Triphenyl-(β-benzenesulfonylethyl)-silane.—A solution of 2.73 g. (0.007 mole) of triphenyl-(β-benzenethioethyl)-silane, 53 ml. (0.47 mole) of 30% hydrogen peroxide and 90 ml. of glacial acetic acid was allowed to stand for 24 hours at room temperature and then refluxed for 45 minutes. On cooling, the pure sulfone crystallized from the solution.

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Analogs of Hexaphenylethane. I. Hexaaryldisilanes Containing Phenyl and *p*-Tolyl Groups

BY HENRY GILMAN AND T. C. WU[1]

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A complete series of ten hexaaryldisilanes containing phenyl and *p*-tolyl groups has been prepared. They were made by coupling a triarylsilylpotassium compound with a triarylchlorosilane; by treating a partially chlorinated organodisilane with an organolithium compound; or by coupling a triarylchlorosilane with sodium. Examination of these compounds shows that, in general, as the degree of symmetry of the disilane decreases the melting point decreases and the solubility increases. The possible dissociation of these hexaaryldisilanes is discussed.

It is known that hexaarylethanes dissociate to give triarylmethyl radicals. However, similar dissociation of hexaaryldisilanes have not been observed.[2,3] One of the difficulties in detecting the degree of dissociation of the hexaarydisilanes is due to the extremely small solubilities in ordinary organic solvents. Accordingly, we prepared a number of hexaaryldisilanes containing two kinds of aryl groups in different positions of the molecules in order to study their solubilities in relation to their structures. There are ten possible structures of hexaaryldisilanes containing phenyl and *p*-tolyl groups. Among them only the simple symmetrical hexaphenyl-[3] and hexa-*p*-tolyldisilane[4] have been described. These two compounds are high-melting solids having low solubilities in most organic solvents.

The new disilanes containing both phenyl and *p*-tolyl groups are lower melting solids with improved solubilities. In general, the less symmetrical the disilane is, the lower is the melting point and the higher is the solubility. Thus, while the simple symmetrical hexaphenyldisilane and hexa-*p*-tolyldisilane melt over 350°, the unsymmetrical 1,1,2-triphenyl-1,2,2-tri-*p*-tolyldisilane melts at 226–227°. It is interesting to observe that although the symmetrical tetraphenyldi-*p*-tolyldisilane has a higher melting point than the unsymmetrical isomer as one might have expected, the melting points of both the symmetrical and unsymmetrical diphenyltetra-*p*-tolyldisilanes are the same. Furthermore, a mixed melting point determination of these two diphenyltetra-*p*-tolyldisilanes showed no depression. The melting points of the hexaaryldisilanes are summarized in Table I.

No quantitative determinations of the solubilities of the hexaaryldisilanes were made in this investigation. However, the solubilities appear to increase with decreasing degree of symmetry of the disilanes. For example, hexaphenyldisilane is only moderately soluble in hot xylene while 1,1,2-triphenyl-1,2,2-tri-*p*-tolyldisilane is very soluble in benzene even at room temperature. The solubilities of these disilanes in various solvents are also given in Table I.

The hexaaryldisilanes described in this paper were prepared by methods outlined below.

$$2R'R''R'''SiCl + 2Na \longrightarrow (R'R''R''')_2Si_2 \quad (1)$$

$$R'R''R'''SiCl + R^{IV}R^{V}R^{VI}SiK \longrightarrow R'R''R'''SiSiR^{IV}R^{V}R^{VI} \quad (2)$$

$$R_3SiSiCl_3 + 3R'Li \longrightarrow R_3SiSiR_3' \quad (3)$$

$$R_3SiSiRCl_2 + 2R'Li \longrightarrow R_3SiSiRR'_2 \quad (4)$$

$$R_3SiSiR_2Cl + R'Li \longrightarrow R_3SiSiR_2R' \quad (5)$$

In the above equations the R's represent phenyl or *p*-tolyl groups, as the case may be. A few disilanes were prepared by two different methods to confirm their structures. Three new chlorine-containing organosilicon compounds were prepared in order to synthesize the disilanes. These are phenyldi-*p*-tolylchlorosilane, 1,1,1-triphenyl-2,2,2-trichlorodisilane and 1,1,1,2-tetraphenyl-2,2-dichlorodisilane. They were made according to the equations

