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

Thermal Rearrangement of Silanecarboxylate Esters[1]

BY A. G. BROOK AND R. J. MAURIS

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The mechanism of the thermal rearrangement of the esters of triarylsilanecarboxylic acids has been investigated by studying the products formed when mixtures of two esters were simultaneously decarbonylated. The reaction is essentially intramolecular, and its mechanism is described in terms of a cyclic three-membered intermediate. Tri-*p*-tolylsilanecarboxylic acid and its methyl and ethyl esters have been prepared.

The evolution of carbon monoxide at or slightly above the melting point appears to be a characteristic property of silanecarboxylic and germanecarboxylic acids and esters. This thermal instability and the attendant rearrangement, as exemplified by triphenylsilanecarboxylic acid,[2,3] triphenylgermanecarboxylic acid,[4] and their esters,[2] appeared to us to be worthy of investigation.

Since the thermal decompositions of the parent acids are complex, as evidenced by the multiplicity of products formed,[2,4] they are obviously not suitable for mechanistic studies. On the other hand, the rearrangements of the esters of triarylsilanecarboxylic acids appear to be extremely clean reactions in which only carbon monoxide and a single rearrangement product are formed, as illustrated by the results given in Table I.

TABLE I

THERMAL REARRANGEMENTS OF SILANECARBOXYLATE ESTERS

Ester	Temp., °C.[a]	Product	Yield, %
Ph$_3$SiCO-OMe	150–230	Ph$_3$SiOMe	98[b]
Ph$_3$SiCO-OEt	122–185	Ph$_3$SiOEt	98
Ph$_3$SiCO-OSiPh$_3$	133–180	Ph$_3$SiOSiPh$_3$	98
p-Tol$_3$SiCO-OMe	140–220	*p*-Tol$_3$SiOMe	98[c]
p-Tol$_3$SiCO-OEt	135–230	*p*-Tol$_3$SiOEt	92

[a] Temperature range over which carbon monoxide was liberated. [b] Yield, after recrystallization of the slightly low-melting material, was 72%. [c] Yield, after recrystallization of the slightly low-melting material, was 50%.

Due to the elevated temperatures at which thermal rearrangement or decarbonylation occurs the kinetics of the reaction cannot be studied readily. However it was felt that an investigation of the products formed when a mixture of two esters was subjected to rearrangement should reveal whether the process was intra- or intermolecular. If the process was intramolecular, the rearrangement would necessarily involve the migration of the alkoxyl group from the carbonyl group to the silicon atom in the same molecule. Hence, from a mixture of two esters only the two corresponding alkoxysilanes would be produced.

$$R_3SiCOOR' + R^{\circ}_3SiCOOR'' \longrightarrow R_3SiOR' + R^{\circ}_3SiOR'' + 2CO$$

On the other hand, an intermolecular process would involve some sort of complex of two or more molecules in which the alkoxyl group from one ester molecule would migrate to the silicon atom of a second molecule. Taking into account the different possible complexes, a mixture of two esters should yield four different alkoxysilanes, of which two would be the same as produced by an intramolecular process, and two would be "mixed" products, each containing a part of both original ester molecules.

$$2R_3SiCOOR' + 2R^{\circ}_3SiCOOR'' \longrightarrow R_3SiOR' + R^{\circ}_3SiOR'' + R_3SiOR'' + R^{\circ}_3SiOR' + 4CO$$

The four products from an intermolecular process should be formed in approximately equal yields, provided that the steric requirements and rates of decomposition of the individual esters were comparable. If these factors differed significantly, the mixed products, which distinguish the intermolecular from the intramolecular process, might be absent or present only in small amounts. It would be expected that the steric requirements of the methyl and ethyl esters of triphenyl- and tri-*p*-tolylsilanecarboxylic acids would be about the same since their structural differences are remote from the site of reaction. Approximate rate studies indicated that these esters also rearranged at about the same rate. Hence, with these esters, it would be expected that if the rearrangement was an intermolecular process all four products would be formed in approximately equal yields. This is less likely, however, in reactions involving triphenylsilyl triphenylsilanecarboxylate which probably has different steric requirements, and which was found to decarbonylate more rapidly than the other esters.

Investigation of the decarbonylation products of a number of pairs of esters (Table II) indicated that the rearrangement occurred predominantly by an intramolecular path.

