the synthesis of 2–(trimethylgermyl)acetic acid (I), diisopropylamine (10.7 mmol, 1.63 ml) and anhydrous tetrahydrofuran (30 ml) were added to an oven dried round-bottomed flask (100 ml) equipped with a magnetic stirring bar. The mixture was cooled to -78 °C prior to a drop-wise addition of n-butyllithium 1.6 M (13 mmol, 8.1 ml). The mixture was allowed to warm at room temperature for 15 min and then cooled to 0 °C trimethylsilyl acetate (11.9 mmol, 1.45 ml) in 5 ml of dry THF was added dropwise over 10 min to LDA solution and the mixture was stirred for 1.5 h at the same temperature to complete the formation of the desired dianion. Then trimethylgermyl chloride (11.9 mmol, 1.45 ml) was added drop-wise to the dianion solution and the mixture was stirred overnight at room temperature. The reaction mixture was diluted by 20 ml of hexane and the organic phase washed twice with a solution of saturated sodium chloride  $(2 \times 30 \text{ ml})$  The aqueous phase was carefully acidified with 1 N HCl to pH = 2 and then extracted with diethyl ether (3  $\times$  20 ml). The combined organic extracts were washed with water, dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated in vacuo. The residual product was crystallized from hexane to give 1.80 gr (80%) of pure 2–(trimethylgermyl)acetic acid (I). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 0.32 (s, 9H, Ge(CH<sub>3</sub>)<sub>3</sub>), 0.57 (s, 1H, Ge(CH<sub>3</sub>)<sub>3</sub>CHCOOH) 1.96 (s, 2H, Ge(CH<sub>3</sub>)<sub>3</sub>CH<sub>2</sub>COOH). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) -0.34 (Ge(CH<sub>3</sub>)<sub>3</sub>), 22.35 ((CH<sub>3</sub>)<sub>3</sub>GeCH<sub>2</sub>), 174.41 ((CH<sub>3</sub>)<sub>3</sub>GeCH<sub>2</sub>COOH). IR (NaCl): v (C= O) 1720 cm<sup>-1</sup>, 2710–3170 cm<sup>-1</sup> (COOH). (ESI negative mode): m/zcalc. for C<sub>5</sub>H<sub>12</sub>O<sub>2</sub>GeH: 179.0122; found 178.9846 [M + H].

Me<sub>3</sub>GeCH(benzyl)COOH. [2–(*trimethylgermyl*)-3-*phenylpropanoic acid*, (**II**)]: trimethylgermylacetic acid (**I**) (2.21 mmol, 390 mg) was reacted with LDA (4.4 mmol, 3.58 ml) and benzylbromide (2.31 mmol, 0.27 ml). After a standard work up procedure the crude product was separated by silica gel column from hexane–ethyl acetate (95:5) to give 1.52 g (80%) of viscous oil of **II**. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  0.31 (s, 9H, Ge(CH<sub>3</sub>)<sub>3</sub>), 2.49–2.52 (dxd, 1H, CH(CH<sub>2</sub>Ph)COOH), 2.73–2.76 (dxd, 1H, CH(CH<sub>2</sub>Ph)COOH), 3.13–3.19 (txd, 1H, CH(CH<sub>2</sub>Ph)COOH), 7.18–7.29 (m, 5H, CH(CH<sub>2</sub>Ph)COOH), 11.13 (br, 1H, CO<sub>2</sub>H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) –2.85 (Ge(CH<sub>3</sub>)<sub>3</sub>), 32.47( CH(CH<sub>2</sub>Ph)COOH), 38.73 (CH(CH<sub>2</sub>Ph)COOH), 126.06, 128.19, 128.37, 141.57 (CH(CH<sub>2</sub>Ph)COOH), 181.58 (CH(CH<sub>2</sub>Ph)COOH). IR (NaCl): v (C=O) 1720 cm<sup>-1</sup>, 2700–3200 cm<sup>-1</sup> cm<sup>-1</sup> (COOH). (ESI negative mode): *m*/*z* calc. for C<sub>12</sub>H<sub>18</sub>O<sub>2</sub>GeNa: 291.0420; found 291.0408 [M + Na].

Me<sub>3</sub>GeCH(allyl)COOH [2–(*trimethylgermyl*)-4-*pentenoic acid*, (**III**)]: trimethylgermylacetic acid (**I**) (2.77 mmol, 490 mg) was reacted with LDA (6.09 mmol, 4.65 ml) and allylbromide (3.05 mmol, 0.28 ml). After standard work up procedure the crude product was was separated by silica gel column from hexane–ethyl acetate (95:5) to give 1.12 g (84%) of pure acid (**III**). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  0.27 (s, 9H, Ge(CH<sub>3</sub>)<sub>3</sub>), 2.61–2.44 (m, 1H, CH(allyl)COOH) 1.96–2.26 (m, 2H, CHCH<sub>2</sub>CH=CH<sub>2</sub>), 4.95–5.11 (t, 2H, CH<sub>2</sub>CH=CH<sub>2</sub>), 5.74–5.94 (m, 1H, CHCH=CH2), 11.11 (br, 1H, CO<sub>2</sub>H).  $\alpha$ -Germyl,  $\alpha$ -silylcarboxylic acid **IV** was prepared by quenching the dianion of Ph<sub>2</sub>(Me)SiCH<sub>2</sub>COOH with Me<sub>3</sub>GeCl, similar to the alkylation of **I** to generate **II**, according to a known procedure [7].

1-(*Trimethylsilyl*)*cyclopropylcarboxylic* acid (**V**) has been prepared according to a known procedure [10] for other similar derivatives: cyclopropane carboxylic acid (13 mmol, 1.0 ml) was reacted with LDA (29 mmol) and then with trimethyl chloro silane (33 mmol, 4.12 ml). After standard work up procedure the crude product was crystallized from hexane to give 1.18 g (60%) of acid (**V**). The siloxane **4c** was formed as a by-product. Spectral data of acid **V** was reported elsewhere [11].

Acids **VI**–**IX** were synthesized according to a known procedure [10]. In all cases, the siloxane **4c** was formed as a by-product. The following quantities have been used:

2-(*Methyldiphenylsilyl*)*cyclopropane carboxylic acid* (**VI**): cyclopropane carboxylic acid (12.7 mmol, 1.0 ml) was reacted with LDA (29 mmol) and then with methyl diphenyl chloro silane (32 mmol, 4.07 ml). After standard work up procedure the crude product was crystallized from hexane to give 1.18 g (66%) of acid (**VI**).

