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CARBOXY-SILANES AND -GERMANES

IV. SYNTHESIS AND PROPERTIES OF TRIORGANOSILYL DERIVATIVES *

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Summary

β-Triorganosilyl derivatives of silane- and germane-carboxylic acids are reported for the first time. Studies are reported on their spectral properties (IR, UV, PMR), acidity and thermolysis. No evidence has been found in support of extended d-orbital participation, $(\pi \rightarrow d \rightarrow d)\pi$ bonding, in the ground state of the polysilanecarboxylic acids and their conjugate base forms. $(d \rightarrow d)\pi$ bonding may be an important factor in lowering the activation energy for the thermal decarbonylation of pentaphenyldisilanecarboxylic acid.

Introduction

Triphenylsilanecarboxylic acid was first synthesized in 1951 [2] and the germanium analogue in 1954 [3]. Since these initial reports, the properties of triorganosilane- and triorganogermane-carboxylic acids have been the subject of a number of papers [1,4—8]. In this paper, we report for the first time the synthesis of triorganosilyl substituted silane- and germane-carboxylic acids and a study of their properties to further elucidate the nature of the interaction between the carboxyl function and the silicon and/or germanium atoms in the substituent group.

Experimental

General

Analyses were performed by Alfred Bernhardt Microanalytical Laboratories, Germany.

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The sources of the starting materials are: trimethylchlorosilane, triphenylchlorosilane and diphenyldichlorosilane (Dow Corning Corp.); lithium wire (Lithium Corp. of America); methyllithium, 1.66 *M* in ether (Alpha Products, Ventron Corp.); diphenylacetylene (Fisher Scientific Co.); methanol-*d*, 99% minimum isotopic purity (Diaprep Incorp.).

Synthesis

1. General. The lithiation reactions were carried out under a nitrogen atmosphere using solvents which were distilled from calcium hydride.

Tetrakis(trimethylsilyl)silane (m.p. 260° C) was prepared by the method of Gilman and Smith [9]. Tetrakis(trimethylsilyl)germane (m.p. 291—293° C) was prepared by the method of Burger and Goetze [10]. The syntheses of trimethylsilanecarboxylic acid, trimethylgermanecarboxylic and tris(trimethylsilyl)acetic acid have been reported previously [5,11].

2. Pentaphenyldisilanecarboxylic acid (I). Triphenylsilyllithium *, prepared from triphenylchlorosilane (23.5 g, 79 mmol) and lithium (2.1 g, 0.30 g-atom) in THF (185 ml) was added to a solution of diphenyldichlorosilane (15.2 g, 60 mmol) dissolved in THF (200 ml) over a period of 3 h. During the addition, the reaction flask was cooled in an ice-water bath (0—5° C).

Finally cut lithium wire (1.4 g, 0.20 g-atom), was added to the reaction mixture. After stirring for 4 h, a deep black color had developed. This mixture was poured through glass wool onto crushed Dry Ice. After 1 h, 5% hydrochloric acid (400 ml) was added, the aqueous layer was extracted several times with ether (200 ml portions) and the combined ethereal solution was dried over Drierite. Removal of the solvent under reduced pressure gave impure I (17.5 g, 36 mmol, 58% yield). Several recrystallizations from benzene/petroleum ether gave crystals of high purity, m.p. 185—188° C dec. (Found: C, 76.71; H, 5.51; Si, 11.60. $C_{31}H_{26}O_2Si_2$ calcd.: C, 76.54; H, 5.35; Si, 11.54%).