TABLE II

PRODUCTS AND YIELDS FROM MIXED ESTER REARRANGEMENTS

Run	Esters	Products	Yield, % Crude	Pure
1	Ph$_3$SiCOOMe	Ph$_3$SiOMe	69	54
	p-Tol$_3$SiCOOEt	*p*-Tol$_3$SiOEt	82	58
2	Ph$_3$SiCOOMe	Ph$_3$SiOMe	85	74
	p-Tol$_3$SiCOOEt	*p*-Tol$_3$SiOEt	77	56
3	Ph$_3$SiCOOEt	Ph$_3$SiOEt		73
	p-Tol$_3$SiCOOMe	*p*-Tol$_3$SiOMe	73	43
4	Ph$_3$SiCOOSiPh$_3$	Ph$_3$SiOSiPh$_3$		96
	p-Tol$_3$SiCOOMe	*p*-Tol$_3$SiOMe	60	
5	Ph$_3$SiCOOSiPh$_3$	Ph$_3$SiOSiPh$_3$		97
	p-Tol$_3$SiCOOEt	*p*-Tol$_3$SiOEt		92
		p-Tol$_3$SiOSiPh$_3$		0.6

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[1] Presented in part before the Division of Organic Chemistry at the 39th Conference of the Chemical Institute of Canada, Montreal, May, 1956.

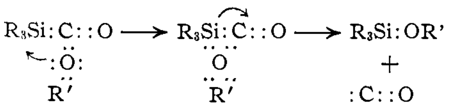
[2] A. G. Brook, THIS JOURNAL, **77**, 4827 (1955).

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

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

In runs 1–3, employing esters where steric and rate effects should be absent, the only products isolated were those expected from intramolecular rearrangement. Unfortunately these alkoxysilanes were extremely soluble, low-melting solids which readily oiled in the presence of traces of impurity, so that the recoveries were far from quantitative. For this reason, "crude" yields, *i.e.*, identified but slightly low-melting material, are included to give a more adequate demonstration of the recoveries of products. In runs 4 and 5, the products were isolated more easily and in higher yield. In these runs, however, the exclusive formation of these products was probably favored by the more rapid decomposition of triphenylsilyl triphenylsilanecarboxylate. In run 5 a trace of the mixed product 1,1,1-triphenyl-3,3,-3-tri-*p*-tolyldisiloxane was isolated, indicating that intermolecular rearrangement occurred to a slight extent (0.6%).

Since the thermal rearrangement is essentially an intramolecular process, it can be depicted as occurring through a three-membered cyclic intermediate formed by attack of the most electronegative atom, oxygen, of the trilogy silicon–carbon–oxygen, on the least electronegative atom, silicon. Subsequent release of electrons to the carbonyl group results in its evolution as carbon monoxide.



No exact analogy appears to be known in organic chemistry for these interesting rearrangements of α-silanecarboxylate esters, although the somewhat related loss of a carbonyl group as carbon monoxide from α-ethoxalyl esters has been reported.[5]

During the course of this work a number of new triarylsilicon compounds have been prepared by conventional methods. These are listed with their melting points, yields and silicon analyses in Table III.

TABLE III

ORGANOSILICON COMPOUNDS

Compound	M.p., °C.	Yield, %	Formula	Silicon, % Calcd.	Found
$Ph_3SiCOOEt$	98.5–100	82	$C_{21}H_{20}O_2Si$	8.47	8.51
p-$Tol_3SiCOOH$	162–163.5	69	$C_{22}H_{22}O_2Si$	8.11	7.89
p-$Tol_3SiCOOMe$	85–86	55	$C_{23}H_{24}O_2Si$	7.79	7.79
p-$Tol_3SiCOOEt$	84.5–85.5	78	$C_{24}H_{26}O_2Si$	7.50	7.45
p-Tol_3SiOMe	52–53	89	$C_{22}H_{24}OSi$	8.44	8.33
p-Tol_3SiOEt	51.5–52	80	$C_{23}H_{26}OSi$	8.11	8.15

Experimental[6]

Tri-*p*-tolylchlorosilane, Hexa-*p*-tolyldisilane and Tri-*p*-tolylsilanecarboxylic Acid.—Tri-*p*-tolylchlorosilane was prepared by treatment of 85.6 g. (0.50 mole) of silicon tetrachloride in 300 ml. of dry ether with 1.50 moles of *p*-tolyllithium in 1.5 l. of dry ether over 3 hours with efficient stirring and cooling. After 11 hours a negative Color Test I[7] was obtained. The pale yellow ether layer was separated from the insoluble white precipitate, the precipitate was washed with ether, and the combined ether layers were evaporated to dryness under reduced pressure. The residual solid was recrystallized from petroleum ether (b.p. 60–70°) to yield 100 g. (61%) of tri-*p*-tolylchlorosilane, m.p. 115–116°.