$$C_6H_5SiCl_3 + 2p\text{-}CH_3C_6H_4Li \longrightarrow (C_6H_5)(p\text{-}CH_3C_6H_4)_2SiCl \quad (6)$$

$$(C_6H_5)_3SiK + SiCl_4 \longrightarrow (C_6H_5)_3SiSiCl_3 \quad (7)$$

$$(C_6H_5)_3SiK + C_6H_5SiCl_3 \longrightarrow (C_6H_5)_3SiSi(C_6H_5)Cl_2 \quad (8)$$

It was observed that the coupling reactions of triarylsilylpotassium compounds with triarylchlorosilanes give better yields than the reactions between an aryllithium compound with a partially chlorinated organodisilane such as pentaphenylchlorodisilane (compare Table I). This is probably due to the ease of cleavage of the chlorinated organodisilanes. The ease of cleavage of hexachlorodisilane has been observed previously. When octachlorotrisilane is treated with phenylmagnesium bromide the products obtained are hexaphenyldisilane and tetraphenylsilane instead of octaphenyltrisilane[4] although the trisilane can be prepared by the reaction of triphenylsilylpotassium with diphenyldichlorosilane.[5] We have also observed that a considerable amount of tetra-*p*-tolylsilane was formed when hexachlorodisilane was treated with *p*-tolyllithium.

The possible dissociation of the hexaaryldisilanes was studied by the treatment of 1,1,2-triphenyl-

(1) Eastman Kodak Company Predoctoral Fellow (1951–1952).
(2) H. Gilman and G. E. Dunn, THIS JOURNAL, 73, 5077 (1951).
(3) W. Schlenk, J. Renning and G. Rackey, *Ber.*, 44, 1178 (1911).
(4) W. C. Schumb and C. M. Saffer, THIS JOURNAL, 61, 363 (1939).
(5) H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman and S. H. Eidt, *ibid.*, 74, 561 (1952).

TABLE I

HEXAARYLDISILANES CONTAINING PHENYL AND *p*-TOLYL GROUPS

Disilane	Formula[a]	M.p., °C.	Method of preparation[b]	Reaction time,[c] hr.	Yield of pure product[d]	Silicon, % Calcd.	Silicon, % Found	Solv. for recrystallization[e]	Solubilities
Hexaphenyl	Y_3SiSiY_3	368–370	(1)	6	92[f]			Dioxane	Sol. hot tributyl phosphate, hot xylene and hot dioxane
			(2)	24	66[g]				
Pentaphenyl-*p*-tolyl	Y_3SiSiY_2Z	283–285	(5)	16	28	10.55	10.50, 10.47	Benzene	Sol. hot benzene; sl. s. hot acetone and hot pet. ether (b.p. 77–115°)
			(2)	5	77				
1,1,2,2-Tetraphenyl-1,2-di-*p*-tolyl	$Y_2ZSiSiY_2Z$	252–253	(1)	6	62	10.28	10.26, 10.28	Benzene	Sol. $CHCl_3$, hot benzene, hot dioxane, hot CCl_4
1,1,1,2-Tetraphenyl-2,2-di-*p*-tolyl	$Y_3SiSiYZ_2$	229–230	(4)	16	14	10.28	10.31, 10.33	Pet. ether	Sol. acetone, benzene, $CHCl_3$, CCl_4, hot pet. ether (b.p. 60–70°)
			(2)	4	72				
1,1,1-Triphenyl-2,2,2-tri-*p*-tolyl	Y_3SiSiZ_3	262–264	(2)	1	26	10.01	9.94, 9.94	Benzene–pet. ether	Sol. ether, benzene, hot acetone, hot pet. ether (b.p. 77–115°)
			(3)	6	11				
1,1,2-Triphenyl-1,2,2-tri-*p*-tolyl	$Y_2ZSiSiYZ_2$	226–227	(2)	2	52	10.01	9.92, 9.95	Benzene–ethanol	Sol. ether, acetone, benzene, $CHCl_3$, hot ethanol, hot pet. ether (b.p. 60–70°)
1,2-Diphenyl-1,1,-2,2-tetra-*p*-tolyl	$YZ_2SiSiYZ_2$	240–241	(1)	15	71	9.77	9.69, 9.76	Benzene–pet. ether	Sol. $CHCl_3$, hot pet. ether (b.p. 77–115°); sl. s. benzene
1,1-Diphenyl-1,2,2,-2-tetra-*p*-tolyl	$Y_2ZSiSiZ_4$	240–241	(2)	20	57	9.77	9.64, 9.65	Benzene–pet. ether	Sol. ether, benzene, acetone, chloroform, hot pet. ether (b.p. 60–70°)
Phenylpenta-*p*-tolyl	YZ_3SiSiZ_3	288–290	(2)	16	19	9.54	9.49, 9.50	Benzene	Sol. hot benzene, $CHCl_3$
Hexa-*p*-tolyl[h]	Z_6SiSiZ_6	354–356	[i]	20	30(31)			Toluene	Sol. hot dioxane, hot toluene
			[j]	16	28(32)				
			[k]	16	27(29)				
			[l]	16	0(42)				

