

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

Thermal Rearrangements of Organosilicon and Organogermanium Compounds¹

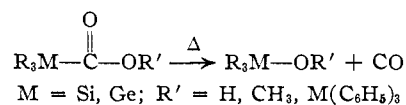
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Organosilicon and organogermanium compounds, in which the metalloïd atom is attached to the carbonyl carbon of a carboxylic acid or ester group, are subject to thermally-induced 1,2-rearrangements in which cleavage of a metalloïd-carbon bond and concomitant formation of a metalloïd-oxygen bond occur, usually accompanied by the elimination of carbon monoxide. Thus, methyl triphenylsilylanecarboxylate, when heated to 150–200°, yields triphenylmethoxysilane and carbon monoxide. A number of other examples and several new organosilicon and organogermanium compounds are described.

Molecular rearrangements are relatively uncommon in organosilicon and organogermanium chemistry. The apparent thermal rearrangement of silicon-substituted phenols has been reported,^{2a} but the majority of rearrangements which have been described have been catalyzed by aluminum chloride^{2b} or by sulfuric acid.^{2c} Each of these rearrangements has involved replacement of an aryl or alkyl group attached to silicon by a more electronegative atom or group.

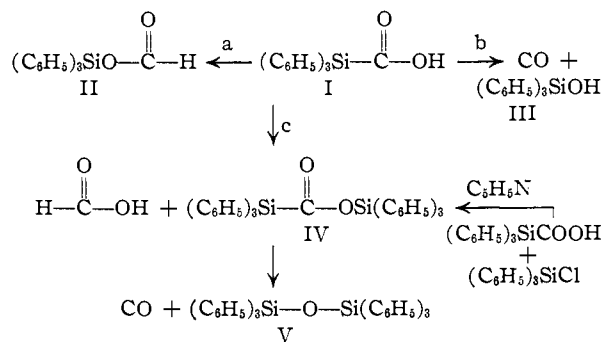
An examination of the thermal decompositions of triphenylsilylanecarboxylic acid³ and triphenylgermanecarboxylic acid,⁴ and their esters, all of which lose carbon monoxide and form a variety of products when heated to their melting points has revealed what appears to be a new type of molecular rearrangement. It has been found that all known organosilicon and organogermanium compounds in which the silicon (or germanium) is attached directly to a carboxylic acid or ester group, undergo thermal rearrangement in which the OH or OR' group of the acid or ester migrates from carbon to silicon (or germanium), accompanied in most cases by the elimination of the carbonyl group as carbon monoxide.



Analogous eliminations of carbon monoxide have recently been reported in base-catalyzed reactions of the same compounds.⁵

A reinvestigation of the thermal decomposition of triphenylsilylanecarboxylic acid (I) at its melting point (180°) has shown that the products formed are carbon monoxide, formic acid, triphenylsilyl formate (II), triphenylsilanol (III) and hexaphenyldisiloxane (V). The formation of these products is best interpreted by the equations shown.

Since none of the reaction products appears to be formed, under the conditions of the reaction, from any of the other products of the reaction, either alone, in pairs, or in combination with the parent acid (see Table II), it must be concluded that each is formed by a separate reaction path. In particular triphenylsilyl formate (II) and triphenylsilanol



(III) must be formed by independent reactions, since these compounds, either alone or as a mixture, can be recovered almost quantitatively after heating to 180° for a few minutes. In addition, when the parent acid (I) is refluxed in toluene for a few hours, triphenylsilyl formate (55%), triphenylsilanol (27%) and carbon monoxide are the only products formed, indicating that their formation *via* reaction paths a and b is independent of reaction c.