3. Tris(trimethylsilyl)silanecarboxylic acid (II). Tris(trimethylsilyl)silyllithium in THF/ether (4/1), prepared from tetrakis(trimethylsilyl)silane, (10.5 g, 32 mmol) and excess methyllithium by the method of Gilman and Smith [13], was poured onto crushed Dry Ice and hydrolyzed with 500 ml of a 5% hydrochloric acid solution. The layers were separated, and the aqueous layer was extracted twice with 200 ml portions of ether. The solvent was removed from the combined extracts under reduced pressure, yielding a crystalline solid. Several crystallizations from pentane at —78° C, gave II (7.0 g, 24 mmol, 75% yield, m.p. 122—126° C dec.) (Found: C, 41.24; H, 9.63; Si, 38.45%; mol. wt. 292. $C_{10}H_{28}O_2Si_4$ calcd.: C, 41.03; H, 9.64; Si, 38.39%; mol. wt. 293.).

4. Tris(trimethylsilyl)germanecarboxylic acid (III). Methyllithium, 5.0 ml of a 1.66 *M* ether solution (9.75 mmol), was injected into a solution of tetrakis(trimethylsilyl)germane (2.0 g, 5.5 mmol) in 20 ml of THF. After stirring for 8 h, the reaction mixture was poured onto powdered Dry Ice. The resulting slurry was poured directly into 50 ml of a 5% hydrochloric acid solution, and the aqueous solution was extracted several times with ether (500 ml). After drying over calcium sulfate, removal of the ether under reduced pressure gave a

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* For general procedures for preparing silyllithium reagents cf. the review article, ref. 4.

solid containing both III and unreacted germane (1.64 g). The mixture was transferred to a chromatographic column (20 mm/280 mm, silica gel, grade 950, 60—200 mesh) using low-boiling petroleum ether. Low-boiling petroleum ether (250 ml) was passed through the column followed by methanol (200 ml). Removal of the solvent from the petroleum ether fraction gave crude III (0.54 g, 1.25 mmol, 23% yield). Three successive crystallizations from pentane at —78°C gave a sample of high purity: m.p. 96—100°C. (Found: C, 35.42; H, 8.36. $C_{10}H_{28}O_2GeSi_3$ calcd.: C, 35.62; H, 8.36%.)

Decarbonylation

1. Pentaphenyldisilanecarboxylic acid (I)

(a) Refluxing toluene. I (4.7 g, 9.7 mmol) was dissolved in toluene (150 ml); the resulting solution was refluxed for 6 h. The gradual darkening of palladium chloride test paper [14] suspended in the reflux condenser to a deep black color indicated the evolution of carbon monoxide. On removing the toluene under reduced pressure, crude pentaphenyldisilanol (4.5 g, 9.8 mmol) was obtained quantitatively. Several crystallizations from petroleum ether gave a sample of high purity: m.p. 133—134.5°C (lit. [15] 134—134.5°C); IR (CCl_4): 3656 cm^{-1}(s) (O—H). (Found: C, 78.38; H, 5.66. $C_{30}H_{26}OSi_2$ calcd.: C, 78.55; H, 5.71%.) No other products were detected.

A second run was carried out as above using I (5.4 g, 11.1 mmol) and toluene (150 ml) in the presence of diphenylacetylene (4.0 g, 22 mmol) yielding pentaphenyldisilanol (3.9 g, 8.8 mmol, 77% yield, m.p. 133—135°C and unreacted diphenylacetylene (3.0 g, 17 mmol) a 77% recovery, m.p. 59—60°C (lit. [16] 60°C). No other products were detected.

(b) Thermally (225°C). I (1.0 g, 2.1 mmol) and diphenylacetylene (0.73 g, 4.1 mmol) were placed in a 10-ml flask equipped with a reflux condenser. The flask was lowered into an oil bath previously heated to 225°C. Carbon monoxide evolution was detected as indicated above during the initial 2 h of reflux. The total reflux time was 4.5 h. After cooling to room temperature, benzene (10 ml), and petroleum ether (10 ml) were added to precipitate the diphenylacetylene (0.66 g, 3.7 mmol, m.p. 58—60°C, 90% recovery). No other pure substances were isolated or identified.

