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Preliminary Communication

Synthesis and reactivity of 3-(triphenylgermyl)propanoic acid

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Abstract

3-(Triphenylgermyl)propanoic acid was synthesized through several reaction steps from germanium tetrachloride. Aromatic Ge–C bonds in the compound can be cleaved selectively by bromine and the β-carboxylic functional group shows some unusual properties.

Key words: Germanium; Organogermanium

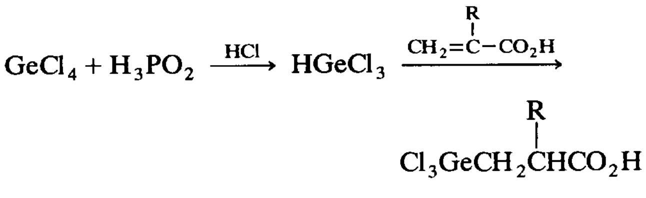
1. Introduction

In tetraalkylgermanes, the aromatic Ge–C bonds are more sensitive than aliphatic Ge–C bonds to the action of halogens, especially of bromine [1]. This difference in reactivity is very useful in the synthesis of organogermanium compounds, for when the mole ratio of the reactants and the reaction conditions are controlled, the aromatic Ge–C bonds can be cleaved selectively by bromine [2,3].

In the molecule of 3-(triphenylgermyl)propanoic acid, there are three aromatic Ge–C bonds, which might be cleaved selectively by bromine, and in the β-position to the metal, a functional group $-CO_2H$, which can also undergo several chemical reactions. So we expect that this compound might present some interesting reactivity and be of importance in the synthesis of a great number of new organogermanium compounds. We have therefore synthesized 3-(triphenylgermyl)propanoic acid and studied its properties. Some special properties of the carboxylic group in 3-(triphenylgermyl)propanoic acid were found and have been related to its interaction with the germanium atom.

2. Results and discussion

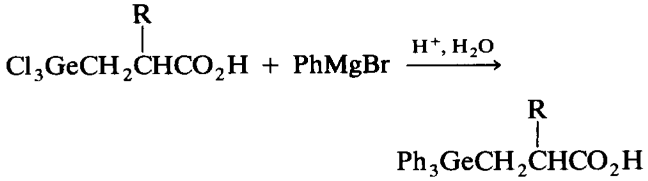
3-(Trichlorogermyl)propanoic acid was prepared from germanium tetrachloride [1,4]:



$$GeCl_4 + H_3PO_2 \xrightarrow{HCl} HGeCl_3 \xrightarrow{CH_2=\overset{R}{\overset{|}{C}}-CO_2H} Cl_3GeCH_2\overset{R}{\overset{|}{C}}HCO_2H$$

$(R = H, CH_3)$

The reaction of 3-(trichlorogermyl)propanoic acid with phenylmagnesium bromide in molar ratio 1:4 led to 3-(triphenylgermyl)propanoic acid:



$$Cl_3GeCH_2\overset{R}{\overset{|}{C}}HCO_2H + PhMgBr \xrightarrow{H^+, H_2O} Ph_3GeCH_2\overset{R}{\overset{|}{C}}HCO_2H$$

$(R = H, CH_3)$

The selective cleavage of Ge–Ph bonds by bromine occurred under mild conditions in good yield. The results are shown in Scheme 1 and Table 1.

The bromination product of 3-(triphenylgermyl)propanoic acid (**1a**) should be 3-(bromodiphenylgermyl)propanoic acid or 3-(dibromophenylgermyl)propanoic acid. Due to the difficulties in purifying some of the bromination products from the reaction mixture, we transformed them to the corresponding hydrides with the $NaBH_4/H_2O$ reduction system. Two hydrides were easily separated.