2-(*Methyldiphenylsilyl*)*cyclobutane carboxylic acid* (**VII**): cyclobutane carboxylic acid (10 mmol, 1.0 g) was reacted with LDA (23 mmol) and then with methyl diphenyl chloro silane (23 mmol, 4.85 ml). After standard work up procedure the crude product was crystallized from hexane to give 2.24 g (52%) of acid (**VII**).

2-(*Methyldiphenylsilyl*)*cyclopentane carboxylic acid* (**VIII**): cyclopentane carboxylic acid (8.76 mmol, 1.0 g) was reacted with LDA (20 mmol) and then with methyl diphenyl chloro silane (20 mmol, 4.25 ml). After standard work up procedure the crude product was crystallized from hexane to give 4.86 g (48%) of acid (**VIII**).

2-(*Methyldiphenylsilyl*)*cyclohexane carboxylic acid* (**IX**): cyclohexane carboxylic acid (8.23 mmol, 1.06 g) was reacted with LDA (18.9 mmol) and then with methyl diphenyl chloro silane (18.9 mmol, 4.0 ml). After standard work up procedure the crude product was crystallized from hexane to give 4.62 g (34%) of acid (**IX**).

1-(*Triisopropylsilyl*-)*cyclohexanecarboxylic acid* (**X**) is a new derivative and was prepared according to reference [10]: 1-(*triisopropylsilyl*)*cyclohexanecarboxylic acid*: cyclohexane carboxylic acid (8.50 mmol, 1.09 g) was reacted with LDA (19.6 mmol) and then with triisopropylchloro silane (19.6 mmol, 4.18 ml). After standard work up procedure the crude product was crystallized from hexane to give 1.56 g (41%) of acid (**10**). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 1.03 (s, 18H, (CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 1.21–1.29 (m, 3H, (CH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>), 1.36–2.27 (m, 5H, cyclohexane), 4.73 (br, 1H, COOH). <sup>13</sup>C (125 MHz, CDCl<sub>3</sub>) 12.26(CH(CH<sub>3</sub>)<sub>2</sub>), 17.63 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.41, 25.74, 28.90, 29.25 (C<sub>6</sub>H<sub>10</sub>), 181.11 (COOH). <sup>29</sup>Si NMR (100 MHz, CDCl<sub>3</sub>) 14.51. IR (NaCl): v (C=O) 1750 cm<sup>-1</sup>, v (OH) 3300 cm<sup>-1</sup> (ESI negative mode): *m/z* calc. for C<sub>16</sub>H<sub>32</sub>O<sub>2</sub>SiNa: 307.2064; found 307.2060 [M + Na].

# 2.3. A general procedure for the synthesis of $\alpha$ -silylcarboxylic acids of type Ph<sub>2</sub>(Me)SiCH(R)COOH (**XI**-**XIII**)

This synthesis has been reported before [7]. The following quantities have been used:  $\alpha$ -*Diphenyl(methyl)silyl*-4-*pentenoic acid* (**XI**): diphenyl(methyl)silylacetic acid (6.98 mmol, 1.79 g) was reacted with LDA (15.4 mmol) and allylbromide (7.68 mmol, 0.66 ml). After standard work up procedure the crude product was crystallized from hexane to give 1.76 g (85%) of acid (**XI**). M.p.: 115–117 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  0.68 (s, 3H, SiCH<sub>3</sub>), 2.18 (m, 1H, CH<sub>2</sub>=CHCH<sub>2</sub>CH), 2.55 (m, 1H, CH<sub>2</sub>=CHCH<sub>2</sub>CH), 2.71 (dxd, <sup>3</sup>J = 7.5 Hz, <sup>3</sup>J = 9.0 Hz, 1H, CH<sub>2</sub>=CHCH<sub>2</sub>CH), 5.00 (m, 2H, CH<sub>2</sub>=CHCH<sub>2</sub>), 5.80 (m, 1H, CH<sub>2</sub>=CHCH<sub>2</sub>), 7.35 (m, 10H, 2Ph), 11.59 (br, 1H, CO<sub>2</sub>H). <sup>13</sup>C (125 MHz, CDCl<sub>3</sub>) – 5.26 (SiCH<sub>3</sub>), 31.29 (CH<sub>2</sub>=CHCH<sub>2</sub>CH), 35.85 (CH<sub>2</sub>=CHCH<sub>2</sub>CH), 115.27 (CH<sub>2</sub>=CH), 127.94, 127.99, 129.84,

133.57, 133.92, 134.43, 134.72, 134.88, 137.27 (2Ph + CH<sub>2</sub>=<u>C</u>H), 180.53 (<u>CO<sub>2</sub>H</u>). <sup>29</sup>Si NMR (100 MHz, CDCl<sub>3</sub>) –5.29. IR (KBr):  $\nu$  (SiCH<u>CO<sub>2</sub>H</u>) 1679 cm<sup>-1</sup>. MS (ESI negative mode): *m/z* calc. for C<sub>18</sub>H<sub>20</sub>O<sub>2</sub>Si: 296.44; found 295.07 [M – H]<sup>-</sup>.

For the preparation of XII, diphenyl(methyl)silylacetic acid (6.75 mmol, 1.73 g) was reacted with LDA (14.8 mmol) and then benzylbromide (7.42 mmol, 0.88 ml) was added drop-wise to the dianion solution. The mixture was stirred overnight at room temperature. After standard work up procedure the crude product was crystallized from hexane to give 2.1 g (90%) of acid (XII). M.p.: 119–121 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.72 (s, 3H, SiCH<sub>3</sub>), 2.76  $(dxd, 3) = 14.5 Hz, 2) = 2.5 Hz, 1H, SiCHCH_2), 2.93 (dxd, 3) = 12.0 Hz,$ 2J = 2.5 Hz, 1H, SiCHCH<sub>2</sub>), 3.11 (dxd, 1H, 3J = 12.0 Hz, 3J = 14.5 Hz, 1H, SiCHCH<sub>2</sub>), 7.40 (m, 15H, 3Ph), 11.35 (br, 1H, COOH). <sup>13</sup>C (125 MHz, CDCl<sub>3</sub>) -5.25 (SiCH<sub>3</sub>), 33.08 (PhCH<sub>2</sub>Si), 38.32 (SiCH-COOH), 126.14, 127.98, 128.06, 128.39, 129.87, 129.93, 133.49, 133.91, 134.74, 134.80, 134.92, 141.53 (2Ph), 179.50(COOH). <sup>29</sup>Si NMR (100 MHz, CDCl<sub>3</sub>) -5.29. IR (KBr): v (SiCHCOOH) 1683 cm<sup>-1</sup>. HRMS (ESI positive mode): m/z calc. for C<sub>22</sub>H<sub>22</sub>O<sub>2</sub>Si [M + Na]+: 369.1287; found 369.1275.

