Experimental details are given in Table I.

TABLE I

Isomer	M.p., °C.	Iodine number Found	Iodine number Calcd.
endo	151–162[a]	3.4	154.7
exo	142–145	151.9	154.7
Mixture 69% *endo* 31% *exo*	118–133	49.6	49.4

[a] This melting point was taken on *endo*-3,6-endomethyleneetetrahydrophthalic anhydride which was fused and allowed to resolidify. The crystals of the *endo*-isomer which separated from methyl ethyl ketone as reaction product of maleic anhydride and cyclopentadiene melted at 164° before fusion.

We wish to thank Mr. E. F. Berger for iodine number determinations.

PAINT DIVISION RESEARCH LABORATORY
PITTSBURGH PLATE GLASS COMPANY
MILWAUKEE, WISCONSIN

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Preparation of Organopolysilanes

BY HENRY GILMAN, TSE CHENG WU, HOWARD A. HARTZFELD, GERALD A. GUTER, ARTHUR G. SMITH, JACK J. GOODMAN AND SCOTT H. EIDT

The silicon–silicon bond is in general much less stable than the carbon–carbon bond (Si–Si, 45 kcal./mole; C–C, 80 kcal./mole[1]). While the length of the carbon–carbon chain is almost unlimited, the silicon–silicon chains known at the present time are relatively short. In the polysilane series the longest silane ever reported[2] is Si_6H_{14}. Silicon chlorides from $SiCl_4$ to Si_6Cl_{14} are well known.[3] Schwarz and co-workers[4,5] reported the preparation of $Si_{10}Cl_{22}$ and $Si_{25}Cl_{52}$ by heating $SiCl_4$ in a hydrogen and in a nitrogen atmosphere, respectively.

The organosubstituted silicon chains which have been made are rather small. Although there are a few known hexasubstituted disilanes, no octasubstituted trisilane has been reported. Schumb and Saffer[6] treated octachlorotrisilane with phenylmagnesium bromide, and they obtained a mixture of tetraphenylsilane and hexaphenyldisilane instead of octaphenyltrisilane. The aryl organosilicon chains of greater length which have been reported were prepared by the action of sodium on diphenyldichlorosilane and closely related compounds. By this method Kipping and co-workers[7a] were able to isolate two compounds with the formula $(C_6H_5)_8Si_4$ and two other substances with the formulas $[(C_6H_5)_2Si]_n$, with *n* having a value of 6 or 8. Recently, Burkhard,[7b] using a similar procedure, showed in an interesting study that polydimethylsilanes can be prepared from dimethyldichlorosilane and sodium.

We are now reporting a new approach for the syntheses of organopolysilanes. When two moles of triphenylsilylpotassium is treated with one mole of diphenyldichlorosilane in ether, octaphenyltrisilane is formed. When one mole of triphenylsilylpotassium is treated with one mole of diphenyldichlorosilane, pentaphenylchlorodisilane can be isolated. Pentaphenylchlorodisilane is an interesting compound because compounds of this type may be coupled to form organopolysilanes by doubling the length of the silicon chain.

$$(C_6H_5)_3SiSi(C_6H_5)_3 \xrightarrow{\text{Na-K}} 2(C_6H_5)_3SiK$$

$$2(C_6H_5)_3SiK + (C_6H_5)_2SiCl_2 \longrightarrow (C_6H_5)_8Si_3 + 2KCl$$

$$(C_6H_5)_3SiK + (C_6H_5)_2SiCl_2 \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_2Cl + KCl$$

Experimental

Triphenylsilylpotassium.—In a previous paper from this Laboratory[8] there was described the preparation of triphenylsilylpotassium from hexaphenyldisilane and sodium–potassium alloy. (Due precautions should be exercised in the preparation and handling of this alloy.) Since then we found that the amount of ether used as a solvent affected the initiation of the reaction. In general an increase in the amount of solvent used increased the time for the appearance of the color of the organosilicon–metallic compound. After some studies the following procedure worked satisfactorily, and it has been checked more than twenty times.