Esterification of 3-(triphenylgermyl)propanoic acid with alcohols seemed especially easy. When 3-(triphenylgermyl)propanoic acid was dissolved in lukewarm methanol, methyl 3-(triphenylgermyl)propanoate formed immediately. The resultant ester can be reduced by $LiAlH_4$ to yield 3-(triphenylgermyl)propanol.

$$Ph_3GeCH_2CH_2CO_2H + HOMe \longrightarrow \underset{(4)}{Ph_3GeCH_2CH_2CO_2Me} \xrightarrow{LiAlH_4/Et_2O} \underset{(5)}{Ph_3GeCH_2CH_2CH_2OH}$$

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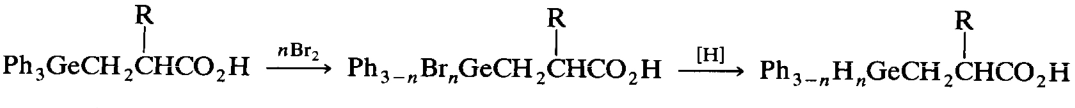
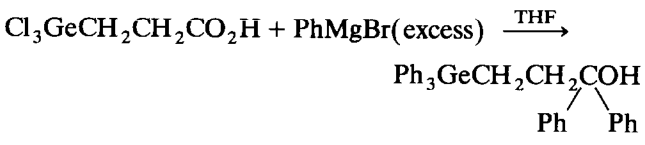


$$Ph_3GeCH_2\overset{R}{C}HCO_2H \xrightarrow{nBr_2} Ph_{3-n}Br_nGeCH_2\overset{R}{C}HCO_2H \xrightarrow{[H]} Ph_{3-n}H_nGeCH_2\overset{R}{C}HCO_2H$$

(1a,b) **(2)** **(3a,b)**

Scheme 1.

The unusual reactivity of the carboxylic group in 3-(triphenylgermyl)propanoic acid was shown again in another reaction. When 3-(trichlorogermyl)propanoic acid reacted with an excess of Grignard reagent, a derivative of 3-(triphenylgermyl)propanol was given in good yield (91%).



$$Cl_3GeCH_2CH_2CO_2H + PhMgBr(excess) \xrightarrow{THF} Ph_3GeCH_2CH_2\underset{Ph\ \ Ph}{C}OH$$

(6)

Here the carboxylic group reacted with phenylmagnesium bromide and gave an alcohol. Under conventional conditions, carboxylic acid is very difficult to react with Grignard reagent to give alcohol, because with the formation of carboxylic salt, the carbon atom in the carboxylic group becomes less electrophilic and the salt is usually insoluble.

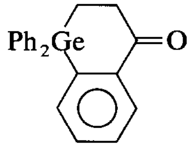
$$RCO_2H + R'MgBr \longrightarrow RCO_2^-MgBr^+ + R'H$$

Considering that there are empty d-orbitals in the outer sphere of the germanium atom, we propose the mechanism illustrated in Scheme 2 to explain the unusual reactivity of the carboxylic group.

The oxygen atoms of the carboxylic group can coordinate with the germanium atom to form a pentacoordinated germanium centred complex. Electrons of the oxygen atom can partly transmit to the empty d-orbital of the germanium atom, thus the carbon atom in the carboxylic group becomes more electrophilic and can be more easily attacked by nucleophiles such as methanol and phenylmagnesium bromide. Here the group Ph_3Ge- acts as an intramolecular Lewis acid catalyst.

When 3-(triphenylgermyl)propanoic acid was transformed into the corresponding acyl chloride, a derivative of germacyclohexanone can be produced through an intramolecular Friedel–Crafts reaction. Here $AlCl_3$ was used as a catalyst. This reaction might be of great use in the synthesis of germacyclo-organic compounds.

$$Ph_3GeCH_2CH_2CO_2H \xrightarrow{PCl_5} Ph_3GeCH_2CH_2COCl \xrightarrow{AlCl_3}$$



(61%) (7)

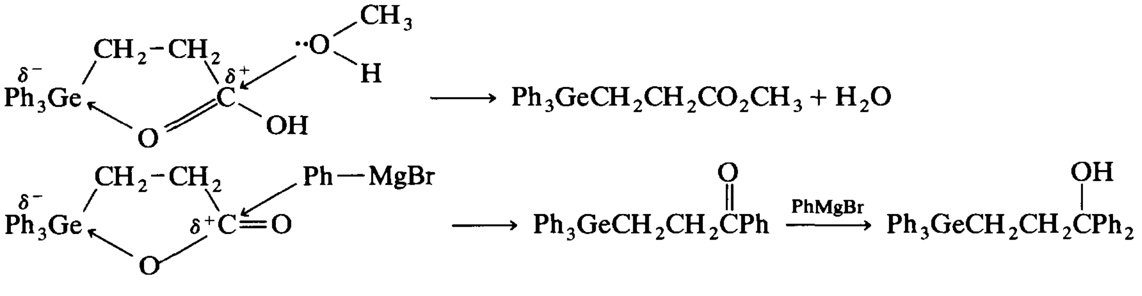
The results of the above-mentioned reactions of the β-carboxylic group in 3-(triphenylgermyl)propanoic acid are summarized in Table 2.