2. Tris(trimethylsilyl)silanecarboxylic acid (III)

(a) Refluxing toluene. II (1.0 g, 3.4 mmol) and diphenylacetylene (1.0 g, 5.6 mmol) were dissolved in toluene (50 ml); the resulting solution was refluxed for 5 h. During this period, no evolution of carbon monoxide was detected. Removal of the toluene under reduced pressure yielded a white crystalline solid. Fractional crystallization from ethanol/water gave diphenylacetylene (0.85 g, 4.8 mmol, 86% recovery, m.p. 59—60°C and II (0.70 g, 2.4 mmol, 71% recovery, m.p. 120—124°C).

(b) Thermally (225°C). II (2.0 g, 6.8 mmol) was heated to 225°C for 1 h as described in section 1-b. Carbon monoxide evolution was detected throughout the heating period. Crystallization from pentane gave a solid, 1.7 g: m.p. 90°C subl.; IR (KBr): 2943, 2905 (C—H), 1245, 830, 748, 680 (Si—CH_3), 1045 cm^{-1} (Si—O—Si). (Found: C, 42.27; H, 10.38; Si, 43.28. $C_{18}H_{54}OSi_8$ calcd.: C, 42.28; H, 10.64; Si, 43.95%). The PMR spectrum (CCl_4) showed five peaks with the

indicated relative ratios: δ 0.07 (1.00), 0.09 (4.75), 0.20 (1.67), 0.27 (8.33), 0.31 (13.0) ppm).

A second run was carried out as above at 250°C using II (1.0 g, 3.4 mmol) in the presence of diphenylacetylene (1.0 g, 5.6 mmol). Crystallization from ethanol/water gave diphenylacetylene (0.9 g, 5.0 mmol, 90% recovery, m.p. 61—63°C and a white solid (0.75 g, m.p. 91°C subl.).

Determination of ionization constants

The ionization constants of the polysilanecarboxylic acids (I and II) were determined in 76 wt. % ethanol/water at 25.0 ± 0.1°C by a spectrophotometric method described previously [1,17]. Specifically, the procedure described as Case I was used with the indicator, sodium 2,4-dinitrophenoxide.

Determination of PMR chemical shifts at infinite dilution for methyl and trimethylsilyl substituted carboxy-methanes, -silanes, -germanes and their anions

1. Apparatus and techniques. All PMR spectra were obtained using a Varian A-60 spectrometer operated at 60 MHz and at ambient temperature, 34 ± 1°C. To assure a resolution of 0.3 Hz the radiofrequency power level was kept well below saturation. Peak positions were measured by means of the standard sideband interpolation method [18] using two Hewlett—Packard Model 201C Audio Oscillators and a Hewlett—Packard Model 522B Electronic Audio Frequency Counter. All chemical shifts were measured relative to TMS.

Solutions of the carboxylic acids and their anions, 0.01—0.03 *M*, were prepared by dissolving a known weight of the acid in 1 ml of methanol-*d* and sodium methoxide/methanol-*d* (prepared by dissolving 0.2847 g of sodium hydroxide in 10 ml of methanol-*d*). Other solutions were prepared by standard dilution procedures.

The chemical shift for each acid and anion concentration was calculated from the average of three separate peak-position determinations. Chemical shifts at infinite dilution, cf. Table 3, were determined for each acid and anion by plotting the chemical shift values for three different concentrations and extrapolating to infinite dilution.

2. Rearrangement and decomposition of $(Me_3Si)_3MCO_2^-$. Samples of the acids, $(Me_3Si)_3MCO_2H$ (M = C, Si, and Ge), were dissolved in the sodium methoxide/methanol-*d* solvent, the resulting solutions were placed in NMR tubes, and the spectra of the anions were recorded within 1 min.

(a) $(Me_3Si)_3CCO_2^-$. The peak position due to the $C\underline{H}_3Si$ group (δ 0.16 ppm) was the same as determined for $(Me_3Si)_2CHCO_2H$ in the above solvent, indicating rearrangement (cf. ref. 11 and 19).