Since hexaphenyldisiloxane (V) does not appear to be formed from either of these compounds under the conditions of the reaction, it must arise from the acid directly, or by way of some unstable intermediate. Triphenylsilyl triphenylsilylanecarboxylate (IV) has been found to be unstable under the conditions of the reaction, decomposing spontaneously at its melting point of 134° to yield hexaphenyldisiloxane and carbon monoxide almost quantitatively. Such an intermediate would account for the hexaphenyldisiloxane isolated from the reaction, and for the formation of formic acid, which also apparently does not arise from any of the other reaction products. Since the ester IV, unlike its germanium analog, does not appear to be formed by condensation of the parent acid with triphenylsilanol, it is therefore inferred that formic acid and triphenylsilyl triphenylsilylanecarboxylate are formed by a bimolecular condensation of the acid I.

Closely related to the behavior of triphenylsilylanecarboxylic acid is the thermal decomposition of triphenylgermanecarboxylic acid (VI) which yields carbon monoxide, water and triphenylgermyl triphenylgermanecarboxylate (VIII).⁴ It has now been found, as was postulated, that the ester VIII is formed, in 84% yield, when a mixture of triphenylgermanol (VII), a postulated intermediate in the reaction, and triphenylgermanecarboxylic acid are heated to 160°, 30° below the temperature at which the acid decomposes. This

(1) Presented in part before the Division of Organic Chemistry at the 126th meeting of the American Chemical Society, New York, 1954.

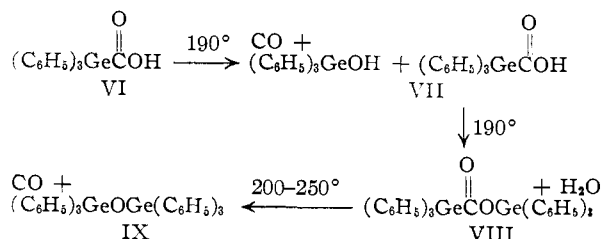
(2) (a) J. L. Speier, *THIS JOURNAL*, **74**, 1003 (1952); (b) F. C. Whitmore, L. H. Sommer and J. R. Gould, *ibid.*, **69**, 1976 (1947); L. H. Sommer, D. C. Bailey, J. R. Gould and F. C. Whitmore, *ibid.*, **76**, 801 (1954); (c) L. H. Sommer and F. J. Evans, *ibid.*, **76**, 1187 (1954).

(3) R. A. Benkeser and R. G. Severson, *ibid.*, **73**, 1424 (1951).

(4) A. G. Brook and H. Gilman, *ibid.*, **76**, 77 (1954).

(5) A. G. Brook and H. Gilman, *ibid.*, **77**, 2322 (1955).

reaction appears to establish the mode of formation of the ester VIII during the thermal decomposition of the acid VI.



It was also found that like its silicon analog IV, triphenylgermyl triphenylgermanecarboxylate rearranges at elevated temperatures to yield hexaphenyldigermoxane (IX) and carbon monoxide. Hence a close analogy exists between the behavior of triphenylsilanecarboxylic acid and triphenylgermanecarboxylic acid in so far as their thermal decompositions are concerned.

Further examples of the 1,2-rearrangements described above include methyl triphenylsilanecarboxylate and methyl triphenylgermanecarboxylate which, at elevated temperatures, lose carbon monoxide and form triphenylmethoxysilane and trimethoxygermane, respectively, in high yields.

It seems reasonable to conclude, on the basis of the examples described, that similar 1,2-rearrangements will occur with all α -silane- and germanecarboxylic acids and their derivatives. It is interesting to observe, despite the fact that bonds to germanium are generally somewhat weaker than the corresponding bonds to silicon,⁶ that triphenylgermanecarboxylic acid and its derivatives are somewhat more stable toward thermal rearrangement than are its silicon analogs, higher temperatures being required to cause elimination of carbon monoxide. This is presumably due to decreased steric strain in the germanium compounds.

Further studies of these compounds are being carried out with the aim of establishing the mechanism of these interesting rearrangements.

Experimental⁷

All thermal rearrangements were carried out in glass tubes made of 5–8 mm. diameter Pyrex tubing about 15 cm. long, sealed at one end. These tubes were placed in a liquid melting-point bath so that the level of the liquid came well above the level of the solid in them. The temperatures reported at which decomposition occurred may not coincide exactly with the reported melting point of the compound, since the rate of heating and the thickness of the glass walls unavoidably introduced some thermal lag.

