[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Thermal Stability of Triphenylsilane, Di- and Tri(aralkyl)silanes, Dibenzylmethane, and Tribenzylmethane

HENRY GILMAN, RICHARD A. TOMASI, AND DIETMAR WITTENBERG

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The thermal stabilities were tested by heating in partially evacuated sealed Pyrex tubes for 24 hr. at approximately 300°. Tribenzylsilane was found to be very stable under these conditions. The other organosilanes tested disproportionated to some extent. Of the di(aralkyl)silanes, dibenzylsilane appeared to be the most stable. Tribenzylmethane was found to be less stable than tribenzylsilane; however, dibenzylmethane proved to be somewhat more stable than dibenzylsilane. The results of isoteniscope studies on dibenzylsilane, dibenzylmethane, tribenzylsilane, and tribenzylmethane nearly parallel those obtained from the sealed tube reactions. The preparations of (β-phenylethyl)silane, di(β-phenylethyl)silane, and di(γ-phenylpropyl)silane are described.

Recently, it was reported that diphenylsilane undergoes a disproportionation reaction when heated in the absence of any added catalyst[1] (Reaction 1). Ethyl-, diethyl- and triethylsilanes

$$(C_6H_5)_2SiH_2 \longrightarrow SiH_4 + C_6H_5SiH_3 + (C_6H_5)_2SiH_2 + (C_6H_5)_3SiH + (C_6H_5)_4Si \quad (1)$$

have also been observed to undergo disproportionation and decomposition when heated in sealed tubes at temperatures in excess of 400°.[2]

Many Lewis acid- catalyzed redistribution reactions of organosilicon compounds may be found scattered throughout the literature. Only within the last few years has interest turned toward disproportionation reactions of compounds containing silicon hydrogen bonds.[3]

This study was primarily concerned with the effects of heating some organosilicon hydrides in partially evacuated sealed Pyrex tubes for 24 hr. at temperatures around 300°. The results of these experiments are summarized in Tables I and II of the Experimental. It is realized that the results of these thermal stability tests may be valid only under the specific reaction conditions used; however, the results obtained are significant in themselves and may apply to other conditions.

With one exception, all of the organosilanes underwent redistribution reactions. Tribenzylsilane, the one exception, was outstanding because it did not disproportionate to any appreciable extent, if at all, under the conditions employed.

Also, it is interesting to note that silane was not formed in detectable amounts in any of the pyrolysis reactions of aralkyl substituted silanes. This is quite contrary to the case of diphenylsilane.[1] There was, however, slight evidence of the formation of silane when triphenylsilane was heated.

Furthermore, in the case of dibenzylsilane,[4] another difference was observed; there was no indication of the formation of tetrabenzylsilane. Further data on the relative thermal stability of dibenzylsilane was obtained in another experiment in which dibenzylsilane was refluxed at 310±5° for 3 hr. on a vacuum line system under a pressure of about 500 mm. of nitrogen. In this experiment, there was no evidence of redistribution or decomposition of the dibenzylsilane.

The infrared spectra of the products obtained from heating di- and tri(*gamma*-phenylpropyl)-silanes contained an additional absorption band at 9.0 microns, indicative of silicon-phenyl bonds. It is believed that these products possibly contain rearranged and/or cyclized compounds.

In view of the uncommon thermal stability of tribenzylsilane and the relative stability of dibenzylsilane, as compared with diphenylsilane,[1] it was of interest to empirically compare the thermal stability of their carbon analogs under similar conditions, even though the modes of decomposition of the two classes of compounds may be quite different. Tribenzylmethane[5] was found to decompose slightly; a small amount of charring was detected, the heated material had a carbonaceous odor, its melting point was depressed 6°, and its infrared spectrum was not quite identical to that of the pure hydrocarbon. Recrystallization of the heated material led to a recovery of 92.2% of pure tribenzylmethane.

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(1) H. Gilman and D. H. Miles, *J. Org. Chem.*, **23**, 326 (1958).

(2) G. Fritz, *Z. anorg. u. allgem. Chem.*, **273**, 275 (1953).