(b) $(Me_3Si)_3SiCO_2^-$. The position and complexity of the resulting $C\underline{H}_3Si$ signals, δ 0.28s, 0.17m ppm, indicated that base-catalyzed decomposition had occurred. During the experiment, gas bubbles appeared, and after standing for approximately 1 h, a white solid precipitated. (Found: C, 10.59; H, 1.47%).

(c) $(Me_3Si)_3GeCO_2^-$. The position and complexity of the resulting $C\underline{H}_3Si$ signals, δ 0.16s, 0.12s, 0.05s, 0.04s, 0.02s ppm, indicated that base-catalyzed decomposition had occurred. During the experiment, gas bubbles appeared, and after standing for approximately 10 min a white solid precipitated. (Found: C, 10.84; H, 1.45%.)

Results and discussion

Synthesis. Since the only method known for synthesizing silane- and germane-carboxylic acids is through carbonation of the organometalloid-alkali metal derivatives [4], this procedure was employed to synthesize the β-triorganosilyl-substituted carboxylic acids. Pentaphenyldisilanyllithium was synthesized directly from the phenylchlorosilanes and carbonated to yield pentaphenyldisilanecarboxylic acid (58%); the intermediate, pentaphenylchlorodisilane, was not isolated.

$$Ph_3SiCl \xrightarrow[THF]{Li} Ph_3SiLi \xrightarrow{Ph_2SiCl_2} Ph_3SiSiPh_2Cl \xrightarrow[THF]{Li}$$

$$Ph_3SiSiPh_2Li \xrightarrow[H_3O^+]{CO_2} Ph_3SiSiPh_2CO_2H$$

The previously reported preparation of pentaphenyldisilanyllithium involves the cleavage of decaphenyltetrasilane by lithium in THF [20].

The tris(trimethylsilyl)-silanecarboxylic acid and -germanecarboxylic acid were prepared by carbonation of the corresponding silyl- and germyl-lithium derivatives. While the preparation of tris(trimethylsilyl)silyllithium by cleavage of a trimethylsilyl group from tetrakis(trimethylsilyl)silane with methyllithium has been reported [13], the preparation of tris(trimethylsilyl)germyllithium from tetrakis(trimethylsilyl)germane by this method is reported for the first time.

Spectral properties. The spectral properties, IR, UV, and PMR, of the β-triorganosilyl derivatives of R_3MCO_2H where M = C, Si and Ge, are given in Table 1.

TABLE 1

SPECTRAL PROPERTIES OF β-TRIORGANOSILYL DERIVATIVES OF R_3MCO_2H (M = C, Si, or Ge)

Compound	IR [a]				PMR [b]		
	ν (C=O) (cm^{-1})		ν (M—CO$_2$H) (cm^{-1})		δ (OH) [c] (ppm)	δ (CH) (ppm)	Peak area ratio
	in CCl_4	*in KBr*	*in* CCl_4	*in KBr*			
$Ph_3SiSiPh_2CO_2H$ [d]	1650	1635	593	597	— [e]	ca. 7.33 [f]	—
$(Me_3Si)_3CCO_2H$ [g, h]	1645	1649	—	—	11.93	0.27	1/27
$(Me_3Si)_3SiCO_2H$ [h]	1633	1633	592	599	11.14	0.26	1/27
$(Me_3Si)_3GeCO_2H$ [h]	1638	1635	574	—	10.93	0.29	1/27

[a] Beckman IR-20 spectrophotometer. [b] Spectra determined in CCl_4, 22—35 w/v% using TMS as an internal standard at 60 MHz, Varian A-60 spectrometer. [c] Position slightly affected by concentration. [d] UV λ_{max}(EtOH) 238 nm (ϵ 19600), 267 nm (4300 (sh)), 274 nm (3120(sh)), determined on a Cary Model 14 spectrophotometer. [e] Not detected because of low solubility. [f] Multiple for Ph groups, acetone solvent. [g] cf., ref. 11 and 19. [h] UV (EtOH), absorption, but no max. above 205 nm for acid and anion forms.