Carbon monoxide was detected by its reaction with filter paper moistened with a dilute (2–3%) palladium chloride solution. The paper rapidly turns black in the presence of carbon monoxide.⁸

Formic acid was identified by its color reaction with chromotropic acid, subsequent to reduction with magnesium and dilute hydrochloric acid,⁹ as well as by its characteristic sharp odor.

The results of the thermal rearrangements of the various compounds are summarized in Table I. Further details will be found below. Table II summarizes the results of a number of experiments involving mixtures of compounds

and various miscellaneous reactions required as background evidence.

Thermal Decomposition of Triphenylsilanecarboxylic Acid.—When 0.04 g. (0.00182 mole) of triphenylsilanecarboxylic acid in a glass tube connected to a mercury-filled gas buret was heated to 180–190°, decomposition occurred and 9.80 ml. (0.00040 mole, 30.4%) of carbon monoxide,⁸ measured at 25° and 758 mm. was liberated. No carbon dioxide could be detected in the gas. Liquid which collected on the walls of the tube gave a strong test for formic acid,⁹ but treatment of it with anhydrous copper sulfate gave the same pale blue color as with 99% formic acid, so that the presence of water is open to question.

Recrystallization of the melt in the tube from petroleum ether (b.p. 90–100°) yielded 0.22 g. (0.00041 mole, 62%) of hexaphenyldisiloxane, m.p. 219–222°, and 0.15 g. (0.00049 mole, 37%) of triphenylsilyl formate, m.p. 67–69°, both identified by mixed melting point. Results from additional experiments are listed in Table I.

Essentially the same results were obtained when the thermal decarbonylation was carried out in the presence of 0.4 mole equivalents of triphenylsilanol, indicating that this compound did not noticeably influence the course of the reaction.

When 0.2 g. (0.00066 mole) of triphenylsilanecarboxylic acid was refluxed in toluene carbon monoxide was eliminated over a 3-hour period. When worked up, 0.11 g. (55%) of triphenylsilyl formate, m.p. 67–70°, and 0.05 g. (27%) of triphenylsilanol, m.p. 149–151°, were recovered.

Triphenylsilyl Formate.—Silver formate was prepared in the dark from silver nitrate and sodium formate. A mixture of 5.5 g. (0.036 mole) of dry silver formate and 9.8 g. (0.035 mole) of triphenylchlorosilane in 50 ml. of dry benzene was stirred for 44 hours in the dark, and then worked up to yield, after recrystallization from petroleum ether (b.p. 60–70°), 8.38 g. (83%) of triphenylsilyl formate, m.p. 68.5–70°.

Anal. Calcd. for $\text{C}_{19}\text{H}_{15}\text{O}_2\text{Si}$: Si, 9.23. Found: Si, 9.19, 9.24.

The compound was readily hydrolyzed in air or in water or dilute base to yield triphenylsilanol and formic acid. It failed to decompose when heated to 220°. When mixed with an equal weight of triphenylsilanol and heated to 220° the mixture softened at 80° and was a clear liquid at 160°, but on working up the melt 88% of the triphenylsilanol and 65% of triphenylsilyl formate were recovered, and no other products were detected.

Triphenylsilyl Triphenylsilanecarboxylate.—A solution of 1.0 g. (0.0033 mole) of triphenylsilanecarboxylic acid in 20 ml. of benzene was added to 0.97 g. (0.0033 mole) of triphenylchlorosilane and 0.4 ml. (0.005 mole) of dry pyridine in 5 ml. of warm benzene. Pyridine hydrochloride slowly precipitated and after 15 minutes was removed (0.32 g., 84%). The clear filtrate was evaporated to dryness under reduced pressure and the resulting solid was recrystallized from chloroform–petroleum ether (b.p. 60–70°) to yield 0.19 g. (19%) of recovered acid, and 0.94 g. (51%) of triphenylsilyl triphenylsilanecarboxylate, m.p. 114–126° with carbon monoxide⁸ evolution, which after recrystallization melted at 133–134°.