[a] In this Table Y represents the phenyl group and Z the *p*-tolyl group. [b] The numbers in parentheses indicate the equation according to which the preparations were carried out. In all reactions between a triarylsilylpotassium compound and a triarylchlorosilane (equation 2) the excess sodium–potassium alloy had been removed from the reaction system by amalgamation procedure (see footnote 14) before the coupling reaction took place. [c] The reaction time for the last step of the synthesis, *i.e.*, the reactions indicated by the equations. [d] The numbers in parentheses indicate the yield of tetra-*p*-tolylsilane. [e] The petroleum ether used for recrystallization has the boiling range of 60–70°. [f] See footnote 14. [g] Prepared by coupling triphenylsilylpotassium with triphenylchlorosilane. [h] Hexa-*p*-tolyldisilane was prepared by Schumb and Saffer (see footnote 4) in 35% yield by adding hexachlorodisilane to *p*-tolylmagnesium bromide. There was no mention of tetra-*p*-tolylsilane. We prepared several batches of hexa-*p*-tolyldisilane by adding *p*-tolyllithium to hexachlorodisilane under various conditions. In all cases, practically equivalent amounts of hexa-*p*-tolyldisilane and tetra-*p*-tolylsilane were obtained. The yields of tetra-*p*-tolylsilane were based on the assumption that for one initial mole of hexachlorodisilane there is obtained one mole of tetra-*p*-tolylsilane. [i] A 10% excess of *p*-tolyllithium was added to hexachlorodisilane in ether at room temperature. [j] A 10% excess of *p*-tolyllithium was added to hexachlorodisilane in benzene at 0°. [k] A 20% excess of *p*-tolyllithium was added to hexachlorodisilane in ether at −65°. [l] An ethereal solution of hexachlorodisilane was added to *p*-tolyllithium solution at 0°. No hexa-*p*-tolyldisilane was isolated in this run.

1,2,2-tri-*p*-tolyldisilane and 1,1,2,2-tetraphenyl-1,2-di-*p*-tolyldisilane with iodine and with oxygen; hexaarylethanes have been found to react with these elements due to dissociation.[6] It was found that, under the experimental conditions, none of the disilanes reacts with oxygen or iodine despite the improved solubilities of these disilanes. These observations confirm previous results that some hexaaryldisilanes were unaffected by oxygen and iodine.[2,8]

The magnetic susceptibility measurements of one of the hexaaryldisilanes, 1,1,2-triphenyl-1,2,2-tri-*p*-tolyldisilane, show that the disilane is diamagnetic with a susceptibility of approximately -0.6×10^{-6} both for the solid and when the substance is in benzene solution.[7] The precision of these results is not sufficient to rule out a dissociation as high as 5% in benzene.[7]