(3) J. L. Speier and R. E. Zimmerman, *J. Am. Chem. Soc.*, **77**, 6395 (1955); S. N. Borisov, M. G. Voronkov, and B. N. Dolgov (Chem. Silicate Inst., Leningrad), *Invest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk*, **1957**, 1396; [*Chem. Abstr.*, **52**, 7136 (1958)]; B. N. Dolgov, S. N. Borisov, and M. G. Voronkov (State Univ., Leningrad), *Zhur. Obshcheĭ Khim.*, **27**, 709 (1957); [*Chem. Abstr.*, **51**, 16283 (1957)]; **27**, 2062 (1957); [*Chem. Abstr.*, **52**, 6160 (1958)]; Dow Corning Ltd. British Patent **663,810**, Dec. 27, 1951; [*Chem. Abstr.*, **46**, 1123 (1952)].

(4) Preparation described by H. Gilman and R. A. Tomasi, *J. Am. Chem. Soc.*, **81**, 137 (1959).

(5) Prepared according to the directions of G. A. Hill, M. H. Little, S. Wray, Jr., and R. J. Trimbey, *J. Am. Chem. Soc.*, **56**, 911 (1934), in an 80% yield. The reported yield was 70%.

The only indications of decomposition of dibenzylmethane after heating were a slight yellow coloration and a decrease in the refractive index by 0.0005. The infrared spectrum of the heated material was identical with that of pure dibenzylmethane. Distillation of the heated material yielded 96.9% of colorless dibenzylmethane boiling over a two-degree range.

Thus, it can be seen that tribenzylsilane is more thermally stable than tribenzylmethane and that dibenzylsilane is somewhat less stable than dibenzylmethane under the reaction conditions employed.

To obtain further data on the thermal stability of dibenzylsilane, dibenzylmethane, tribenzylsilane, and tribenzylmethane, these compounds were subjected to isoteniscopic studies. Dibenzylsilane gave no evidence of decomposition during the measurement, which was carried out over the temperature range between 83.7 and 304.5°. Similar results were obtained with dibenzylmethane over the temperature range of 69.0 to 303.5°. Furthermore, when the logarithms of the pressures were plotted against the reciprocals of the absolute temperatures for both dibenzylsilane and dibenzylmethane, nearly straight lines were obtained. In neither case did these plots exhibit a break, which indicates that the temperatures at which these compounds begin to decompose are above 300°.

Tribenzylsilane gave results similar to those obtained for dibenzylsilane and dibenzylmethane over the temperature range between 117.2 and 363.9°, with the exception that it turned slightly yellow during the measurement. A plot of $\log_{10}P$ *vs.* $1/T$ was also nearly a straight line which did not show a break, again indicating that the decomposition temperature of tribenzylsilane had not been reached during the determination. Tribenzylmethane also yellowed slightly during the isoteniscopic measurement which covered the temperature range of 121.8 to 364.1°. Furthermore, the plot of $\log_{10}P$ *vs.* $1/T$ was nearly a straight line which exhibited a break at 349°, indicating thermal decomposition began at that temperature.

Thus, the results of the isoteniscopic measurements on dibenzylsilane, dibenzylmethane, tribenzylsilane, and tribenzylmethane nearly parallel the results obtained from the other thermal stability tests on these compounds.

EXPERIMENTAL[6]

General procedures for pyrolysis reactions. The reactions were carried out in Pyrex Schlenk tubes of approximately 50 ml. volume, which were dried in an oven,[7] flushed with oxygen-free, dry nitrogen, charged with the sample to be tested, evacuated, filled again with nitrogen, evacuated again to pressures varying from 1 to 10 mm., and sealed. The sealed tubes were heated slowly in an oil bath to the reported temperatures (temperature of the oil bath) for 24 hr.