In a dry three-necked flask fitted with a Trubore glass blade stirrer, a gas inlet tube, and a glass stopper were placed 4 g. (0.0077 mole) of hexaphenyldisilane,[9] 1 ml. of sodium–potassium alloy (1:5) and 10 ml. of anhydrous ether, after the flask had been swept with dry, oxygen-free nitrogen. The slurry was stirred vigorously at room temperature. Usually, after 5 to 10 minutes a greenish-yellow color began to form, indicating the start of the reaction. About 30 minutes later a distinct tan mixture was formed. Then 50 ml. of anhydrous ether was added to the reaction mixture against a stream of nitrogen.[10] The mixture was stirred at room temperature for about 20 hours. At the end of this period a suspension with a color ranging from dark greenish-brown to tan was formed. Mercury was added (caution!) dropwise to the reaction mixture until a liquid amalgam was formed. The amalgam was then stirred with the reaction mixture for one and one-half hours in order to dissolve all the excess sodium–potassium alloy. The triphenylsilylpotassium suspension was separated from the liquid amalgam by forcing it through a glass tubing by the pressure of nitrogen into a dry nitrogen-filled dropping funnel. Color Test I[11] for the clear supernatant liquid was negative, whereas the precipitate gave an intense bluish-violet color in both organic and aqueous layers of the Color Test.

Octaphenyltrisilane.—A triphenylsilylpotassium suspension prepared according to the procedure described in the last paragraph was added fairly rapidly to 1.5 g. (0.0059 mole) of diphenyldichlorosilane dissolved in 20 ml. of anhydrous ether (in a nitrogen atmosphere). Some heat was evolved, and there was very little color change. The reaction mixture was stirred for 9 hours at room temperature. Color Test I[11] at this stage was positive (bluish-green), probably due to the slight excess of triphenylsilylpotassium present. The reaction mixture was filtered by suction. The gray residue was boiled 30 minutes with 50 ml. of dry benzene and filtered hot. On standing, a small amount of white precipitate was formed. This was removed by filtration. The solids melted at about 270° to form a turbid

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[1] K. S. Pitzer, THIS JOURNAL, **70**, 2140 (1948).

[2] A. Stock and C. Somieski, *Ber.*, **49**, 111 (1916).

[3] See, for example, J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VI, Longmans, Green and Co., New York, N. Y., 1940, p. 960 ff.

[4] R. Schwarz and H. Meckbach, *Z. anorg. u. allgem. Chem.*, **232**, 241 (1937).

[5] R. Schwarz and C. Danders, *Chem. Ber.*, **80**, 444 (1947).

[6] W. C. Schumb and C. M. Saffer, Jr., THIS JOURNAL, **61**, 363 (1939).

[7a] F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 830, 848 (1921); F. S. Kipping, *ibid.*, **123**, 2590, 2598 (1923); *ibid.*, **125**, 2291 (1924).

[7b] C. A. Burkhard, THIS JOURNAL, **71**, 963 (1949).

[8] H. Gilman and T. C. Wu, THIS JOURNAL, **73**, 4031 (1951).

[9] Hexaphenyldisilane was prepared according to the method described by H. Gilman and G. E. Dunn, *ibid.*, **73**, 5077 (1951). It appears desirable to extend the reflux period to about 12 hours.

[10] It was observed that if the remainder of the ether was added before about 30 minutes, the yellow color which had formed faded away. It took some time for the reappearance of the color.

[11] H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

melt which became clear liquid at about 320°. It was believed to be impure hexaphenyldisilane. The benzene extract was concentrated to about 10 ml., and to this was added 20 ml. of petroleum ether (b.p. 60–70°). On cooling to room temperature 2.2 g. (53% based on diphenyldichlorosilane) of white solids melting at 238–244° was obtained by filtration. The crude product was recrystallized three times from a mixture of benzene and ethanol to give 1.2 g. (29%) of colorless needles melting at 260–262° to form a somewhat gelatinous mass which became water-clear liquid at 266° (uncor.).

Anal. Calcd. for $C_{48}H_{40}Si_3$: Si, 12.00. Found: Si, 11.98, 11.84.

Three check runs were made. In two of these runs a product melting at 302–303° was isolated. Analysis showed that it, too, had the composition of octaphenyltrisilane. From molecular model studies we suspected that this inconsistency in the melting points of these two products might possibly be due to the existence of isomeric forms. Further studies are now in progress.

Pentaphenylchlorodisilane.—A triphenylsilylpotassium suspension prepared according to the procedure described above was added fairly rapidly to 4 g. (0.016 mole) of diphenyldichlorosilane dissolved in 20 ml. of ether. It was noticed that the first few drops of triphenylsilylpotassium was decolorized immediately when it was added to the diphenyldichlorosilane solution. When addition was completed, a gray suspension was formed. Color Test I[11] immediately after the addition was negative. The mixture was stirred 1 hour at room temperature and was filtered by suction. The solvent was distilled from the filtrate to give 7.1 g. of colorless solids melting at 120–140°. The crude product was recrystallized twice from petroleum ether (b.p. 60–70°) to give colorless granular crystals melting at 154–155° (uncor.). The yield of pure product was 3.7 g. (50%).

Anal. Calcd. for $C_{30}H_{25}Si_2Cl$: Si, 11.79; Cl, 7.43. Found: Si, 11.76, 11.81; Cl, 7.42, 7.36.