The apparent lack of dissociation of hexaaryldisilanes is probably due to the small resonance stabilization of the triarylsilyl groups which necessitates a structure containing a silicon-to-carbon double bond, the contribution of which is considered to be small.[2] However, dipole moment measurements of trimethylaryl silanes favor the postulation of structures involving a double bond between a carbon and a silicon atom.[8] Perhaps one might say that structures containing silicon–carbon double bonds may form under certain favorable conditions, but the contribution of these structures in the hexaaryldisilanes appears to be too small to stabilize the triarylsilyl radical to any appreciable extent. Nevertheless, if the six aryl groups of the disilane (preferably an unsymmetrical one because of higher solubility) have very bulky ortho-substituted groups to increase the steric hindrance of the molecule, the chances of dissociation of the silicon–silicon bond may be appreciably increased. The bond energy of the silicon–silicon bond is considerably smaller than that of the carbon–carbon bond (Si–Si, 45 kcal./mole[9]; C–C, 80 kcal./mole[9]) and it has been shown that the silicon–silicon bond of some hexasubstituted disilanes can be easily cleaved by some reagents such as sodium–potassium alloy[10] or bromine.[11]

(6) See W. E. Bachmann in H. Gilman's "Organic Chemistry, An Advanced Treatise," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1943, Ch. 6.

(7) The authors are grateful to Professor P. W. Selwood of Northwestern University for the measurements of magnetic susceptibility of this compound.

(8) H. Soffer and T. De Vries, THIS JOURNAL, **73**, 5817 (1951).

(9) K. S. Pitzer, *ibid.*, **70**, 2140 (1948).

(10) H. Gilman and T. C. Wu, *ibid.*, **73**, 4031 (1951).

(11) Unpublished studies by T. C. Wu.

The infrared spectra of the hexaaryldisilanes containing phenyl and *p*-tolyl groups have been studied by Dr. V. A. Fassel and Mr. M. Margoshes. The results will be published elsewhere.

Experimental

In all experiments involving the use of organolithium compounds and triarylsilylpotassium compounds the reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. All melting points are uncorrected. The silicon analyses were made in accordance with a published procedure.[12] All reactions were carried out at room temperature when ether was used as the reaction medium.

Following are a few examples illustrating the types of reactions which were used in the preparation of chlorosilanes and hexaaryldisilanes. Other results are compiled in Table I.

Phenyldi-*p*-tolylchlorosilane (equation 6).—This compound was prepared by the reaction of 2 equivalents of *p*-tolyllithium with 1 equivalent of phenyltrichlorosilane in ether using the procedure for the preparation of diphenyl-*p*-tolylchlorosilane.[13] The product was obtained by vacuum distillation to give a 92% yield of colorless liquid (b.p. 190–192° (1.2 mm.)) which solidified on standing, m.p. 99–100°.

Anal. Calcd. for $C_{20}H_{19}ClSi$: Si, 8.70. Found: Si, 8.54, 8.63.

1,1,1,2-Tetraphenyl-2,2-dichlorodisilane (equation 7).—A triphenylsilylpotassium suspension in ether was prepared by cleaving 10.0 g. (0.019 mole) of hexaphenyldisilane with 2 ml. of sodium–potassium alloy according to the recently described procedure.[14] The excess alloy was removed by amalgamation and was separated from the suspension. The triphenylsilylpotassium suspension was transferred into a nitrogen-filled dropping funnel from which it was added slowly to 8.0 g. (0.038 mole) of phenyltrichlorosilane dissolved in 30 ml. of ether during a period of 30 minutes. Some heat was evolved, and the reaction mixture turned gray. After 1.5 hours of stirring at room temperature the reaction mixture was filtered. The insoluble gray solid residue was extracted twice with hot benzene to give 1.6 g. (16%) of hexaphenyldisilane (mixed m.p.) melting at 362°. The ethereal solution was distilled to yield 13.5 g. of gummy residue which solidified on standing. This solid was very soluble in benzene, acetone and chloroform and was partially soluble in ethanol and petroleum ether (b.p. 28–40°). Attempts to recrystallize this product were unsuccessful, so it was crushed to a powder, washed with cold petroleum ether (b.p. 28–40°), and filtered. The solid residue after such treatment melted at 98–101°. The yield of this partially purified product was 5.6 g. (34%). This product was used for the preparation of 1,1,1,2-tetraphenyl-2,2-di-*p*-tolyldisilane without further purification.