The tubes were allowed to cool to room temperature and were then cooled in a Dry Ice–acetone bath before opening. The tubes were examined for the presence of silica which would be indicative of the combustion of silane formed during the reaction. Infrared spectra were run on all reaction mixtures; melting points or refractive indices were also determined. With the exceptions of tribenzylsilane and tribenzylmethane, which were recrystallized from petroleum ether (b.p. 60–70°), the products were distilled under reduced pressure. Identification of all pyrolysis products was made by comparisons of infrared spectra with those of authentic samples; in the case of liquids, refractive indices, and in the case of solids, melting points and mixed melting points were also used for identifications. The results of these experiments are summarized in Tables I and II.

TABLE I

PYROLYSIS[a] OF DI(ARALKYL)SILANES

Compound	Types of Products, %			
	$RSiH_3$	R_2SiH_2	R_3SiH	R_4Si
$(C_6H_5CH_2)_2SiH_2$[b]	1[c]	20.2[d] 59.3[c,e]	0.4[c,e]	0
$(C_6H_5CH_2CH_2)_2SiH_2$	3[c]	13[d] 58.6[c]	10.5[c,f]	—[f]
$(C_6H_5CH_2CH_2CH_2)_2SiH_2$	—[g,h]	84[c,h]	2.8[c,h]	—[h,i]

[a] Heated in partially evacuated sealed tubes for 24 hr. at 310–320°. See Experimental for details. [b] Heated to 400° for 1 hr., cooled to and maintained at 310–320° for 23 hr. [c] Product not quite pure. [d] Pure product. [e] The distillation residue contained an additional 6.8% of a mixture of R_2SiH_2 and R_3SiH, from which the R_3SiH was isolated. [f] No products were isolated from the distillation residue. The infrared spectrum indicated the presence of some R_3SiH with a high probability of the presence of R_4Si. [g] A low boiling fraction containing 2.8% of a mixture of $RSiH_3$ and R_2SiH_2. [h] The infrared spectra contained an additional absorption band at 9.0 microns. [i] The distillation residue contained 3.5% of a yellow oil which appeared to be mainly R_4Si; however, the infrared spectrum indicated the presence of a small amount of R_3SiH.

TABLE II

PYROLYSIS[a] OF TRIPHENYLSILANE AND TRI(ARALKYL)SILANES

Compound	Types of Products, %			
	$RSiH_3$	R_2SiH_2	R_3SiH	R_4Si
$(C_6H_5)_3SiH$[b]	0.5	4.5	69	16
$(C_6H_5CH_2)_3SiH$	0	0	100[c]	0
$(C_6H_5CH_2CH_2)_3SiH$	Traces	5.8	72.5	8.5
$(C_6H_5CH_2CH_2CH_2)_3SiH$	Traces	2.5[d]	88.5	4.7

[a] Heated in partially evacuated sealed tubes for 24 hr. at 300–310°. See Experimental for details. [b] A small explosion occurred upon opening the tube, indicating the possible formation of SiH_4. No evidence in other reactions. [c] Melting point lowered by 0.5°. [d] Two fractions were obtained; n_D^{20} 1.5460 and n_D^{20} 1.5512 compared to n_D^{20} 1.5444 for di(*gamma*-phenylpropyl)silane. The infrared spectra of these fractions contained additional absorption bands at 8.0 and 9.0 microns.

Isoteniscopic studies (by A. Dobry).[8] Dibenzylsilane, dibenzylmethane, tribenzylsilane, and tribenzylmethane

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[6] Temperatures reported are uncorrected.

[7] In the cases of the tri(aralkyl)silanes and the hydrocarbons, before drying, the tubes were rinsed with dilute alkali and then with distilled water until the rinse water was neutral to litmus.

[8] The isoteniscopic measurements and calculations were made through the courtesy of Dr. Alan Dobry, Standard Oil Co. of Indiana, Whiting, Ind.

were tested on a conventional Smith-Menzies type isoteniscope. The temperatures were found with an iron-constantan thermocouple and a Rubicon Type 2745 portable precision potentiometer. Pressures were measured with an Ace Type C tilting McLeod gauge and a Wallace and Tiernan Type FA-135-173 manometer. The temperature ranges covered and the corresponding vapor pressures are listed in Table III.

