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TRIPHENYLSILYLPOTASSIUM

HENRY GILMAN AND T. C. WU

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INTRODUCTION

Triphenylsilylpotassium has been prepared by the reaction of phenylisopropyltriphenylsilane (1), hexaphenyldisilane (2), triphenylchlorosilane (2), triphenylethoxysilane (2), triphenylmethoxysilane (3), or triphenylsilane (3) with sodium-potassium alloy and by the reaction of hexaphenyldisilane with potassium (2) It has been shown that triphenylsilylpotassium is a very reactive organosiliconmetallic compound. Thus, it reacts with bromobenzene to give tetraphenylsilane (1–3), with trimethylchlorosilane to give 1,1,1-triphenyl-2,2,2-trimethyldisilane (1, 2), with triethylchlorosilane to give 1,1,1-triphenyl-2,2,2-triethyldisilane (1, 3), with diphenyldichlorosilane to give pentaphenylchlorodisilane and octaphenyltrisilane (4), and with methyl iodide to give triphenylmethylsilane (3). It also adds to the carbon-carbon double bond of *trans*-stilbene (5), yielding a silicon-containing organometallic compound which is hydrolyzed to give triphenyl-α,β-diphenylethylsilane, $(C_6H_5)_3SiCH(C_6H_5)CH_2(C_6H_5)$. The addition reaction to an olefinic linkage shows that triphenylsilylpotassium has a distinctly high order of reactivity (6).

Among various procedures studied in this investigation it now appears that the best method of preparation of the uncommonly useful and important triphenylsilylpotassium is to cleave hexaphenyldisilane with sodium-potassium alloy in ether. The use of hexaphenyldisilane as the starting material has some advantages which are not found in any other compound such as triphenylchlorosilane, triphenylethoxysilane, or tetraphenylsilane.

Hexaphenyldisilane can be prepared in excellent yields and high purity by coupling triphenylchlorosilane with sodium in boiling xylene (7). The procedure is very simple and the product obtained directly from the reaction is good enough for the preparation of triphenylsilylpotassium without further purification. The finely divided hexaphenyldisilane thus prepared provides a large surface area to facilitate the cleavage reaction. Other starting materials are either not available or are more difficult to prepare or to keep. Thus triphenylethoxysilane has to be made and purified, and triphenylchlorosilane, although commercially available, is difficult to keep well due to its ease of hydrolysis. Furthermore, hexaphenyldisilane can be dried very conveniently in an oven at 110° while this can not be done with other possible starting materials, like triphenylsilane and triphenylchlorosilane. The stability of hexaphenyldisilane makes it possible to keep it indefinitely without special precautions.

Another advantage in the use of hexaphenyldisilane is the essential absence of by-products in the preparation of triphenylsilylpotassium. The reaction of

TABLE I

Reactions of Triphenylsilylpotassium Prepared From Hexaphenyldisilane

No.	Compound added for derivatization	Product isolated	Reaction time	Crude product		Purified product		Solvent for recrystallization
				Yield, %	M.P., °C. (Uncorr.)	Yield, %	M.P., °C. (Uncorr.)	
1	$(CH_3)_3SiCl$ [a]	$(C_6H_5)_3SiSi(CH_3)_3$	15 min.	86	101–104	75	107–108	95% Ethanol
2	$(CH_3)_3SiCl$ [b]	$(C_6H_5)_3SiSi(CH_3)_3$	45 min.	70	97–102	47	107–108	95% Ethanol
3	H_2O	$(C_6H_5)_3SiOH$	15 min.	—	—	58	150–152	Pet. ether (b.p. 60–70°)
4	$C_6H_5CH_2Cl$	$(C_6H_5)_3SiCH_2C_6H_5$	5 min.	33	85–92	22	98–99	Pet. ether (b.p. 60–70°)
5	$C_6H_5CH_2Cl$	$(C_6H_5)_3SiCH_2C_6H_5$	16 hr.	39	94–97	32	97–99	Pet. ether (b.p. 60–70°)
6	*o*-$BrC_6H_4CH_3$	$(C_6H_5)_3SiC_6H_4CH_3$-*o*	4 hr.	57	155–170	24	188–190	Benzene-ethanol
7	*p*-$IC_6H_4CH_3$ [a]	$(C_6H_5)_3SiC_6H_4CH_3$-*p*	10 min.	95	125–135	73	138–140	Pet. ether (b.p. 60–70°)
8	$(C_6H_5)_2SiCl_2$ [c]	$(C_6H_5)_3SiSi(C_6H_5)_2Cl$	1 hr.	—	120–140	50	154–155	Pet. ether (b.p. 60–70°)
9	$(C_6H_5)_2SiCl_2$ [d]	$(C_6H_5)_8Si_3$	9 hr.	53	238–244	29	260–262	Benzene-ethanol
10	$(C_6H_5)_3SnCl$	$(C_6H_5)_3SiSn(C_6H_5)_3$	6 hr.	86	280–286	76	296–298	Benzene-dioxane