Anal. Calcd. for $C_{24}H_{20}Cl_2Si_2$: Si, 12.90. Found: Si, 13.35, 13.42.

1,1,1-Triphenyl-2,2,2-trichlorodisilane (equation 8).—A triphenylsilylpotassium suspension of the same amount as that in the previous section was prepared and added to 6.5 g. (0.038 mole) of silicon tetrachloride in 25 ml. of ether. After 2 hours, Color Test I[15] was negative. The mixture was filtered by suction. The insoluble solid was shaken with dilute aqueous ethanol and filtered again in order to separate the inorganic material. There was obtained 3.7 g. of solid residue melting at 360°, and was identified after recrystallization as hexaphenyldisilane. From the ethereal solution 9.0 g. of solid melting at 140–145° was obtained. One recrystallization from 40 ml. of petroleum ether (b.p. 60–70°) gave 4.1 g. (27%) of colorless crystals melting at 143–145°. From the mother liquor an impure product melting at 140–143° was recovered. It was noticed that the compound was not very stable. On standing the melting point was lowered.

Anal. Calcd. for $C_{18}H_{15}Cl_3Si_2$: Si, 14.27. Found: Si, 14.38, 14.41.

(12) H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, THIS JOURNAL, **72**, 5767 (1950). For micro analysis of silicon in organosilicon compounds, see H. Gilman and L. S. Miller, *ibid.*, **73**, 968 (1951).

(13) H. Gilman and G. E. Dunn, *ibid.*, **73**, 3404 (1951).

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

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

1,1,2,2-Tetraphenyl-1,2-di-*p*-tolyldisilane (equation 1).—A mixture of 22.4 g. (0.0725 mole) of diphenyl-*p*-tolylchlorosilane,[13] 4.8 g. (0.21 g. atom) of sodium and 50 ml. of dry xylene was stirred at the refluxing temperature for 6 hours. The mixture was cooled to room temperature and filtered by suction. The residue was treated with 50 ml. of 95% ethanol in order to react with the unused sodium. The solid was now washed first with water, then with 20% ethanol, filtered and dried. There was obtained 16.6 g. (84%) of colorless solid melting at 250–252°. Two recrystallizations from benzene yielded 12.3 g. (62%) of pure product melting at 252–253°. From the mother liquor 1.9 g. (10%) of impure product melting at 248–250° was recovered.

Anal. Calcd. for $C_{38}H_{34}Si_2$: Si, 10.28. Found: Si, 10.26, 10.28.

1,1,2-Triphenyl-1,2,2-tri-*p*-tolyldisilane (equation 2).—A mixture of 4.6 g. (0.0082 mole) of 1,1,2,2-tetraphenyl-1,2-di-*p*-tolyldisilane, 1 ml. of sodium-potassium alloy and 10 ml. of ether was stirred at room temperature. Fifteen minutes later another 40 ml. of ether was added to the deep yellow diphenyl-*p*-tolylsilylpotassium suspension thus formed. The color of the mixture partially faded during the addition but resumed a bright orange color after another 1 hour of stirring. The mixture was then allowed to stir for 40 hours and the excess alloy in the mixture was removed by amalgamation.[14] The diphenyl-*p*-tolylsilylpotassium suspension was separated from the amalgam and it was added to 5.2 g. (0.016 mole) of phenyldi-*p*-tolylchlorosilane dissolved in 40 ml. of ether. There was very little heat evolved during the addition. After 2 hours of stirring at room temperature the gray suspension was hydrolyzed and filtered to remove a trace of gray residue. The ethereal solution was washed with water, dried with sodium sulfate, and distilled. There was obtained 8.3 g. of colorless sticky solids melting at 215–225°. The crude product was recrystallized twice from benzene–ethanol to yield 4.7 g. (52%) of shining, fluffy crystals melting at 226–227°.

Anal. Calcd. for $C_{39}H_{36}Si_2$: Si, 10.01. Found: Si, 9.92, 9.95.