α-Diphenyl(methyl)silylvaleric acid (**XIII**): Diphenyl(methyl) silylacetic acid (4.36 mmol, 1.12 g) was reacted with LDA (9.6 mmol) and propyliodide (4.80 mmol, 0.47 ml). After standard work up procedure the crude product was crystallized from hexane to give 1.05 g (81%) of pure acid (**XIII**). M.p.: 82–83 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.67 (s, 3H, SiCH<sub>3</sub>), 0.85 (t, <sup>3</sup>*J* = 7.5 Hz, 3H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>) 1.28 (m, 1H, CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.42 (m, 2H, CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.84 (m, 1H, CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.60 (dxd, <sup>3</sup>*J* = 12.0 Hz, <sup>3</sup>*J* = 11.5 Hz, CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 7.34 (m, 6H, 2Ph), 7.56 (m, 4H, 2Ph), 11,11 (br, 1H, CO<sub>2</sub>H). <sup>13</sup>C (125 MHz, CDCl<sub>3</sub>) –5.34 (SiCH<sub>3</sub>), 13.61 (CH<sub>2</sub>CH<sub>3</sub>), 23.54 (CH<sub>2</sub>CH<sub>3</sub>), 29.56 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 36.17 (CHCO<sub>2</sub>H), 127.86, 127.93, 129.70, 129.74, 134.01, 134.35, 134.73, 134.88 (2Ph), 180.86 (CO<sub>2</sub>H). <sup>29</sup>Si NMR (100 MHz, CDCl<sub>3</sub>) –5.76. IR (KBr): v (SiCHCO<sub>2</sub>H) 1667 cm<sup>-1</sup> (ESI negative mode): *m/z* calc. for C<sub>18</sub>H<sub>22</sub>O<sub>2</sub>Si: 298.14; found 296.78 [M – H]<sup>-</sup>.

#### 2.3.1. The "bromo derivative" (XIV)

The procedure for the synthesis of 2-bromo-2-(diphenylmethysilyl)acetic acid is representative for all a-silylcarboxylic acids of type Ph<sub>2</sub>(Me)SiCH(halogen)CO<sub>2</sub>H. Diisopropylamine (8.4 mmol, 1.2 ml) and anhydrous tetrahydrofuran (30 ml) were added to an oven dried round-bottomed flask (100 ml) equipped with a magnetic stirring bar. The mixture was cooled to -78 °C prior of drop-wise addition of n-butyllithium 1.6 M (8.4 mmol, 5.3 ml). The mixture was warmed at room temperature for 15 min and cooled to 0 °C. Diphenyl(methyl)silylacetic acid (3.8 mmol, 0.98 gr) in 5 ml of dry THF was added drop-wise over 10 min to LDA solution and the mixture was stirred for 1.5 h at the same temperature to complete the formation of the dianion. Then CBr<sub>4</sub> (4.2 mmol, 1.39 gr) was added drop-wise to the dianion solution and the mixture was stirred overnight at room temperature. The reaction mixture was diluted by 20 ml of hexane and the organic phase washed twice with a solution of saturated sodium chloride (2  $\times$  30 ml) The aqueous phase was carefully acidified with 1 N HCl to pH = 2 and then extracted with diethyl ether (20 ml  $\times$  3). The combined organic extracts were washed with water, dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated in vacuo. The residual product was contained 0.59gr of 2-bromo-2-(diphenylmethysilyl)acetic acid and siloxane Ph<sub>2</sub>(Me)SiOSi(Me)Ph<sub>2</sub> as a by-product. Separation by column chromatography resulted in decomposition of the acid (desilylation). IR (NaCl): v (C=O) 1720 cm<sup>-1</sup>, 2710-3170 cm<sup>-1</sup> (COOH). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  0.60 (s, 3H, SiCH<sub>3</sub>), 3.90 (s, 1H, SiCHBr), 7.32–7.55 (m, 10H, 2Ph), 11.35 (br, 1H, CO<sub>2</sub>H); <sup>13</sup>C (125 MHz, CDCl<sub>3</sub>) -0.60 (SiCH<sub>3</sub>), 32.34 (BrCHSi), 127.70, 129.55, 133.97, 137.43, (2Ph), 167.52 (CO<sub>2</sub>H).

#### 2.3.2. The "iodo derivative" (XV)

2-iodo-2-diphenylmethylsilylacetic acid: Diphenyl(methyl)silylacetic acid (4.29 mmol, 1.10 g) was reacted with LDA (9.4 mmol) and I<sub>2</sub> (17.3 mmol, 2.2 gr). After standard work up procedure the crude product contained 1.46 g of the acid and siloxane Ph<sub>2</sub>(Me)SiOSi(Me) Ph<sub>2</sub> as a by-product. Separation by column chromatography resulted in decomposition of the acid (desilylation). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  0.68 (s, 3H, SiC<u>H</u><sub>3</sub>), 3.72 (s, 1H, SiC<u>H</u>I), 7.35–7.64 (m, 10H, 2Ph), 11.59 (br, 1H, COOH).

# 2.4. A general procedure for the anodic oxidation of I, II, IV, VI–IX, XI–XVI

The following procedure is given as a representative example for all other oxidations: Substrate I (0.3 mmol) was electrolized in a wall-jacketed (to allow a steady flow of tab water during electrolysis) undivided cell, equipped with two carbon rods  $(\varphi = 5 \text{ mm})$  as electrodes. The electrolyte included 3.33 mL a mixture of MeOH:MeCN (1:9, v/v) and 30  $\mu$ L of KOH solution (3 N in methanol) which is equivalent to 30% of the substrate, namely 0.09 mmol. No additional electrolyte was used. Constant current electrolysis of  $\sim 30 \text{ mA/cm}^2$  was conducted with magnetic stirring. After the desired electricity was consumed (3 F) the solvents were removed by evaporation and the remaining solid was dissolved in diethyl ether and washed with 5% of aqueous sodium bicarbonate. After phase separation the ethereal solution was dried over magnesium sulfate and filtered. Evaporation of the ether gave a crude mixture of products that was subjected to GC-MS and NMR as is (or after chromatography separation on silica gel, using hexane-ethyl acetate as eluent).

After electrolysis, a slight acidification of the aqueous phase with HCl 2 N enabled the detection of the corresponding carboxylic acid. For example, in the case of electrolysis of **VII**, cyclobutylcarboxylic acid was observed.