To prepare hexa-*p*-tolyldisilane, a mixture of 19.7 g. (0.058 mole) of tri-*p*-tolylchlorosilane in 90 ml. of dry xylene and 6.5 g. (0.28 g. atom) of sodium was refluxed for 22 hours. After cooling, the resulting solid was added to ethanol to remove excess sodium. Water was then added and the insoluble material was removed and recrystallized from benzene to yield 10.15 g. (58%) of hexa-*p*-tolyldisilane, m.p. 350–353°.

Tri-*p*-tolylsilanecarboxylic acid was prepared by cleavage of 3.0 g. (0.005 mole) of hexa-*p*-tolyldisilane with 1 ml. of 1:5 sodium–potassium alloy and just enough anhydrous ether to make a thick paste. The mixture was stirred and after 3 hours was of a pale yellow color. After 6 hours stirring, 75 ml. of dry ether was added to the green suspension and the reaction mixture was stirred for a total of 51 hours. The suspension was treated with mercury to remove excess alloy,[8] and was then poured onto excess powdered Dry Ice. After the excess carbon dioxide had evaporated, the resulting suspension was poured into 150 ml. of iced 1% hydrochloric acid. The ether layer was removed by evaporation in an air stream. The resulting suspension was filtered, the solid was washed with cold water, and then was dried under vacuum. The dry solid was dissolved in boiling benzene (15 ml. per g.) and, after filtration, the filtrate was diluted with one volume of petroleum ether (b.p. 60–70°). A total of 1.96 g. (56%) of tri-*p*-tolylsilanecarboxylic acid, m.p. 162–163.5° dec. precipitated, evolving carbon monoxide[9] at its melting point.

Alternatively, the acid could be prepared, in somewhat better yield, directly from tri-*p*-tolylchlorosilane and sodium–potassium alloy. It was necessary to use a large excess of the alloy to give a good yield of the tri-*p*-tolylsilylpotassium; otherwise, the product was contaminated with large amounts of hexa-*p*-tolyldisilane. When 3.37 g. (0.01 mole) of tri-*p*-tolylchlorosilane in 18 ml. of dry ether was stirred vigorously with 3 ml. of sodium–potassium alloy, with cooling, the system became violet-black and then dark green in 5 minutes. Two 25-ml. portions of dry ether were added within the next hour, and the mixture was stirred an additional 23 hours. After amalgamation, carbonation and separation of the solid as before, 3.4 g. of crude acid, m.p. 133–138°, was isolated. Recrystallization from benzene-petroleum ether (b.p. 60–70°) gave 2.4 g. (69%) of tri-*p*-tolylsilanecarboxylic acid, m.p. 162–163°.

Methyl and Ethyl Tri-*p*-tolylsilanecarboxylate.—To 1 g. (0.0032 mole) of tri-*p*-tolylsilanecarboxylic acid was added slowly excess diazomethane in ether. After nitrogen evolution had ceased (10 minutes) the solvent was removed under reduced pressure. The resulting solid, m.p. 79–81°, was recrystallized from petroleum ether (b.p. 40–60°) to yield 0.58 g. (55%) of methyl tri-*p*-tolylsilanecarboxylate, m.p. 85–86°.

The ethyl ester was similarly prepared using ethereal diazoethane and gave, after recrystallization from petroleum ether (b.p. 40–60°), a 78% yield of white crystals, m.p. 84.5–85.5°.

Esters of Triphenylsilanecarboxylic Acid.—Methyl triphenylsilanecarboxylate, m.p. 110–111°, was prepared as previously described,[10] as was triphenylsilyl triphenylsilanecarboxylate,[2] m.p. 133–134°. Ethyl triphenylsilanecarboxylate was prepared by treatment of the acid with ethereal diazoethane analogously to the preparation described above, to give, after recrystallization from petroleum ether (b.p. 60–70°), an 82% yield of white solid, m.p. 98.5–100°.