1,1,1-Triphenyl-2,2,2-tri-*p*-tolyldisilane (equation 3).—An ethereal solution containing 0.022 mole of *p*-tolyllithium was added rapidly to 2.0 g. (0.0051 mole) of 1,1,1-triphenyl-2,2,2-trichlorodisilane dissolved in 40 ml. of ether. Heat was evolved while some white solids were formed. After 6 hours of stirring at room temperature the reaction mixture was hydrolyzed with water. From the sodium sulfate-dried ethereal solution there was obtained 2.7 g. of glassy residue. This was dissolved in a solution containing 50 ml. of petroleum ether (b.p. 60–70°) and 10 ml. of benzene. On cooling 0.3 g. (11%) of colorless crystals melting at 260–264° separated. Evaporation of the mother liquor resulted in a gummy residue.

In another reaction triphenylchlorosilane was treated with tri-*p*-tolylsilylpotassium prepared by cleaving hexa-*p*-tolyldisilane with sodium–potassium alloy with the same procedure for the preparation of triphenylsilylpotassium.[14] From this reaction there was obtained a 53% yield of crude product melting at 258–262°. This was recrystallized from a mixed solvent of benzene and petroleum ether (b.p. 60–70°) to give colorless fine needles melting at 262–264°. A mixed melting point determination with the product obtained by treating 1,1,1-triphenyl-2,2,2-trichlorodisilane with *p*-tolyllithium was not depressed. The yield of pure 1,1,1-triphenyl-2,2,2-tri-*p*-tolyldisilane for this run was 26%.

Anal. Calcd. for $C_{39}H_{36}Si_2$: Si, 10.01. Found: Si, 9.94, 9.94.

From the ethereal solution of the reaction mixture there were obtained triphenylsilanol and 1,1,1-triphenyl-3,3,3-tri-*p*-tolyldisiloxane as by-products.

1,1,1,2-Tetraphenyl-2,2-di-*p*-tolyldisilane (equation 4).—A solution containing 4.0 g. (0.0092 mole) of partially purified 1,1,1,2-tetraphenyl-2,2-dichlorodisilane in 40 ml. of ether was added, over a period of 10 minutes, to 0.0205 mole of freshly prepared *p*-tolyllithium in ether. A small amount of heat was evolved during the addition. The reaction mixture after the addition was pale yellow and a little cloudy. On stirring more and more white precipitate formed. Color Test I[15] after 5 hours was positive, so the reaction mixture was stirred at room temperature overnight. After 16 hours a large amount of white precipitate was

formed, and Color Test I[15] became negative. The reaction mixture was filtered by suction, and the solid residue was extracted with hot benzene. The benzene extract was evaporated to give 1.2 g. of white solid melting at 217–222°. Two recrystallizations from petroleum ether (b.p. 60–70°) gave 0.7 g. (14%) of colorless fine needles melting at 229–230°. From the ethereal solution of the reaction mixture a large amount of gummy residue was obtained from which only a small amount of impure product could be isolated.

Anal. Calcd. for $C_{38}H_{34}Si_2$: Si, 10.28. Found: Si, 10.31, 10.33.

The same product was obtained from the reaction of triphenylsilylpotassium with phenyldi-*p*-tolylchlorosilane (equation 2) to give an 85% crude yield of 1,1,1,2-tetraphenyl-2,2-di-*p*-tolyldisilane melting at 228°. One recrystallization from a mixed solvent of benzene–petroleum ether (b.p. 60–70°) gave 72% of pure product melting at 229–230°. A mixed melting point determination with the product obtained from 1,1,1,2-tetraphenyl-2,2-dichlorodisilane and *p*-tolyllithium was not depressed.

Pentaphenyl-*p*-tolyldisilane (equation 5).—An ethereal solution containing 0.011 mole of *p*-tolyllithium was added rapidly to 4.8 g. (0.01 mole) of pentaphenylchlorodisilane.[6] The reaction mixture became more and more turbid, but very little heat was evolved. After 16 hours of stirring at room temperature, Color Test I[15] was negative. The reaction mixture was hydrolyzed with water and filtered to separate 2.8 g. (53%) of white powder melting at 270° to a turbid liquid. Two recrystallizations from benzene yielded small needles (1.5 g., 28%) melting at 283–285°.

Anal. Calcd. for $C_{37}H_{32}Si_2$: Si, 10.55. Found: Si, 10.50, 10.47.