Electrolyses at Pt electrodes involved two foils ( $2 \times 1.2$  cm each), current density of 250 mA/cm<sup>2</sup>, in MeOH:MeCN (1:3, v/v) using 0.09 mmol of KOH (3 N in methanol) for 0.3 mmol of I.

# 2.5. Spectral data of major products (for minor products only GC-MS data are reported)

Me<sub>3</sub>GeOGeMe<sub>3</sub> (**1a**): GC-MS (m/z) (%): 253  $(M - 1)^+$ , 237, 145, 119 (100). <sup>1</sup>H NMR: 0.49 for 'Me<sub>3</sub>Ge'; Me<sub>3</sub>GeOGe(Me)<sub>2</sub>OGeMe<sub>2</sub> (1b): GC-MS (m/z) (%): 371 (M - 1)<sup>+</sup>, 253, 207 (100), 119. <sup>1</sup>H NMR: 0.10-0.28 for 'Me<sub>3</sub>GeO' and 'Me<sub>2</sub>GeO' groups; Me<sub>3</sub>GeCH<sub>2</sub>CH<sub>2</sub>GeMe<sub>3</sub> (1c): <sup>1</sup>H NMR: 0.49 for Me<sub>3</sub>Ge; 1.43 for 'CH<sub>2</sub>'; GC–MS (*m*/*z*) (%): 263 (M<sup>+</sup>), 237 (100), 119; Data for PhCH<sub>2</sub>CH<sub>2</sub>COOMe (**2a**) were compared with literature [12]; <sup>1</sup>H NMR: 3.67 for OMe 2.95 for PhCH<sub>2</sub>; 2.63 for CH<sub>2</sub>CO<sub>2</sub>Me; GC–MS (*m*/*z*) (%): 164 (M<sup>+</sup>), 133, 104 (100), 91; Data for PhCH<sub>2</sub>CH(OMe)<sub>2</sub> (**2b**) were compared with literature [13]; <sup>1</sup>H NMR: 5.23 for CH; 3.34 for OMe. GC–MS (m/z) (%): 135 (M-OMe)<sup>+</sup>, 91, 75 (100); Me<sub>3</sub>GeCH(CH<sub>2</sub>Ph)OMe (**2c**), GC-MS (m/z) (%): 253 (M - 1)<sup>+</sup>, 222, 207(100), 104. Me<sub>3</sub>GeOH (2d); GC-MS (m/z) (%): 135 (M - 1)<sup>+</sup>, 119, 104 (100). Ph<sub>2</sub>(Me)SiOH (4a): Spectral data were compared with published data [14]. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 0.68$  (s, 3H), 2.18 (s, 1H), 7.38–7.44(m, 6H), 7.59–7.64(m, 4H);  $^{13}$ C NMR:  $\delta = -1.09, 128.05,$  $130.03, 134.49, 137.19; GC-MS(m/z)(\%): 214(M^+), 199(100), 151, 183,$ 151, 121, 105; Ph<sub>2</sub>(Me)SiOCH<sub>3</sub> (**4b**): Spectral data were compared with published data [14].  $^{1}$ H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.64 (s, 3H), 3.54 (s, 3H), 7.37–7.43 (m, 6H), 7.57–7.62 (m, 4H); GC–MS (m/z) (%): 228 (M<sup>+</sup>), 213 (100), 183, 151, 121, 105; Ph<sub>2</sub>(Me)SiOSi(Me)Ph<sub>2</sub>(**4c**): Spectral data were compared with published data [14]. <sup>1</sup>H NMR:  $\delta = 0.59$  (s, 6H), 7.29–7.40 (m, 6H), 7.51–7.56 (m, 4H);  $^{13}$ C NMR:  $\delta = -0.43$ , 127.87, 129.71, 134.14, 137.72; GC-MS(m/z)(%): 410(M<sup>+</sup>), 395(100), 317, 255, 195, 151; Ph<sub>2</sub>(Me)SiGeMe<sub>3</sub>(**4d**); GC-MS(m/z)(%): 315 $(M-1)^+$ (100), 237, 197; Me<sub>3</sub>GeOSi(Me)Ph<sub>2</sub> (**4e**); GC-MS (*m*/*z*) (%): 332 (M+), 317 (100), 239, 197; 1,1-[Ph<sub>2</sub>(Me)Si](OMe)cyclopropane (**6a**): <sup>1</sup>H NMR: 0.60 (MeSi), 3.47 (OMe). GC–MS (*m*/*z*) (%): 268 (M<sup>+</sup>), 151 (100), 121; 1,1-[Ph<sub>2</sub>(Me)Si](OH)cyclopropane (**6b**) GC–MS (m/z) (%): 253(M - 1)<sup>+</sup>, 213 (100), 197, 151; IR (NaCl): ν (OH) 3300 cm<sup>-1</sup>: 1.1-[Ph<sub>2</sub>(Me)Si](NHCOCH<sub>3</sub>)cyclopropane (**6c**): <sup>1</sup>H NMR: 0.42 (MeSi), 2.10 (COMe). GC-MS (*m*/*z*) (%): 268(M)<sup>+</sup>, 151 (100), 121; Ph<sub>2</sub>(Me) SiCH(allyl)OMe (11a); <sup>1</sup>H NMR: 0.59 (MeSi); 3.13 (OMe); 4.99–5.11 (2H); 5.61–5.75 (1H). GC–MS (m/z) (%): 281(M – 1)<sup>+</sup>, 235 (100), 172, 105;  $Ph_2(Me)SiCH(allyl)OH(11b):GC-MS(m/z)(\%): 267(M-1)^+$ , 213 (100), 197, 151; Ph<sub>2</sub>(Me)SiCH<sub>2</sub>OH (12a): Spectral data were compared with published data [14]. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 0.33$  (s, 3H), 3.58 (s, 2H), 7.36–7.40 (m, 6H), 7.48–7.53 (m, 4H); GC-MS(*m*/*z*)(%): 227 (M<sup>+</sup> – 1), 197 (100), 151, 105; MS (MALDI-TOF): m/z calc. for C<sub>14</sub>H<sub>16</sub>OSi: 228.097; found for [M + Ag]: 335.111; PhMeSi(OMe)<sub>2</sub> (**13a**): Spectral data were compared with published data [14]. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.38 (s, 3H), 3.59 (s, 6H), 7.38-7.43 (m, 6H), 7.59-7.64 (m, 4H); GC-MS(m/z)(%): 182 (M<sup>+</sup>), 167 (100), 137, 107, 91, 75, 59; Ph<sub>2</sub>(Me)SiCH(*n*-Pr)OH (**13b**): GC-MS (*m*/*z*) (%): 269 (M – 1)<sup>+</sup>, 213, 197 (100), 151; Me<sub>2</sub>(allyl)SiCH<sub>2</sub>CH<sub>2</sub>Si(allyl)Me<sub>2</sub> (16a); <sup>1</sup>H NMR: 0.07 (MeSi); 1.25 (SiCH<sub>2</sub>); allyl: 2.00-2.10 (2H). GC-MS (*m*/*z*) (%): 226 (M<sup>+</sup>-allyl), 185 (100), 143, 99; 4.76-4.87 (2H); 5.71–5.84 (1H); Me<sub>2</sub>(allyl)SiOSi(allyl)Me<sub>2</sub> (**16b**): <sup>1</sup>H NMR: 0.03 (MeSi); allyl group:1.88-2.04 (2H); 4.77-4.86 (2H); 5.69-5.83 (1H). GC-MS (*m*/*z*) (%): 214 (M<sup>+</sup>-allyl), 173 (100), 133, 73.