Alkoxysilanes.—Triphenylmethoxysilane, m.p. 54–55°, was prepared as previously described.[10] Triphenylethoxysilane was similarly prepared in 74% yield, m.p. 64–65°. Identical procedures using tri-*p*-tolylchlorosilane with sodium methoxide and sodium ethoxide gave, respectively, an 89% yield of tri-*p*-tolylmethoxysilane, m.p. 52–53°, and an 80% yield of tri-*p*-tolylethoxysilane, m.p. 51.5–52°. The mixed melting points of all possible pairs of these compounds were depressed, and melted in the range 25–40°.

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(5) E. E. Royals, "Advanced Organic Chemistry," Prentice–Hall, Inc., New York, N. Y., 1954, p. 810.

(6) All reactions involving organometallic reagents were carried out in a dry, oxygen-free nitrogen atmosphere. All melting points are corrected.

(7) H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

(8) H. Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953).

(9) R. Nowicki, *Chem. Ztg.*, **35**, 1120 (1911).

(10) A. G. Brook and H. Gilman THIS JOURNAL, **77**, 2322 (1955).

Thermal Rearrangements of Silanecarboxylate Esters. A. Individual Esters.—The following is typical of the method used in studying the thermal rearrangements of the individual esters; the results obtained are summarized in Table I.[11] In a dry glass tube 15 × 0.9 cm., sealed at one end, was placed 0.42 g. (0.00125 mole) of finely powdered ethyl triphenylsilanecarboxylate. The open end of the tube was connected to a mercury-filled gas buret. The tube was immersed above the level of the solid in an oil-bath, and the temperature was slowly raised. At 122° a slow evolution of gas began which became faster as the temperature rose to 185°, by which time (about 12 minutes) gas evolution had ceased. A total of 29.5 ml. (94%) of gas, measured at S.T.P., was evolved, and this was shown to be carbon monoxide by the palladium chloride test.[9] The tube contents were removed and this 0.39 g. (98%) of triphenylethoxysilane melted at 63–64°. Recrystallization from 95% ethanol failed to raise the melting point. A mixed melting point with an authentic specimen was not lowered.

B. Mixtures of Esters.—Equimolar amounts of the well-mixed, finely powdered esters were placed, either in a tube similar to that described above or in a 10 ml. flask to which was attached a 10 cm. Vigreaux column. The mixture of esters was either heated by an oil-bath fairly rapidly (10°/min.) to 200–250°, or else the mixture was plunged into the oil bath preheated to 200–250°. No appreciable difference was observed from either method of thermal rearrangement. After rearrangement, the reaction mixture was worked up; the following examples are illustrative.

Ethyl Tri-*p*-tolylsilanecarboxylate and Methyl Triphenylsilanecarboxylate.—A mixture of 2.7 g. (0.0072 mole) of ethyl tri-*p*-tolylsilanecarboxylate and 2.3 g. (0.0072 mole) of methyl triphenylsilanecarboxylic was placed in a small flask bearing a Vigreux column. The flask was plunged into a pre-heated bath at 205°. After 2 minutes, gas evolution began, and continued vigorously for 8 minutes, at which time it ceased. The liquid residue was distilled at 0.1 mm. pressure, and the following fractions (b.p., wt.) were collected: 1, 120–133°, 0.11 g.; 2, 133–138°, 0.58 g.; 3, 138–141°, 0.68 g.; 4, 141–143°, 0.78 g.; 5, 143–152°, 0.67 g.; 6, 152–160°, 0.60 g.; 7, 160–164°, 0.83 g.; 8, pot residue, 0.20 g. Fractions 1–4 were seeded with triphenylmethoxysilane; the first three crystallized completely; fraction 4 remained a mush. The combined fractions 1–3, 1.37 g. (66%), melted at 53–55°, and a mixed melting point with authentic triphenylmethoxysilane, m.p. 54–55°, was not depressed. The mixed melting point of this material with any of the three other possible alkoxysilanes was a mush melting in the range 25–40°. Crystallization of the combined material from methanol yielded 1.14 g. (55%) of pure triphenylmethoxysilane, m.p. 54–55°, mixed melting point with an authentic sample undepressed. Fractional crystallization of fraction 4 from methanol eventually yielded an additional 0.40 g. (19%) of triphenylmethoxysilane, m.p. 52–54°, whose mixed melting point with authentic triphenylmethoxysilane was 53–55°, but whose mixed melting point with tri-*p*-tolylethoxysilane was lowered to 25–30°.