TABLE III

TEMPERATURE RANGES AND CORRESPONDING VAPOR PRESSURES

	Temp., °C.		Vapor Pressure, Mm.	
Compound	Initial	Final	Initial	Final
Dibenzylsilane	83.7	304.5	1.10	794.6
Dibenzylmethane	69.0	303.5	0.17	776.7
Tribenzylsilane[a]	117.2	363.9	0.55	777.1
Tribenzylmethane[a]	121.8	364.1	0.13	780.7

[a] Slight yellowing of the sample occurred during the measurement.

Plots of $\log_{10}P$ *vs.* $1/T$ were nearly straight lines in all cases. Only in the case of tribenzylmethane did the plot exhibit a break, which was at 349°.

The data obtained from the isoteniscopic studies were fitted to the regression equation $\log_{10}P\ (\text{mm.}) = -A/T(°\text{K.}) + C$. The values of A and C, as well as Lv, the latent heat of vaporization, were calculated and are tabulated in Table IV.

TABLE IV

CONSTANTS CALCULATED FROM ISOTENISCOPE DATA

	Dibenzylsilane[a]	Dibenzylmethane[b]	Tribenzylsilane[c]	Tribenzylmethane[d]
A	2926	3211	4280	4128
C	7.94	8.49	9.61	9.26
Lv (K cal./mole)	13.4	14.7	19.6	18.9

[a] Points below 3.1 mm. were left out of this calculation. [b] Only the observation at 0.17 mm. was rejected. [c] Points below 2.1 mm. were rejected. [d] Points below 1.47 mm. and above 497.7 mm. were rejected.

Refluxing of dibenzylsilane. In a dry 25 ml., round-bottomed flask, equipped with a reflux condenser was placed 0.85 g. (0.004 mole) of dibenzylsilane, n_{D}^{20} 1.5742. This was attached to a vacuum line system and cooled with a liquid nitrogen bath. The system was evacuated and filled with nitrogen to a pressure of *ca.* 500 mm. The dibenzylsilane was heated to 310 ± 5° for 3 hr. and cooled to room temperature. The heated material, 0.84 g. (98.0%), had a refractive index and infrared spectrum identical to those of the starting material.

Di(β-phenylethyl)silane.[9] A solution of 0.1 mole of β-phenylethylmagnesium bromide in 100 ml. of tetrahydrofuran was added rapidly to 13.6 g. (0.1 mole) of (β-phenylethyl)silane (see next experiment), and stirred overnight. The reaction mixture was hydrolyzed by the slow addition of 50 ml. of 5% hydrochloric acid. The work-up consisted of separating the aqueous layer from the organic layer, washing it twice with 75-ml. portions of ether, drying the combined organic layer and ether washings over sodium sulfate, filtering, removal of the solvents by distillation, and distilling the products under reduced pressure. Di(β-phenylethyl)silane, 15.4 g. (64.3%), was collected at 140–144° (0.9–0.95 mm.), n_{D}^{20} 1.5562, D_4^{20} 0.9728.

Anal. Calcd. for $C_{16}H_{20}Si$: Si, 11.68; MR$_{\text{D}}$, 79.56. Found: Si, 11.55, 11.58; MR$_{\text{D}}$, 79.47.

(β-Phenylethyl)silane. To 13.5 g. (0.356 mole) of lithium aluminum hydride suspended in 100 ml. of sodium-dried ether was added 102 g. (0.426 mole) of β-phenylethyltrichlorosilane in 150 ml. of ether at a rate which maintained refluxing of the ether. The reaction mixture was refluxed for 16 hr., and hydrolyzed by pouring cautiously onto a mixture of cracked ice and 50 ml. of concentrated sulfuric acid. The work-up was the same as described in the previous reaction. Two fractions of (β-phenylethyl)silane were collected: 16.2 g. (26.9%), b.p. 82–85° (45–48 mm.), n_{D}^{20} 1.5122; and 20.4 g. (35.2%), b.p. 85–86° (48–49 mm.), n_{D}^{20} 1.5119, D_4^{20} 0.8815. The infrared spectra had absorption bands characteristic of silanes of the type $RSiH_3$.[10]

Anal. Calcd. for $C_8H_{12}Si$: Si, 20.61; MR$_{\text{D}}$, 46.12. Found: Si, 20.18, 20.23; MR$_{\text{D}}$, 46.48.