## 3. Results and discussion

The various  $\alpha$ -germylated and  $\alpha$ -silylated carboxylic acids discussed in this work are summarized in Table 1. Some of them are newly made and some have been studied electrochemically by their anodic oxidation under various experimental conditions. The table includes four parts: acids **I**–**IV** involve  $\alpha$ -germylated derivatives; acids **V**–**X** involve  $\alpha$ -silylatedcycloalkyl derivatives; acids **XI**–**XV** involve  $\alpha$ -silylated derivatives with alkyl or halo groups at the  $\alpha$  position; compound **XVI** is an  $\alpha$ -silylacetic acid with an allyl group attached to the silicon moiety.

#### Table 1

Synthesized  $\alpha$ -germylcarboxylic and  $\alpha$ -silylcarboxylic acids.

Me <sub>3</sub> GeCH <sub>2</sub> COOH (I) <sup>a</sup>
Me <sub>3</sub> GeCH(benzyl)COOH (II) <sup>a</sup>
Me <sub>3</sub> GeCH(allyl)COOH (III) <sup>a</sup>
Me <sub>3</sub> GeCH[SiPh <sub>2</sub> (Me)]COOH ( <b>IV</b> ) <sup>b</sup>
Me <sub>3</sub> Si(cyclopropyl)COOH ( <b>V</b> ) <sup>c</sup>
Ph <sub>2</sub> (Me)Si(cyclopropyl)COOH (VI) <sup>c</sup>
Ph <sub>2</sub> (Me)Si(cyclobutyl)COOH (VII) <sup>c</sup>
Ph <sub>2</sub> (Me)Si(cyclopentyl)COOH ( <b>VIII</b> ) <sup>c</sup>
Ph <sub>2</sub> (Me)Si(cyclohexyl)COOH ( <b>IX</b> ) <sup>c</sup>
(i-Pr) <sub>3</sub> Si(cyclohexyl)COOH ( <b>X</b> ) <sup>a, c</sup>
Ph <sub>2</sub> (Me)SiCH(allyl)COOH ( <b>XI</b> ) <sup>b</sup>
Ph <sub>2</sub> (Me)SiCH(benzyl)COOH (XII) <sup>b</sup>
Ph <sub>2</sub> (Me)SiCH( <i>n</i> -Pr)COOH ( <b>XIII</b> ) <sup>b</sup>
Ph <sub>2</sub> (Me)SiCH(Br)COOH ( <b>XIV</b> ) <sup>a, b</sup>
Ph <sub>2</sub> (Me)SiCH(I)COOH ( <b>XV</b> ) <sup>a, b</sup>
Me <sub>2</sub> (allyl)SiCH <sub>2</sub> COOH (XVI) <sup>d</sup>

<sup>a</sup> A new compound.

<sup>b</sup> Synthesized according to a known procedure [7].

<sup>c</sup> Synthesized according to a known procedure [10].

<sup>d</sup> Commercially available.

#### 3.1. Synthesis

Based on the recently reported new synthetic method to obtain C-silylation in preference over O-silylation, trimethylgermylacetic acid I has been prepared according to the procedure used to synthesize its silicon analog, Me<sub>3</sub>SiCH<sub>2</sub>COOH [6] (Scheme 2):

Scheme 2. Experimental conditions for trimethylgermylation at the  $\alpha$  position of trimethylsilyl acetate.

Acid I could be further transformed into other carboxylic acids (II and III) by direct alkylation of its dianion, similar to the procedure for the silyl analog [7] (Scheme 3).



Scheme 3. Alkylation of Me<sub>3</sub>GeCH<sub>2</sub>CO<sub>2</sub>H.

The synthesis of  $\alpha$ -silyl(cycloalkyl)carboxylic acids (**VI–IX**) has been carried out by a different synthetic procedure [10] than for **I**, starting from the carboxylic acid itself. Initially, the  $\alpha$ -carbanion of the corresponding cycloalkylcarboxylic acid was formed, followed by its quenching with a silyl reagent (Scheme 4).



Scheme 4. Silylation of cycloalkylcarboxylic acids.

Cyclic acids **V** and **X** with different substitution pattern at the silicon moiety were also synthesized according to Scheme 4. However, whereas **V** is already a known and characterized compound [11], derivative **X** is a new one.

Similar to the alkylation of I (Scheme 3),  $\alpha$ -germyl,  $\alpha$ -silylcarboxylic acid (IV),  $\alpha$ -alkyl- $\alpha$ -silylcarboxylic acids (XI–XIII) and  $\alpha$ halo- $\alpha$ -silylcarboxylic acids (XIV and XV) have been prepared in good yields ( $\sim$  70 – 90%) (Scheme 5).



Scheme 5. Germylation/alkylation/halogenation of Ph<sub>2</sub>MeSiCH<sub>2</sub>CO<sub>2</sub>H.

#### 3.2. Electrochemistry of selected examples of acids

It has been reported that the anodic oxidation of  $\alpha \alpha'$ -dialkylcarboxylic acids (*R'R''*CHCOOH) and cycloalkylcarboxylic acids afford poor yields (0–8% and 0–30%, respectively) of Kolbe 'dimers' (*R'R''*CHCH*R'R''*) [15], mainly due to the inductive effect exerted by the alkyl groups, favoring a carbocation formation rather than a radical intermediate. As to the silyl moiety, there are two contradictive effects. On the one hand, it has been known [16] that a silyl group at the  $\alpha$ -position stabilizes radicals (The " $\alpha$ -effect"), but on the other hand, the polarity of the Si–C bond causes the silyl group at the  $\alpha$  position to be as electron-donating group in nature. This property causes the carboxylic group to be less acidic, and therefore, more reluctant to form a carboxylate anion, which is necessary for the Kolbe reaction to take place.