The C=O stretching frequency for silane- and germane-carboxylic acids occurs at a lower energy than for the analogous carbon acids, $\Delta\nu$ 28—51 cm^{-1} [5]. The position of this band also is affected by the type of atom in the β position to the carboxyl group. β-Substitution of a silicon atom for carbon results in a shift of the C=O stretching frequency to lower energy, the effect being two to three times larger in the acid, R_3MCO_2H, where M = C, than for the acids where M = Si and Ge (for comparison purposes, cf. ref. 5 and 19).

A similar β effect has been reported for the ketones, R_3MCOR' [21—24], and esters, R_3CCO_2R' [25] and has been attributed to a direct intramolecular interaction between the metalloid in the β position and the carbonyl oxygen [22,26]. The larger effect of β-R_3Si groups in the compounds where M = C is ascribed to the smaller non-bonded distance between the silicon atom and the carbonyl oxygen in comparison to the compounds where M = Si [26].

The position of the M—CO_2H stretching frequency (M = Si, 572—600 cm^{-1}; M = Ge, 563—580 cm^{-1} [5] remains substantially unchanged in the carboxylic acids with β-R_3Si groups.

The UV spectrum of pentaphenyldisilanecarboxylic acid (cf. Table 1) shows a strong absorption, λ_{max} 238 nm, characteristic of the pentaphenyldisilanyl group * with two shoulders in the phenyl region. The carboxyl absorption ($n \rightarrow \pi^*$) of R_3MCO_2H, where M = Si and Ge, (λ_{max} 240—250 nm [5]) is completely masked by the above absorption bands. The carboxylic acids, $(M_3Si)_3MCO_2H$, where M = Si and Ge, and the corresponding anions show a continuously rising absorption below 270 nm with no maxima above 205 nm which is characteristic of related systems [30,31]. In these species the carboxyl absorption also is completely masked. An end absorption also obscures the carboxy $n \rightarrow \pi^*$ transition in the acid where M = C.

The spectral data on the compounds $(Me_3Si)_3MCO_2H$, where M = Si and Ge, and their anions do indicate that there is no extensive bathochromic shift of the carboxyl or carboxylate absorption bands to $\lambda_{max} > 270$ nm when β-silyl groups are present. Similar observations have been reported for the ketones, R_3SiSiR_2COR', and their implications have been discussed [24,27].

The PMR spectra of the acids, $(Me_3Si)_3MCO_2H$, where M = C, Si or Ge, consist of two singlet resonance lines, $MC\underline{H}_3$ and $MCO_2\underline{H}$. The chemical shifts of the acidic protons are in accord with the electronegativities of the Group IVB elements, $C > Si \approx Ge$, as observed for the acids, Me_3MCO_2H [5]. The main difference between the two series is that the presence of the β-Me_3Si groups results in a shift to higher field which can be ascribed to the greater $+I$ effect of Me_3Si group as compared to the Me group.

Ionization constants. The presence of an α-silicon or -germanium atom in carboxylic acids leads to enhanced acidity over the analogous carbon derivatives [1]. Three mechanisms have been proposed to explain the increased stability of the carboxylate ion over the conjugate acid form in the carboxysilanes and -germanes: (1) $(\pi \rightarrow d)\pi$ bonding between the carboxylate group and the metalloid [1]; (2) 1,3-$(p \rightarrow d)\pi$ bonding between the oxygen in the anion

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* For a discussion of the UV spectra of polysilanes, polygermanes, α-silyl ketones and related compounds cf. ref. 27—29.