The same product, pentaphenyl-*p*-tolyldisilane, was obtained in an 82% crude yield (m.p. 276–282°) and a 77% pure yield (m.p. 283–285°) by the reaction of triphenylsilylpotassium with diphenyl-*p*-tolylchlorosilane (equation 2). A mixed melting point determination of these two products showed no depression.

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[CONTRIBUTION FROM THE WHITMORE LABORATORY, THE PENNSYLVANIA STATE COLLEGE]

Kinetics and Mechanism of Methyl–Silicon Cleavage by Sulfuric Acid[1]

BY LEO H. SOMMER, WALTER P. BARIE AND JACK R. GOULD

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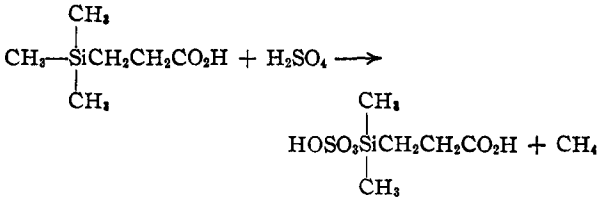
The kinetics of the reaction of β-trimethylsilylpropionic acid with sulfuric acid to give selective cleavage of one methyl group from silicon as methane has been studied. A mechanism involving electrophilic attack on carbon and formation of a siliconium ion in the rate-determining step is advanced.

Introduction

The reaction of certain organosilicon structures with concentrated sulfuric acid to give selective cleavage of one methyl group from trimethylsilyl, Me_3Si, as methane, has provided an important synthetic route to new types of aliphatic organofunctional siloxanes.[2,3] Thus, the mechanism of this reaction is of interest from both theoretical and practical standpoints. The present paper reports a kinetic study of the methyl–silicon cleavage given by β-trimethylsilylpropionic acid. The reaction is homogeneous, and quantitative.



Discussion and Results

The pseudo first-order character of the reaction (sulfuric acid in large excess) is clearly shown for sulfuric acid concentrations of 85–97% by Fig. 1. *These good straight-line plots were obtained after initial difficulty, due to the formation of supersaturated solutions of methane in sulfuric acid, was overcome by more efficient stirring.* This somewhat surprising phenomenon is well-illustrated by Fig. 2 in the experimental part.

Having established the fact that the reaction follows a pseudo first-order rate law, *e.g.*, is first order in the silicon acid, it was of interest to determine whether the decrease of rate with decreasing concentration of sulfuric acid could be correlated in terms of a simple mechanism.

No correlation between the pseudo first-order rate constants and stoichiometric concentration of sulfuric acid was available.

In order to determine whether the concentration of molecular or non-ionized sulfuric acid might be the critical factor use was made of the (approximately correct) assumption that the following reaction proceeds to completion[4]

$$H_2SO_4 + H_2O \longrightarrow H_3O^{\oplus} + HSO_4^{\ominus} \qquad (1)$$

Table I gives the pseudo first-order rate constants, the concentrations of molecular sulfuric acid calculated on the above approximation, and also lists values of second-order rate constants obtained by dividing out the concentration of molecular sulfuric acid. These latter values have been calculated for the range 87–97% sulfuric acid since equation (1) becomes seriously in error below 87% sulfuric acid.[4] Taking into consideration the approximations involved in calculating the concentration of molecular sulfuric acid, as well as the very serious medium effects to be expected on changing the solvent–reactant from 97% sulfuric acid to 87% sulfuric acid, the relative constancy of the second-order rate constants is here considered to be quite good. For example, a change from 87 to 97% sulfuric acid increases the pseudo first-order constant by a factor of 4.7, the same change

(1) Paper 34 in a series on organosilicon chemistry; for 33 see THIS JOURNAL, 75, 2932 (1953).

(2) L. H. Sommer, N. S. Marans, G. M. Goldberg, J. Rockett and R. P. Pioch, *ibid.*, 73, 882 (1951).

(3) L. H. Sommer, R. P. Pioch, N. S. Marans, G. M. Goldberg, J. Rockett and J. Kerlin, *ibid.*, 75, 2932 (1953).

(4) For a good discussion and pertinent references see J. C. D. Brand, *J. Chem. Soc.*, 997 (1950).