Recently we discovered [14] that the anodic decarboxylation of  $\alpha$ -silylacetic acids under non-Kolbe conditions (e.g., at C anodes and low current density) undergoes a competing desilylation reaction, as shown in Scheme 6.

reactions the anodic degermylation process prevails over the decarboxylation one. Acid I afforded two germoxanes on a Pt anode, Me<sub>3</sub>GeOGeMe<sub>3</sub> (**1a**, 18%) and Me<sub>3</sub>GeOGe(Me)<sub>2</sub>OGeMe<sub>2</sub> (**1b**, 41%) as the major products along with a small amount of a Kolbe 'dimer', Me<sub>3</sub>GeCH<sub>2</sub>CH<sub>2</sub>GeMe<sub>3</sub> (**1c**, 6%) and a mixture of other germoxanes. These results are somewhat surprising because under



Scheme 6. Products by anodic oxidation of Ph<sub>2</sub>(Me)SiCH<sub>2</sub>CO<sub>2</sub>H.

Therefore, due to the above described contradictive effects and the summary of previous results outlined in Scheme 6, it is interesting to investigate the anodic oxidation of  $\alpha$ -germylated acids and the various types of  $\alpha$ -silylated acids listed in Table 1 in order to explore what pathways these types of acids will undergo.

For clarity, all types of products generated by the various anodic oxidations of the slected acids from the list in Table 1 are described in Scheme 7 with their proper assignments, as they appear in the text and Tables 2–8.

Me <sub>3</sub> GeOGeMe <sub>3</sub> (1a)	1,1-[Ph <sub>2</sub> (Me)Si](OMe)cyclopropane (6a)
Me <sub>3</sub> GeOGe(Me <sub>2</sub> )OGeMe <sub>3</sub> (1b)	1,1-[Ph <sub>2</sub> (Me)Si](OH)cyclopropane (6b)
(Me <sub>3</sub> GeCH <sub>2</sub> -) <sub>2</sub> (1c)	$1,1\text{-}[Ph_2(Me)Si](NHCOCH_3) cyclopropane~(\textbf{6c})$
PhCH <sub>2</sub> CH <sub>2</sub> COOCH <sub>3</sub> (2a)	Ph2(Me)SiCH(allyl)OMe (11a)
PhCH <sub>2</sub> CH(OMe) <sub>2</sub> (2b)	Ph2(Me)SiCH(allyl)OH (11b)
Me <sub>3</sub> GeCH(CH <sub>2</sub> Ph)OMe ( <b>2</b> c)	
Me <sub>3</sub> GeOH ( <b>2d</b> )	Ph <sub>2</sub> (Me)SiCH <sub>2</sub> OH (12a)
Ph <sub>2</sub> (Me)SiOH (4a)	Ph(Me)Si(OMe) <sub>2</sub> (13a)
Ph <sub>2</sub> (Me)SiOMe (4b)	Ph2(Me)SiCH(n-Pr)OH (13b)
Ph2(Me)SiOSi(Me)Ph2 (4c)	
Ph <sub>2</sub> (Me)SiGeMe <sub>3</sub> (4d)	$(Me_2(allyl)SiCH_2)_2$ (16a)
Me <sub>3</sub> GeOSi(Me)Ph <sub>2</sub> (4e)	$Me_2(allyl)SiOSi(allyl)Me_2(16b)$

Scheme 7. Products from anodic oxidations.

#### 3.2.1. Anodic oxidation of $\alpha$ -germylcarboxylic acids (I–IV)

The titled acids have been electrolyzed under both Kolbe conditions (a Pt anode, high current density of 250 mA/cm<sup>2</sup>) and non-Kolbe conditions (a C anode, low current density of 32 mA/cm<sup>2</sup>) and the results are summarized in Table 2. Apparently in all

#### Table 2

Results from anodic oxidation of I.<sup>a</sup>

Main identified products <sup>b</sup>	% at Pt <sup>c</sup>	% at C <sup>d</sup>
Me <sub>3</sub> GeOGeMe <sub>3</sub> ( <b>1a</b> )	18	30
Me <sub>3</sub> GeOGe(Me <sub>2</sub> )OGeMe <sub>3</sub> (1b)	41	18
$(Me_3GeCH_2-)_2$ (1c)	6 (8) <sup>e</sup>	_
Other germoxanes	25	29

<sup>a</sup> At room temperature; undivided cell; [I] = 0.09 M.

<sup>b</sup> Relative yields based on GLC integration.

<sup>c</sup> In MeCN:MeOH (3:1); 0.3 mol-equiv (relative to I) of KOH 3 N; 250 mA/cm<sup>2</sup>; terminated after 3F electricity consumption.

<sup>d</sup> In MeCN:MeOH (9:1); 0.3 mol-equiv (relative to I) of KOH 3 N; 30 mA/cm<sup>2</sup>; terminated after 3F electricity consumption.

<sup>e</sup> Yield of the Kolbe dimer when the concentration of the substrate was tripled.

similar experimental conditions [4], the silicon analog of **I** gave a Kolbe dimer in good yield (70%) at a Pt anode. Since the C–Ge bond is weaker than the C–Si one bond energies of C–Si and C–Ge are 301 and 255 kJ/mol, respectively [17] it is not surprising that the former is more labile towards anodic cleavage. This observation is also supported by the fact that oxidation on a C anode resulted in an exclusive mixture of germoxanes **1a** (34%) and **1b** (29%) with no trace of Kolbe or non-Kolbe products.

In the case of the alkylated acid **II** (Table 3), again the major product on a Pt anode was germoxane **1b** (66%) without detection of any Kolbe 'dimer'. However, this time a non-Kolbe product, PhCH<sub>2</sub>CH<sub>2</sub>COOMe (**2a**, 18%) was observed at this anode. This latter product was also detected (18%) at a C anode along with other products such as PhCH<sub>2</sub>CH(OMe)<sub>2</sub> (**2b**, 10%), a non-Kolbe product, Me<sub>3</sub>GeCH(CH<sub>2</sub>Ph)OMe (**2c**, 6%), and small amounts of germanol Me<sub>3</sub>GeOH (**2d**, 5%) and a Kolbe dimer **1c** (4%).