TABLE 2

pK_a VALUES OF R_3MCO_2H IN 76 wt% ETHANOL/WATER AT 25°C [a]

Acid	Number of determinations	pK_a(σ) [b]
Me_3CCO_2H [c]	19	7.96 (0.05)
Me_3SiCO_2H [c]	24	7.74 (0.02)
$(Me_3Si)_3SiCO_2H$	15	9.33 (0.02)
Ph_3SiCO_2H [c]	9	6.10 (0.10)
$Ph_3SiSiPh_2CO_2H$	10	7.95 (0.10)

[a] Determined by a spectrophotometric method described previously, ref. 17. [b] Standard deviation. [c] Ref. 1.

and the metalloid [32]; (3) the greater diffuseness and polarizability of the valence atomic orbitals of the metalloid [7]. The relative merits of these approaches have been discussed in terms of MO calculations [7]. In the light of the recent studies on the acidity of the hydroxy derivatives, R_3MOH and $R_3MM'R_2OH$ (where M and M' = C, Si or Ge) [33], one would expect that 1,3-$(p \rightarrow d)\pi$ bonding, i.e., $n_0 \rightarrow$ LUMO$_M$ bonding, plays the predominant role. However, poorer matching of the energy levels between the nonbonding electrons on oxygen and the lowest unoccupied orbital on the metalloid in the carboxy-silanes and -germanes due to electron delocalization in the carboxylate ion and the spatial arrangement (wider bond angles in the carboxylate group) result in a smaller effect than observed for the hydroxy compounds.

The presence of a β-R_3Si group in the acids, R_3CCO_2H, is known to exert an acid weakening effect through electron release by silicon ($+I$) and perhaps steric hindrance to anion solvation [34—36]. A similar effect is observed for the polysilanecarboxylic acids, cf. Table 2. These results rule out any extensive extended d-orbital participation, i.e., $(\pi \rightarrow d \rightarrow d)\pi$ bonding, in the ground state of polysilanecarboxylic acids and their conjugate base forms. Also, in terms of the 1,3-$(n_O \rightarrow$ LUMO$_M)$ interaction model, extension of the chain to Si_2 must have a small effect on the energy of the LUMO$_M$ [28].

In order to compare charge delocalization in the anions, $R_3MCO_2^-$ (where M = C, Si and Ge) relative to their conjugate acid forms, the chemical shifts of MHH_3 were determined in CH_3OD and CH_3OD containing CH_3O^- at infinite dilution, for both R_3MCO_2H and $R_3MCO_2^-$, cf. Table 3. The shift to higher field for the anion, $-\Delta\delta$, is roughly in the order expected based on acidity mea-

TABLE 3

PMR DATA FOR $MC\underline{H}_3$ IN R_3MCO_2H AND $R_3MCO_2^-$ [a]

R	M	$\delta(R_3MCO_2H)$ (ppm)	$\delta(R_3MCO_2^-)$ (ppm)	$\Delta\delta$ [b] (ppm)
Me	C	1.199	1.177	0.022
Me	Si	0.245	0.200	0.045
Me	Ge	0.389	0.327	0.062
Me_3Si	C	0.268	— [c]	
Me_3Si	Si	0.256	— [c]	
Me_3Si	Ge	0.300	— [c]	

[a] Chemical shifts at infinite dilution, precision ±0.005 ppm, cf. experimental section. [b] $\delta(R_3MCO_2H - \delta(R_3MCO_2^-)$. [c] Base-catalyzed decomposition.

surements and the mechanisms for charge delocalization, Ge ≈ Si > C. However, one must be somewhat cautious in interpreting these results since the magnitude of the spectral shifts are small and magnetic anisotropic effects may be important.