3. Experimental section

All the melting points were determined with a Yanagimoto micro-melting point apparatus and are

TABLE 1. The selective cleavage of Ge–Ph bonds by bromine

Compound No.	R	n	M.p./B.p. (°C)	Yield(%)	Elementary analysis Found (calcd.)(%) C	H	MS (m/z)
1a	H		136–7	60	66.80 (66.67)	5.20 (5.29)	
1b	CH_3		151–2	62	67.49 (67.35)	5.57 (5.61)	315 (M^+− ph)
2	CH_3	2	78–9	83	30.20 (30.20)	2.86 (3.02)	317 (M^+− Br)
3a	H	1	83–4	83	59.60 (59.60)	5.42 (5.30)	301 (M^+− 1)
3b	CH_3	2	142–3/1 torr	85	50.19 (50.02)	6.11 (5.83)	239 (M^+− 1)



Scheme 2.

uncorrected. IR spectra were recorded with a Nicolet-5-MX, FT-IR. ^{1}H-NMR spectra were recorded on a Varian FT-80A spectrometer using tetramethylsilane as an internal standard. Mass spectra were recorded with a VG-ZAB-HS spectrometer.

3.1. *3-(Triphenylgermyl)propanoic acid (**1a**) and 2-methyl-3-(triphenylgermyl)propanoic acid (**1b**)*

Magnesium (0.180 mol) and bromobenzene (0.185 mol) in THF (100 ml) were made into phenylmagnesium bromide. The reaction mixture was cooled with ice water and stirred. To this mixture was added 3-(trichlorogermyl)propanoic acid (0.040 mol) in small portions. The mixture was refluxed for 12 h and THF was distilled. Then toluene (100 ml) was added and the remaining THF was distilled again. The mixture was then kept at 110°C for 3 h, cooled and dissolved with the solution of hydrochloric acid (40 ml) in ice water. The organic layer was separated and the water layer extracted with toluene. The organic layers were combined, dried with anhydrous magnesium sulfate and concentrated. A solid substance formed, which was recrystallized from cyclohexane to give 3-(triphenylgermyl)propanoic acid (9.5 g) in 63% yield.

M.p. 136–7°C. IR (cm^{-1}): 1710 (C=O), 622 (Ge–C). ^{1}H-NMR (δ ppm, $CDCl_3$): 1.80 (t, 2H, CH_2Ge), 2.50 (t, 2H, CH_2CO), 7.38 (m, 15H, 5ph), 10.3 (s, 1H, COOH). Elemental analysis Found: C 66.80, H 5.20; Calcd.: C 66.67, H 5.29%.

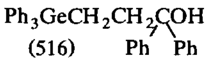
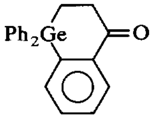
The same method was used for the synthesis of 2-methyl-3-(triphenylgermyl)propanoic acid (**1b**) which was obtained in 62% yield.

M.p. 151–2°C. IR (cm^{-1}) 1710 (C=O). ^{1}H-NMR (δ ppm, $CDCl_3$): 1.15 (d, 3H, CH_3), 1.84 (m, 2H, $GeCH_2$), 2.08 (m, 1H, CHCO), 7.38 (m, 15H, 5ph). MS(*m/z*): 315 (M^+ – ph). Elemental analysis Found: C 67.49, H 5.57; Calcd.: C 67.35, H 5.61%.