### Table 3

Results from anodic oxidation of II.<sup>a</sup>

Main identified products	% at Pt	% at C <sup>b</sup>
1b	66	_
1c	_	6
$PhCH_2CH_2COOCH_3$ ( <b>2a</b> )	18	18
$PhCH_2CH(OMe)_2$ ( <b>2b</b> )	_	10
Me <sub>3</sub> GeCH(CH <sub>2</sub> Ph)OMe ( <b>2c</b> )	_	6
Me <sub>3</sub> GeOH ( <b>2d</b> )	-	5

<sup>a</sup> See footnotes 'a-d' underneath Table 1.

<sup>b</sup> A complex mixture of products was obtained.

As expected, based on the above and previous results, in the case of the  $\alpha$ -germyl,  $\alpha$ -silylcarboxylic acid **IV** both anodic degermylation and desilylation took place (Table 4). Indeed, the main products at a Pt anode are silanol Ph<sub>2</sub>MeSiOH (**4a**, 26%), siloxane methoxysilane Ph<sub>2</sub>(Me)SiOMe (**4b**, 11%), siloxane Ph<sub>2</sub>(Me)SiO-Si(Me)Ph<sub>2</sub> (**4c**, 24%) and a mixed radical-coupled product, Me<sub>3</sub>GeSi(Me)Ph<sub>2</sub> (**4d**, 7%) together with germoxane **1b** (19%). A similar mixture of products was formed at a C anode but in

# Table 4

Results from anodic oxidation of IV.ª

Products	% at Pt	% at C
1b	19	_
Ph <sub>2</sub> (Me)SiOH ( <b>4a</b> )	26	11
Ph <sub>2</sub> (Me)SiOMe ( <b>4b</b> )	11	36
$Ph_2(Me)SiOSi(Me)Ph_2(4c)$	24	28
Ph <sub>2</sub> (Me)SiGeMe <sub>3</sub> ( <b>4d</b> )	7	8
Me <sub>3</sub> GeOSi(Me)Ph <sub>2</sub> ( <b>4e</b> )	-	11

<sup>a</sup> See footnotes 'a-d' underneath Table 1.

different ratios: **4a** (11%), **4b** (36%), **4c** (28%) and **4d** (8%). This time an additional mixed oxygenated product was detected,  $Me_3GeO-Si(Me)Ph_2$  (**4e**, 11%).

Scheme 8 outlines plausible mechanisms for obtaining the major products from electrolysis of **I**–**IV**.



Scheme 8. Mechanistic schemes.

Actually, germoxanes are not direct electrochemical products and their formation could be postulated by the following chemical reactions:



R<sub>3</sub>GeOGe(R)<sub>2</sub>OGeR<sub>3</sub>

# 3.2.2. Anodic oxidation of Ph<sub>2</sub>(Me)SiCH(cycloalkyl)COOH (VI-IX)

 $\alpha$ -Silyl(cycloalkyl)carboxylic acids (**VI–IX**), bearing the same substitution pattern at the Si atom, were also oxidized under Kolbe and non-Kolbe experimental conditions. The results of selected examples are summarized in Table 5. In all cases, there were three silyl products of which the major one was the siloxane Ph<sub>2</sub>(Me)SiOSi(Me) Ph<sub>2</sub> (**4c**, 27–76%) and the other two products: Ph<sub>2</sub>(Me)SiOH (**4a**, 3–13%) and Ph<sub>2</sub>(Me)SiOMe (**4b**, 14–22%). The yields of the latter two were higher at a C than a Pt anode, at the expense of **4b** (not shown).

	Pt anode/ 250 mA/cm <sup>2</sup>
	or:
	C anode/ 32 mA/cm <sup>2</sup>
SiPh <sub>2</sub> Me	MeOH-MeCN (9:1)
(n = 2 - 5)	

Table 5	
Results from anodic oxidation of VI-IX at a C anode. <sup>a</sup>	

Substrate	Products ( <b>4a–4c</b> )				
	Ph <sub>2</sub> (Me)SiOH ( <b>4a</b> )	Ph <sub>2</sub> (Me)SiOMe ( <b>4b</b> )	Ph <sub>2</sub> (Me)SiOSi(Me)Ph <sub>2</sub> ( <b>4c</b> )		
VI <sup>b</sup>	12	14	27		
VII <sup>c</sup>	3	21	76		
VIII	_	22	70		
IX	13	16	67		

<sup>a</sup> In MeCN:MeOH (9:1); 0.3 mol-equiv (relative to I) of KOH 3 N; 30 mA/cm<sup>2</sup>; terminated after 3F electricity consumption.

 $^b$  Other products (non-Kolbe) were obtained: 1,1-[Ph<sub>2</sub>(Me)Si](OMe)cyclopropane (**6a**, 18%); 1,1-[Ph<sub>2</sub>(Me)Si](OH)cyclopropane (**6b**, 13%) and 1,1-[Ph<sub>2</sub>(Me)Si](NH-COCH<sub>3</sub>)cyclopropane (**6c**, 10%).

<sup>c</sup> After electrolysis, when acidification took place cyclobutylcarboxylic acid was detected together with a minute amount of bicyclobutane.

As to the Ph<sub>2</sub>(Me)SiCH(cyclopropyl)COOH (**VI**) it also yielded siloxane **4c** (27%), silanol **4a** (12%) and methoxysilane **4b** (14%) at a C anode. However also three non-Kolbe products were formed: Ph<sub>2</sub>(Me)Si(cyclopropyl)OMe (**6a**) (18%), Ph<sub>2</sub>(Me)Si(cyclopropyl)OH (**6b**) (13%) and Ph<sub>2</sub>(Me)Si(cyclopropyl)NHCOCH<sub>3</sub> (**6c**) (2%). Interestingly, at a Pt anode no siloxane was formed and the major product was a Ph<sub>2</sub>(Me)Si(cyclopropyl)H (65%) (not shown) stemming from a hydrogen abstraction of the radical intermediate.

The effect of temperature was investigated for the anodic oxidation of **VII** at a C anode and the results are summarized in Table 6. Evidently, in the temperature range of +22 to -40 °C there is no meaningful effect on the spectrum of products and their relative yields, but a minor trend could be observed. Upon increasing the temperature the yield of **4b** decreases whereas that of **4c** increases.

#### Table 6

Effect of temperature on the anodic oxidation of VII at a C anode.<sup>a</sup>

Temperature (°C)	Products		
	4a	4b	4c
22–23	3	21	76
0	4	14	82
-40	9	2	89

<sup>a</sup> See footnote 'a' underneath Table 4.