Anal. Calcd. for $\text{C}_{37}\text{H}_{30}\text{O}_2\text{Si}_2$: Si, 9.99. Found: Si, 9.88, 10.01.

If the above reaction was refluxed, the yield of product was decreased—4 hours reflux in the absence of pyridine led to a 60% recovery of the parent acid.

Treatment of 0.10 g. (0.00018 mole) of the ester in 5 ml. of ethanol and 1 ml. of 10% aqueous sodium hydroxide led to rapid evolution of carbon monoxide,⁸ and 0.095 g. (97%) of triphenylsilanol, m.p. 148–151°, was isolated when the reaction mixture was worked up.

When 0.15 g. (0.00027 mole) of the ester was heated above its melting point, it melted at 133°, evolving carbon monoxide, resolidified by 150°, and remelted at 180°. When the melt was worked up the only product isolated was 0.14 g. (98%) of hexaphenyldisiloxane, m.p. 223–225°.

Attempts to prepare the ester by heating together mixtures of triphenylsilanol and triphenylsilanecarboxylic acid (Table II) failed. Miscellaneous experiments are listed in Table II which demonstrate that under the conditions of the reaction, triphenylsilanol is not converted to hexaphenyldisiloxane, and that mixtures of triphenylsilyl formate and triphenylsilanecarboxylic acid do not react with each other.

(6) M. L. Huggins, *THIS JOURNAL*, **75**, 4123 (1953).

(7) All melting points have been corrected against reliable standards.

(8) R. Nowicki, *Chem. Z.*, **35**, 1120 (1911).

(9) F. Feigl, "Qualitative Analysis by Spot Tests," Nordemann Publishing Co., Inc., New York, N. Y., 1939, p. 329.

TABLE I

THERMAL REARRANGEMENTS OF ORGANOSILICON AND ORGANOGERMANIUM COMPOUNDS, $R_3M-\overset{\text{O}}{\parallel}{C}-O-R'$, $R = C_6H_5$				
M	OR'	Temp., °C. ^a	Products and yields (%)	Remarks
Si	OH	190	CO (30), R_6Si_2O (62), $R_3SiOOCH$ (37), HCOOH	
Si	OH	190	R_6Si_2O (19), R_3SiOH (22), $R_3SiOOCH$ (38), CO, HCOOH	
Si	OH	110	R_3SiOH (27), $R_3SiOOCH$ (55), CO	Refluxed in toluene for 3 hr.
Si	OSiR ₃	133-180	CO, R_6Si_2O (98)	Resolidified 150°, remelted 180°
Si	OCH ₃	150-230	CO, R_3SiOMe (72)	
Ge	OH	200	CO, $R_3GeCOOGeR_3$ (92), H ₂ O	
Ge	OGeR ₃	200-250	CO, R_6Ge_2O (69), $R_3GeCOOGeR_3$ (27 recovered)	
Ge	OMe	250	CO, R_3GeOMe (73)	

^a A temperature range denotes decomposition temperature and maximum temperature.