3.2. *3-(Dibromophenylgermyl)-2-methylpropanoic acid (**2**)*

2-Methyl-3-(triphenylgermyl)propanoic acid (0.117 mol) was dissolved in dry chloroform (50 ml), cooled

TABLE 2. Results of the reactions of the carboxylic group in 3-(triphenylgermyl)propanoic acid

No.	Compound (Mw)	M.p. (°C)	Yield(%)	Elementary analysis Found (calcd.)(%) C	H	MS (*m/z*)
4	$Ph_3GeCH_2CH_2CO_2Me$ (392)	65–7	94	67.37 (67.35)	5.61 (5.63)	393 (M^+ + 1)
5	$Ph_3GeCH_2CH_2CH_2OH$ (364)	135–6	72	69.34 (69.23)	6.12 (6.04)	365 (M^+ + 1)
6	 $Ph_3GeCH_2CH_2\underset{Ph\ \ Ph}{C}OH$ (516)	163–4	91	76.85 (76.74)	5.89 (5.62)	517 (M^+ + 1)
7	 (360)	– *	61	69.85 (70.00)	4.82 (5.00)	361 (M^+ + 1)

* The compound is a very dense and sticky liquid separated on a silica gel chromatographic column.

with ice water and stirred. Bromine (0.234 mol) was added dropwise. The mixture was stirred for 12 h and the solvent distilled. The residue was recrystallized from cyclohexane and gave the product (11.0 g) in 83% yield.

M.p. 78–9°C. IR (cm^{-1}): 1640 (C=O), 625 (Ge–C). ^1H-NMR (δ ppm, $CDCl_3$): 1.35 (d, 3H, CH_3), 2.22 (m, 2H, $GeCH_2$), 2.74 (m, 1H, CHCO), 7.67 (m, 5H, ph), 11.00 (s, 1H, COOH). MS (m/z): 317 ($M^+ - Br$). Elemental analysis Found: C 30.20, H 2.86; Calcd.: C 30.20, H 3.02%.

3.3. 3-(Hydrodiphenylgermyl)propanoic acid (3a) and 3-(dihydrophenylgermyl)-2-methyl-propanoic acid (3b)

Bromine (0.036 mol) was added dropwise to the stirred solution of 3-(triphenylgermyl)propanoic acid (**1a**) (0.035 mol) in chloroform (100 ml) cooled in an ice bath. The mixture was stirred for about 2–3 h at room temperature. Then the solution was concentrated and the solution of sodium borohydride (1.05 mol) in 100 ml water was added. The mixture was stirred at room temperature for 1 h, acidified with dilute hydrochloric acid and extracted with ether. The ether layer was dried with anhydrous magnesium sulfate, and concentrated to give crystals (10.0 g) in 83% yield. M.p. 83–4°C. IR (cm^{-1}): 2050 (Ge–H), 1700 (C=O), 620 (Ge–C). ^1H-NMR (δ ppm, $CDCl_3$): 1.47–1.72 (m, 2H, CH_2Ge), 2.53 (t, 2H, CH_2CO), 5.08 (t, 1H, HGe), 7.37 (m, 5H, ph), 11.1 (s, 1H, COOH). MS(m/z): 301 ($M^+ - 1$). Elemental analysis Found: C 59.60, H 5.42; Calcd.: C 59.60, H 5.30%.

3-(Dibromophenylgermyl)-2-methylpropanoic acid (0.027 mol) was reduced with sodium borohydride (0.120 mol) in 100 ml water. The product (4.8 g) was obtained by vacuum distillation in 85% yield.

B.p. 142–3°C/1 Torr. ^1H-NMR (δ ppm, $CDCl_3$): 1.21–1.55 (m, 5H, CH_3, CH_2Ge), 2.63 (m, 1H, CHCO), 7.25–7.50 (m, 5H, ph), 4.45 (t, 2H, H_2Ge), 11.48 (s, 1H, COOH). IR (cm^{-1}): 2050 (Ge–H), 1700 (C=O), 840 (Ge–C). MS(m/z): 239 ($M^+ - 1$). Elemental analysis Found: C 50.19, H 6.11; Calcd.: C 50.02, H 5.83%.