# 3.2.3. Anodic oxidation of $Ph_2MeSiCH(R)CO_2H$ [R = allyl (**XI**); benzyl (**XII**), n-Pr (**XIII**), Br (**XIV**), I,(**XV**)]

It has been claimed that the yields of Kolbe 'dimers' are very low when the  $\alpha$  position of the acid bears an electron-donating substituent capable of stabilizing carbenium ions [8]. In this respect, the titled silylcarboxylic acids contain both alkyl and silyl subsituents at the  $\alpha$  position. Since it has been known that  $\alpha$  silyl groups stabilize alkyl radicals, this effect contradicts with the one exerted by an alkyl substituent, which favors carbenium ion stabilization, leading to non-Kolbe products via follow up reactions with nucleophiles. Therefore, it is not surprising that no Kolbe 'dimer' was detected from the electrolysis of Ph<sub>2</sub>MeSiCH(*n*-Pr)CO<sub>2</sub>H

Ph<sub>2</sub>(Me)SiOSi(Me)Ph<sub>2</sub> (**4c**, major) + Ph<sub>2</sub>MeSiOH (**4a**) + Ph<sub>2</sub>MeSiOMe (**4b**)

(**XIII**) at a Pt anode, unlike the  $\alpha$ -unalkylated acids [5]. It afforded 35% of a non-Kolbe product, as shown in Scheme 9, and 50% of recovered starting material.



Scheme 9. A major non-Kolbe product from anodic oxidation of Ph<sub>2</sub>(Me)SiCH<sub>2</sub>CO<sub>2</sub>H.

On the other hand, electrolysis of  $Ph_2MeSiCH(benzyl)CO_2H$  (**XII**) at a Pt anode led to a complete desilylation under the same experimental conditions [5].

Table 7 Results from anodic oxidation of XI-XV<sup>a</sup>

$R$ at $\alpha$ position	Pro	ducts			
	4a	4b	4c	Ph(Me)Si(OMe) <sub>2</sub> (13a)	Non-Kolbe Products
Allyl	_	48	11	-	36 <sup>b</sup>
Benzyl	4	42	18	-	14 <sup>c</sup>
n-Pr	4	35	_	24	17 <sup>d</sup>
Br	_	_	100	-	-
Ι	-	-	86 <sup>e</sup>	-	-

<sup>a</sup> In MeCN:MeOH (9:1); 0.3 equiv (relative to I) of KOH 3 N; C anode; 30 mA/cm<sup>2</sup>; terminated after 3F electricity consumption.

Ph<sub>2</sub>(Me)SiCH(allyl)OMe (11a, 22%) and Ph<sub>2</sub>(Me)SiCH(allyl)OH (11b, 14%).

Ph2(Me)SiCH2OH (12a).

<sup>d</sup> Ph<sub>2</sub>(Me)SiCH<sub>2</sub>OH (**12a**, 14%) and Ph<sub>2</sub>(Me)SiCH(*n*-Pr)OH (**13b**, 3%).

On a Pt anode.

Table 7 summarizes the results obtained from anodic oxidation of the titled acids at C anodes. It can be seen that all alkylated acids (XI-XV) afford silvlated products of type 4a-4c, in addition to non-Kolbe products involving "SiCH(R)(OH)", "SiCH(R)(OMe)" and "SiCH2OH" moieties. The oxidation of acid XIII also yielded Ph(Me) Si(OMe)<sub>2</sub> (13a) exclusively. As anticipated, no Kolbe 'dimers' were detected for all this type of alkylated acids.

In the cases of the halogenated acids **XIV** and **XV**, they both afforded siloxane 4c in high yields with no observation of any kind of a non-Kolbe product.

# 3.2.4. Anodic oxidation of Me<sub>2</sub>(allyl)SiCH<sub>2</sub>COOH (XVI)

The idea behind the anodic oxidation of acid **XVI** in which an allyl group is attached to the silicon moiety has been to obtain a five-membered cyclic silane by intramolecular cyclization through the electrogenerated radical intermediate. It turned out



Scheme 10. Products from XVI.

#### Table 8

Results from anodic oxidation of XVI.<sup>a</sup>

Main products <sup>b</sup>	% at Pt (250 mA/cm <sup>2</sup> )	% at Pt (21 mA/cm <sup>2</sup> )
Kolbe 'dimer'( <b>16a</b> )	61	15
Siloxanes <sup>c</sup>	25	8
	% at C (30 mA/cm <sup>2</sup> )	% at C (13 mA/cm <sup>2</sup> )
Kolbe 'dimer'	37	9
Siloxanes	29	14

At room temperature; in MeCN:MeOH (9:1); 3F; R.T.; [XVI] = 0.045 M.

b The remaining contains a complex mixture of unidentified 4-15 products.

<sup>c</sup> Major siloxane: Me<sub>2</sub>(allyl)SiOSi(allyl)Me<sub>2</sub> (16b).

that at both Pt and C anodes and even with a diluted solution of **XVI** (0.045 M), the preferred reaction pathway was to form a Kolbe 'dimer' rather than a cyclized product (Scheme 10). Surprisingly, a higher yield of the Kolbe 'dimer' Me<sub>2</sub>(allyl) SiCH<sub>2</sub>CH<sub>2</sub>Si(allyl)Me<sub>2</sub> (16a) was formed at a C anode (61%) than at a Pt anode (19%) (Table 8), even though it has been known that radical intermediates undergo further oxidation to carbenium ions at C anodes [8]. Eventually, the silvl group at the  $\alpha$  position stabilizes radical intermediates even at this type of anodes. In addition, siloxanes were formed at both anodes, particularly Me<sub>2</sub>(allyl)SiOSi(allyl)Me<sub>2</sub> (16b).

### 4. Conclusions

The synthesis of new a-germylcarboxylic acids and  $\alpha$ -silylcarboxylic acids, among some known  $\alpha$ -silyl(cycloalkyl)carboxylic ones, has been performed. Selected examples of these acids were electrolyzed anodically at C anodes in basic methanol solutions. The anodic process indicates that the major pathway involves degermylation for  $\alpha$ -germyl acids I–IV, and desilylation for the  $\alpha$ -silyl acids VI–IX and  $\alpha$ -halo,  $\alpha$ -silyl acids XIV and XV. However, for acids **XI**–**XIII** (with an alkyl group at the  $\alpha$  position), a competing anodic decarboxylation reaction takes place to afford non-Kolbe type of products, and for XVI (with an allyl group attached to the silicon moiety), a Kolbe type 'dimer'.

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