Di(γ-phenylpropyl)silane. γ-Phenylpropylmagnesium bromide, 0.97 mole in 1000 ml. of ether solution, was added to 75.4 g. (0.44 mole) of silicon tetrachloride in 100 ml. of ether at a rate which maintained refluxing. The reaction mixture was refluxed for 1 hr. and cooled to room temperature. The magnesium salts were removed by filtration under nitrogen pressure and washed with 300 ml. of ether. The combined filtrate and ether washings were added to 9.47 g. (0.25 mole) of lithium aluminum hydride suspended in 100 ml. of ether at a rate which maintained refluxing. The reaction mixture was refluxed for 2 hr., and worked up as described in the previous reaction. The products were distilled under a pressure of 25 mm. until the temperature of the distillate was 100°. The infrared spectrum of this low-boiling material indicated the presence of (γ-phenylpropyl)silane. The distillation was continued at a lesser pressure to give 58.5 g. (49.2%) of di(γ-phenylpropyl)silane, b.p. 139–145° (0.2–0.3 mm.), n_{D}^{20} 1.5445. A portion of this material was redistilled and was collected at 153–154° (0.55 mm.), n_{D}^{20} 1.5444, D_4^{20} 0.9530.

Anal. Calcd. for $C_{18}H_{25}Si$: Si, 10.46; MR$_{\text{D}}$, 88.82. Found: Si, 10.34, 10.24; MR$_{\text{D}}$, 88.98.

Dibenzylmethane (1,3-diphenylpropane). 1,3-Diphenyl-2-propanone, b.p. 142–146° (0.16 mm.), m.p. 36°, was reduced to the hydrocarbon by a Wolff-Kischner reaction using the modified, general procedure of Huang-Minlon[11] for other ketones. A mixture of 31.9 g. (0.15 mole) of the ketone, 20 g. (0.36 mole) of potassium hydroxide, 13.5 ml. of 95% hydrazine and 150 ml. of triethylene glycol was heated slowly to 140° over a period of 2 hr. The temperature was slowly raised to 190°, during which the aqueous distillate was removed by means of a take-off adapter on the reflux condenser. The reaction mixture was refluxed for 16 hr. and cooled to room temperature. The aqueous distillate and the reaction mixture were combined with 100 ml. of water and extracted four times with 50-ml. portions of ether. The combined ether extracts were washed twice with 100-ml. portions of water, dried over sodium sulfate, and filtered. The ether was removed by distillation and the product distilled under reduced pressure to give two fractions of dibenzylmethane: 4.81 g. (16.4%), b.p. 123–124° (1.7 mm.); and 22.92 g. (77.8%), b.p. 124° (1.7 mm.). The infrared spectra and physical constants of the two fractions were identical: n_{D}^{20} 1.5595,[12] D_4^{20} 0.9818.

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(9) The tetrahydrofuran used was dried by refluxing over sodium for at least 24 hr. and distilling, immediately before use, from lithium aluminum hydride. The reaction was carried out under an atmosphere of dry oxygen-free nitrogen.

(10) Unpublished studies.

(11) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

(12) Wide variations of the value for the refractive index of 1,3-diphenylpropane have been reported in the literature. However, a refractive index of n_{D}^{15} 1.5634 with a temperature dependence of 0.0008 per degree was reported by J. F. Sirks, *Rec. trav. chim.*, **62**, 193 (1943). His value, when corrected to 20°, is n_{D}^{20} 1.5594.

Anal. Calcd. for $C_{15}H_{16}$: MR_D, 64.80. Found: MR_D, 64.61.