TABLE II
MISCELLANEOUS REACTIONS OF ORGANOSILICON AND ORGANOGERMANIUM COMPOUNDS
 $R = C_6H_5$

Compd(s). and molar ratio	Temp., °C. ^a	Products and yields (%)	Remarks
$R_3SiCOOH$	190	R_6Si_2O (57), $R_3SiOOCH$ (40), CO, HCOOH	Identical conditions to
$R_3SiCOOH + R_3SiOH$ (1:0.4)	190	R_6Si_2O (46), $R_3SiOOCH$ (50), R_3SiOH (94 recovered), CO, HCOOH	show independence of reaction to R_3SiOH
$R_3SiCOOH + R_3SiOH$ (1:1)	125	R_3SiOH (78, of total moles of reagents), CO	
$R_3SiOOCH$	220	$R_3SiOOCH$ (74 recovered)	No CO or HCOOH
$R_3SiOOCH + R_3SiOH$ (1:1)	200	$R_3SiOOCH$ (65 recovered), R_3SiOH (88 recovered)	
R_3SiOH	200	R_3SiOH (89 recovered)	
$R_3SiOH + HCOOH$ (1:1.5)	240	R_3SiOH (76 recovered)	
$R_3SiOH + HCOOH$	80	R_3SiOH (62 recovered), R_6Si_2O (21)	Refluxed in benzene for 10 min.
$R_3SiCOOH + R_3SiOOCH$ (1:1)	105	$R_3SiCOOH$ (80 recovered), $R_3SiOOCH$ (55 recovered)	
$R_3SiCOOH + R_3SiOOCH$ (1:1)	127-160	HCOOH (17), R_6Si_2O (80, based on acid), $R_3SiOOCH$ (80 recovered), CO	
$R_3GeCOOH + R_3GeOH$ (1:1)	157	$R_3GeCOOGeR_3$ (84), H ₂ O	
R_3GeOMe	250	R_3GeOMe (90+)	
R_3GeOMe	230	R_6Ge_2O (60+), R_3GeOMe	Hydrolysis due to moisture in solvents

^a A temperature range denotes decomposition temperature and maximum temperature.

Triphenylgermyl Triphenylgermanecarboxylate.—An intimate mixture of 0.032 g. (0.0001 mole) of triphenylgermanol⁴ and 0.035 g. (0.0001 mole) of triphenylgermanecarboxylic acid⁴ was heated slowly to 157° to give a clear liquid. No gas was evolved and the liquid which collected on the walls of the tube was shown to be water with anhydrous copper sulfate. Recrystallization of the melt from benzene-petroleum ether (b.p. 60-70°) yielded 0.055 g. (84%) of triphenylgermyl triphenylgermanecarboxylate, m.p. 161-163°, identified by mixed melting point.

When 0.15 g. (0.00023 mole) of the ester was heated slowly to 250°, it melted at 165°, and evolved carbon monoxide⁸ over the range 200-245° during 15 minutes. Recrystallization of the residue yielded 0.10 g. (69%) of hexaphenyldigermoxane, m.p. 179-181°, and 0.04 g. (27%) of recovered ester, m.p. 161-163°.

Thermal Decomposition of Methyl Triphenylgermanecarboxylate.⁴—A 0.31-g. (0.0086 mole) sample of the ester was heated to 250°. Melting occurred at 110° and evolution of carbon monoxide⁸ started slowly at 210° and accelerated up to 250°. After 20 minutes at 250°, gas evolution ceased, and the melt was worked up to yield, after recrystallization from petroleum ether (b.p. 60-70°), 0.21 g. (73%) of triphenylmethoxygermane, m.p. 66-67°, identified by mixed melting point with an authentic sample.

Triphenylmethoxygermane.—A solution of 0.64 g. (0.028 g. atom) of sodium in 200 ml. of anhydrous methanol was treated with 10.5 g. (0.027 mole) of triphenylbromogermane. The solution was kept at room temperature for 18 hours,

the solvent was removed under reduced pressure, and the resultant solid, m.p. 59-62°, was recrystallized from petroleum ether (b.p. 60-70°) to yield 8.9 g. (97%) of triphenylmethoxygermane, m.p. 66-67°.

Anal. Calcd. for $C_{19}H_{18}OGe$: Ge, 21.6. Found: Ge, 20.9, 21.3.

It was found¹⁰ that triphenylmethoxygermane was very susceptible to hydrolysis, even by moist air. When 0.5 g. of finely powdered triphenylmethoxygermane was left exposed to the air for 3 hours the melting point changed from 66 to 156°. Recrystallization from petroleum ether (b.p. 60-70°) gave 0.40 g. (83%) of pure hexaphenyldigermoxane, m.p. 178-180°, identified by mixed melting point. When 0.1 g. of triphenylmethoxygermane was dissolved in 10 ml. of commercial absolute ethanol and the solvent was immediately removed, hexaphenyldigermoxane was quantitatively isolated.

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(10) Studies by H. M. Barrett of this Laboratory.