The chemical shifts of the anions, $(Me_3Si)_3MCO_2^-$, could not be determined because of base-catalyzed decomposition. Where M = C, the anion is rapidly converted to $(Me_3Si)_2CHCO_2^-$ [11]. When M = Si and Ge, rapid Si—Si and Si—Ge bond cleavage occurs resulting in an insoluble polymeric material. From the C and H content and the C/H ratio, the composition of these polymeric materials are most likely formulated as polysiloxanes and polygermoxanes containing approximately an equal number of MeO and CO_2Na substituted groups.

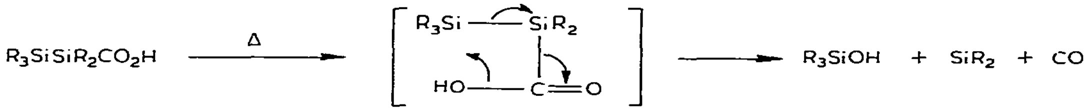
Thermolysis. Thermal rearrangements have been reported for carboxylic acids which have a silicon atom in either the α- or the β-position [6]. Three competing reactions have been detected for the thermolysis of the acid, Ph_3SiCO_2H [12]. In refluxing toluene only two of the competing processes are observed:

$$Ph_3SiO_2CH \xleftarrow[a]{\overset{\Delta}{\text{toluene}}} Ph_3SiCO_2H \xrightarrow[b]{\overset{\Delta}{\text{toluene}}} Ph_3SiOH + CO$$

β-Triorganosilyl substituted carboxylic acids rearrange thermally to their corresponding silyl esters [37]:

$$R_3SiCR'_2CO_2H \xrightarrow{\Delta} HCR'_2CO_2SiR_3$$

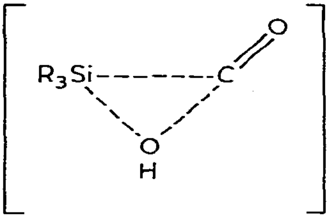
We investigated the thermolysis of the polysilanecarboxylic acids to determine which of the above processes were operative. Also, we speculated that silylene may be one of the products if attack by oxygen occurred at the beta silicon.



To test this hypothesis, several of the thermolyses were carried out in the presence of diphenylacetylene, a silylene trapping agent [38].

The thermolysis of $Ph_3SiSiPh_2CO_2H$ (I) and $(Me_3Si)_3SiCO_2H$ (II) was carried out in refluxing toluene (110°C) and neat (225—250°C) with and without diphenylacetylene. No evidence was found which would indicate the presence of a silylene intermediate. I decarbonylates quantitatively in refluxing toluene yielding $Ph_3SiSiPh_2OH$ (pathway b) while II is recovered unchanged. Both I and II decarbonylate at 225—250°C, yielding products which as yet are not completely characterized. Elemental analysis and the infrared spectrum of the material isolated on decarbonylation of II are consistent with the expected product, hexakis(trimethylsilyl)disiloxane. The PMR spectrum of this material consists of five peaks in the $C\underline{H}_3Si$ region which would indicate that more than one species is present and/or there is restricted rotation in the disiloxane. Further work is in progress to differentiate between the above possibilities and to determine the nature of the skeletal rearrangement if one occurs.

The observation that I rearrange quantitatively by pathway b while Ph_3SiCO_2H rearranges by both pathways, a (55%) and b (27%) [12] suggests that the presence of a β-silyl group lowers the activation energy for the decarbonylation process in relation to the ester-forming process. The decarbonylation reaction is proposed to proceed via intermediate A [6].



(A)

The formation of A involves nucleophilic attack at silicon by a non-bonding electron pair on oxygen; a silicon(V) species may be formed initially. The presence of a β-silyl group could lower the energy of the transition state through $(d \rightarrow d)\pi$ bonding. A similar explanation has been proposed for the enhanced rate of solvolysis of $Me_3SiSiMe_2H$ [39], a reaction which undoubtedly proceeds via a silicon(V) intermediate [40]. The greater thermal stability of II as compared to Ph_3SiCO_2H and I could arise from steric factors and/or the higher energy of the $LUMO_{Si}$ [41].

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