Pentaphenylchlorodisilane is an interesting compound because even though it can be hydrolyzed in aqueous basic solution to give the corresponding hydroxy compound, still, unlike the triphenylchlorosilane, it is quite stable in air. A sample of this compound was put in a vial loosely plugged with cotton. After 3 months there was no depression in its melting point. Its preparation has been checked several times.

From some preliminary work it was found that pentaphenylchlorodisilane can be treated with sodium in boiling xylene to give a white solid, presumably decaphenyltetrasilane. Further work is now in progress.

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Phenylphosphine[1]

BY ROBERT J. HORVAT AND ARTHUR FURST

Phenylphosphine has been previously prepared by reducing dichlorophenylphosphine directly with anhydrous hydrogen iodide,[2,3] or by first converting the dichlorophenylphosphine to diiodophenylphosphine hydrogen iodide and treating this with absolute alcohol.[4] Yields were increased only after many hours of reaction.

It is possible to obtain phenylphosphine in much shorter time and in comparable over-all yields by simply reducing the dichlorophenylphosphine with lithium aluminum hydride.

Experimental

To an ice-cold solution of 4.18 g. (0.11 mole) of lithium aluminum hydride in 200 ml. of absolute ether was added drop by drop 35.5 g. (0.2 mole) of dichlorophenylphosphine (Victor Chemical Works) dissolved in 200 ml. of absolute ether. The reaction mixture turned yellow and soon began to reflux. After the addition was complete the mixture was refluxed for one hour, cooled and filtered through glass wool. In an atmosphere of nitrogen the ether was first removed; then the phenylphosphine was distilled and collected as a colorless liquid at 160–161°. The yield was 5.6 g. (25.4%); hydrogen iodide salt, m.p. 136° (uncor.).

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[1] A grant-in-aid from Research Corporation is gratefully acknowledged; also the technical assistance of O. Clark Chisim.

[2] A. Michaelis, *Ber.*, **7**, 6 (1874).

[3] H. Lecoq, *Bull. soc. chim. Belg.*, **42**, 199 (1933).

[4] H. Kohler and A. Michaelis, *Ber.*, **10**, 807 (1877).

The Solubility of Aniline Hydrochloride in Water

BY EDWARD H. HOUSE AND JOHN H. WOLFENDEN

Three values for the solubility of aniline hydrochloride are recorded in the literature and regularly quoted in works of reference. Two of these relate to 25° and are in fair agreement; at this temperature C. J. Peddle and W. E. S. Turner[1] report that 100 g. of water dissolves 107.1 g. of the salt while N. V. Sidgwick, P. Pickford and B. H. Wilsdon[2] report that 100 g. of the saturated solution contains 52.1 g. of the salt. The third solubility determination relates to 15°, at which temperature S. v. Niementowski and J. v. Roszkowski[3] report that 100 cc. of water dissolves 17.762 g. of aniline hydrochloride. This last figure is at variance with common observation in the purification of the salt by recrystallization, and suggests a remarkably high temperature coefficient of solubility. The molal heat of solution computed from the recorded solubilities at 15° and 25° implies an absorption of about 29 kcal. of heat, a value much larger than the value of 2.7 kcal. measured by Louguinine,[4] than the heats of solution of other amine hydrochlorides, which commonly range between 1 and 4 kcal. per mole, and than the heat of fusion of the salt as deduced from the cryoscopic data of Leopold[5] (*ca.* 2 kcal. per mole).

The paucity of information about the solubility of this common organic compound and the implausibility of the only determination at any temperature other than 25° prompted us to measure the solubility over the temperature range from 0° to 100°. Saturated solutions of the pure recrystallized salt in water containing 0.2% of aniline to repress hydrolysis were analyzed by titration with

TABLE I

SOLUBILITY OF ANILINE HYDROCHLORIDE

Temp., °C.	g./100 g. H_2O	Mole fraction
0	63.50	0.08112
15	88.36	.1094
25	107.35	.1299
40	143.7	.1665
100	396	.355

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[1] C. J. Peddle and W. E. S. Turner, *J. Chem. Soc.*, **103**, 1202 (1913).

[2] N. V. Sidgwick, P. Pickford and B. H. Wilsdon, *ibid.*, **99**, 1122 (1911).

[3] S. v. Niementowski and J. v. Roszkowski, *Z. physik. Chem.*, **22**, 145 (1897).

[4] Cited by M. Berthelot, *Ann. chim. Phys.*, 6e. ser., **21**, 355 (1890).

[5] G. H. Leopold, *Z. physik. Chem.*, **71**, 59 (1910).