3.4. Methyl 3-(triphenylgermyl)propanoate (4)

3-(Triphenylgermyl)propanoic acid (0.0132 mol) was dissolved in lukewarm methanol (40 ml). The solvent was evaporated and white crystals of methyl 3-(triphenylgermyl)propanoate (5 g) were obtained in 94% yield. M.p. 65–7°C. ^1H-NMR (δ ppm, $CDCl_3$): 1.92 (t, 2H, CH_2Ge), 2.39 (t, 2H, CH_2CO), 3.54 (s, 3H, CH_3), 7.39 (m, 15H, 3ph). MS(m/z): 393 ($M^+ + 1$). Elemental analysis Found: C 67.37, H 5.61; Calcd.: C 67.35, H 5.63%.

3.5. 3-(Triphenylgermyl)propanol (5)

To the stirred solution of lithium aluminium hydride (0.026 mol) in ether (250 ml) protected under nitrogen, methyl 3-(triphenylgermyl)propanate (0.020 mol) was added in small portions. The reaction mixture was refluxed for 2 h, then cooled, dissolved with 10% aqueous sodium hydroxide and extracted with ether. The ether layer was washed with water and dried with anhydrous sodium sulfate. When the solvent was evaporated, white crystals of 3-(triphenylgermyl)propanol (6.8 g) were obtained in 72% yield. M.p. 135–6°C. IR (cm^{-1}): 3331s, 1418s, 1070m, 779s, 698s. ^1H-NMR (δ ppm, $CDCl_3$): 1.63 (m, 5H, $GeCH_2CH_2OH$), 3.62 (t, 2H, CH_2O), 7.83 (m, 15H, ph). MS(m/z): 365 ($M^+ + 1$). Elemental analysis Found: C 69.34, H 6.12; Calcd.: C 69.23, H 6.04%.

3.6. 1,1-Diphenyl-3-(triphenylgermyl)propanol (6)

Magnesium (1.28 mol) and bromobenzene (1.30 mol) in THF (360 ml) were made into phenylmagnesium bromide. While the reaction mixture was cooled in an ice bath and stirred, a solution of 3-(trichlorogermyl)-propanoic acid (0.080 mol) in THF (150 ml) was added. The mixture was then refluxed for 12 h, cooled, dissolved with dilute hydrochloric acid and extracted with THF. The organic layer was dried with anhydrous sodium sulfate and concentrated. 1,1-Diphenyl-3-(triphenylgermyl)propanol (38 g) was obtained as crystals from the solution in 91% yield. M.p. 163–4°C. IR (cm^{-1}): 3353s, 3050s, 1431s, 700s. ^1H-NMR (δ ppm, $CDCl_3$): 1.52 (m, 2H, CH_2Ge), 1.85 (s, 1H, –OH), 2.40 (m, 2H, CH_2COH), 7.37 (m, 25H, 5ph). MS(m/z): 517 ($M^+ + 1$). Elemental analysis Found: C 76.85, H 5.89; Calcd.: C 76.74, H 5.62%.

3.7. Derivative of germacyclohexanone (7)

3-(Triphenylgermyl)propanoic acid (0.013 mol) in 40 ml cyclohexane was added in small portions to a mixture of PCl_5 (0.013 mol) and cyclohexane (5 ml). After 10 min under reflux, the solvent and phosphorous oxide trichloride were distilled under reduced pressure. To the residue, cyclohexane (15 ml) and aluminium trichloride (0.014 mol) were added. The mixture was stirred at 40°C for 30 min and at 60°C for 30 min, cooled, dissolved with hydrochloric acid in ice water and extracted with ether. The organic layer was separated, washed with dilute hydrochloric acid, water, dilute sodium hydroxide solution and brine water, and dried with anhydrous sodium sulfate. The solvent was evaporated to give a sticky substance which was purified with a silica gel column (ether as eluent); the sticky product (**7**) (2.9 g) was obtained in 61% yield. IR

(cm^{-1}): 3053m, 1432s, 1230s, 690s, 463m. ^{1}H-NMR (δ ppm, $CDCl_3$): 2.00 (t, 2H, $GeCH_2$), 3.30 (t, 2H, CH_2CO), 7.30–7.60 (m, 14H, 3Ph). MS(m/z): 361 ($M^+ + 1$). Elemental analysis Found: C 69.85, H 4.82; Calcd.: C 70.00, H 5.00%.

Acknowledgement

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