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AMES, IOWA

[CONTRIBUTION FROM THE MATERIALS LABORATORY, WRIGHT AIR DEVELOPMENT CENTER]

Derivatives of Ferrocene. VI. Heteroannular Disubstitution of Ferrocene[1]

STANLEY I. GOLDBERG, DANA W. MAYO, MARTIN VOGEL, HAROLD ROSENBERG, AND MARVIN RAUSCH

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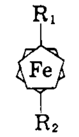
Confirmation of previous postulates regarding the steric course of two metalation reactions of ferrocene is presented. It is rigorously shown that treatment of ferrocene with *n*-butyllithium or with phenylsodium gives rise to 1,1′-dilithioferrocene or 1,1′-disodioferrocene, respectively. Dilithio- and disodioferrocene were converted to silyl derivatives which are identical to those obtained from reactions of correspondingly substituted cyclopentadienes and iron(II) chloride.

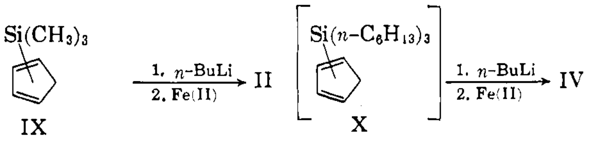
In a previous publication from this laboratory[2] some work concerning the metalation of ferrocene was described. Included in that report was the preparation of two silylferrocenes which were obtained from treatment of the reaction mixture of ferrocene and *n*-butyllithium with trimethylchlorosilane. Analytical values obtained from these products were consistent with a monosubstituted ferrocene, trimethylsilylferrocene (I), and a disubstituted ferrocene which was assigned the structure, 1,1′-bis(trimethylsilyl)ferrocene (II). The assignment had as its basis the absence of absorption near 9 and 10 μ in the infrared spectrum of the compound (9–10 Rule[3]).



	R_1	R_2
I.	$(CH_3)_3Si—$	H—
II.	$(CH_3)_3Si—$	$(CH_3)_3Si—$
III.	$(n\text{-}C_6H_{13})_3Si—$	H—
IV.	$(n\text{-}C_6H_{13})_3Si—$	$(n\text{-}C_6H_{13})_3Si—$
V.	Li—	H—
VI.	Li—	Li—
VII.	Na—	H—
VIII.	Na—	Na—

In the present study, treatment of the mixture of lithioferrocenes (V and VI) with tri-*n*-hexylbromosilane also yielded a mono- and disubstituted silylferrocene. The infrared spectra of both compounds, in this case, exhibited strong absorption at 9 and 10 μ. This observation, therefore, caused us to consider the correctness of the previous structural assignment for II.[2] The fact that the spectrum of tri-*n*-hexylbromosilane also showed strong absorption at 9 and 10 μ, could not, at first, be taken to mean that these bands were the ones present in the spectrum of IV since it was not possible to preclude the absence of 9–10 absorption due to the ferrocene nucleus of IV. Additional experimental work, however, conclusively showed both disubstituted silylferrocenes, II and IV, to possess heteroannular orientation; so that the absorption at 9 and 10 μ in the spectrum of IV was, in fact attributed to the substituents and not to a possible inconsistency with the 9–10 Rule.

The heteroannular locations of the silyl functions in II and IV were proven by synthesis of both compounds from the correspondingly substituted cyclopentadiene derivatives, IX and X.



Trimethylsilylcyclopentadiene (IX) was prepared according to the procedure reported by Frisch.[4] This material was treated with *n*-butyllithium followed by iron(II) chloride to yield 1,1′-bis(trimethylsilyl)ferrocene (II). The product gave rise to an infrared spectrum identical to that obtained from the disubstituted product previously prepared *via* lithiation of ferrocene.[2]

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[1] Presented before the Division of Organic Chemistry, 134th Meeting, ACS, Chicago, September 1958.

[2] M. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, **22**, 900 (1957).

[3] M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, **80**, 5443 (1958); *cf.* M. Rosenblum, doctoral dissertation, Harvard University 1953.

[4] K. C. Frisch, *J. Am. Chem. Soc.*, **75**, 6050 (1953).