Fractions 5–8 were seeded with authentic tri-*p*-tolylethoxysilane; fractions 6–8 crystallized completely to yield a total of 1.63 g. (66%) of crude tri-*p*-tolylethoxysilane, m.p. 49–52°. The mixed melting point with authentic tri-*p*-tolylethoxysilane (m.p. 51.5–52°) was 51–52°; the mixed melting points with any of the other three possible alkoxysilanes were lowered to about 25–40°. Crystallization of the combined fractions 6–8 from absolute ethanol yielded 1.08 g. (44%) of pure tri-*p*-tolylethoxysilane, m.p. and mixed m.p. with an authentic specimen each 51–52°.

Fraction 5 after seeding partially crystallized. Fractional crystallization from absolute ethanol eventually yielded an additional 0.29 g. (12%) of pure tri-*p*-tolylethoxysilane, m.p. 49–51°, identified by mixed melting point with an authentic specimen.

The total combined yields of pure material were: triphenylmethoxysilane, 74%; tri-*p*-tolylethoxysilane, 56%. No other alkoxysilanes could be detected.

Triphenylsilyl Triphenylsilanecarboxylate and Ethyl Tri-*p*-tolylsilanecarboxylate.—A mixture of 1.69 g. (0.003 mole) of triphenylsilyl triphenylsilanecarboxylate and 1.12 g. (0.003 mole) of ethyl tri-*p*-tolylsilanecarboxylate were mixed well and placed in a small flask, which was plunged into an oil-bath preheated to 200°. The temperature was raised to 220° and maintained for about 10 minutes, by which time gas evolution had ceased. On cooling the flask contents solidified. The solid was triturated with 6 ml. of cold petroleum ether (b.p. 60–70°), and the mixture filtered to yield 1.53 g. (96%) of hexaphenyldisiloxane, m.p. 226–227.5°, identified by mixed melting point with an authentic specimen. An additional 0.02 g. (1%) of hexaphenyldisiloxane was obtained on evaporation of the petroleum ether filtrate, m.p. 225–227°; total yield of hexaphenyldisiloxane 97%. A trace of material, 0.01 g. (0.6%) melting at 153–160°, next precipitated. After recrystallization from absolute ethanol the white solid melted at 163–165°, and a mixed melting point with authentic 1,1,1-triphenyl-3,3,3-tri-*p*-tolyldisiloxane, m.p. 164–165°, melted at 163–165°.[12]

The petroleum ether filtrate was further evaporated, and the residue was dissolved in absolute ethanol and seeded with authentic tri-*p*-tolylethoxysilane. A total of 0.95 g. (92%) of tri-*p*-tolylethoxysilane, m.p. 50–51.5°, was isolated. A mixed melting point with authentic tri-*p*-tolylethoxysilane was not depressed, but the mixed melting point with triphenylethoxysilane was depressed to 30–35°.

Relative Rates of Thermal Decomposition.—A rough estimate of the relative rates of rearrangement of the various esters used above was determined as follows: (a) by observing the total time required for carbon monoxide to be eliminated when samples of each pure ester were plunged into an oil-bath preheated to 200°, and (b) by observing the total time in minutes required for carbon monoxide to be eliminated when individual samples of the esters were heated from 30 to 210°. In neither study were the times closely reproducible, and the results reported from method (a) are ranges, in minutes, of three or more determinations.

Ester	Method (a) time, min.	Method (b) time, min.
$Ph_3SiCOOMe$	5–7.5	12
$Ph_3SiCOOEt$	4–6	11
p-$Tol_3SiCOOMe$	4–6.5	12
p-$Tol_3SiCOOEt$	4–6	10
$Ph_3SiCOOSiPh_3$	1–2	2–12[a]

[a] After 2 min. CO evolution slowed down, a solid having formed. After 12 min. this solid melted, and additional CO was liberated.

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TORONTO, CANADA

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(11) See also ref. 2.

(12) We are indebted to Dr. Henry Gilman, Iowa State College, for supplying an authentic specimen of this material.