[a] The excess sodium-potassium was not removed by amalgamation (2). [b] The triphenylsilylpotassium was prepared by the cleavage of hexaphenyldisilane with potassium in *n*-butyl ether (2). [c] One equivalent of triphenylsilylpotassium per mole of diphenyldichlorosilane (4). [d] Two equivalents of triphenylsilylpotassium per mole of diphenyldichlorosilane (4).

TABLE II

THE PREPARATION OF TRIPHENYLSILYLPOTASSIUM FROM COMPOUNDS OTHER THAN HEXAPHENYLDISILANE

No.	COMPOUND CLEAVED BY SODIUM-POTASSIUM ALLOY	COMPOUND ADDED FOR DERIVATIZATION OF TRIPHENYLSILYLPOTASSIUM	PRODUCT ISOLATED	REACTION TIME (min.)	CRUDE PRODUCT		PURIFIED PRODUCT	
					YIELD, %	M.P., °C. (uncorr.)	YIELD, %	M.P., °C. (Uncorr.)
1	$(C_6H_5)_3SiOC_2H_5$[a]	C_6H_5Br	$(C_6H_5)_4Si$	15	48	218–231	24	233–235
2	$(C_6H_5)_3SiCl$[a, b]	$(CH_3)_3SiCl$	$(C_6H_5)_3SiSi(CH_3)_3$	30	95	96–102	65	107–108
3	$(C_6H_5)_3SiCl$[a, c]	$(CH_3)_3SiCl$	$(C_6H_5)_3SiSi(CH_3)_3$	15	97	95–101	67	107–108
4	$(C_6H_5)_3SiCl$[a, d, e]	$(CH_3)_3SiCl$	$(C_6H_5)_3SiSi(CH_3)_3$	30	98	96–100	45	105–107
5	$(C_6H_5)_3SiCl$[a, d, f]	$(CH_3)_3SiCl$	$(C_6H_5)_3SiSi(CH_3)_3$	30	98	98–106	57	107–108
6	$(C_6H_5)_3SiCl$[a, g]	$(C_2H_5)_3SiCl$	$(C_6H_5)_3SiSi(C_2H_5)_3$[h]	15	92	80–85	60	98–99
7	$(C_6H_5)_4Si$[i]	$(C_6H_5)_3SiCl$	$(C_6H_5)_3SiSi(C_6H_5)_3$	20	83	350–355	70	360–362
8	$(C_6H_5)_3SiSi(CH_3)_3$[a]	C_6H_5Br	$(C_6H_5)_4Si$	15	60	230–232	50	233–234

[a] Without removal of excess sodium-potassium alloy by amalgamation. [b] The reaction period of triphenylchlorosilane and sodium-potassium alloy was 48 hours. [c] The reaction period of triphenylchlorosilane and sodium-potassium alloy was 36 hours. [d] Unpublished studies of J. B. Honeycutt, Jr. [e] 48 hours of continuous stirring. [f] 48 hours of intermittent stirring. [g] 24 hours of stirring with redistilled (vacuum) triphenylchlorosilane and sodium-potassium alloy. [h] 5 percent of hexaphenyldisilane was also isolated. [i] The excess alloy was removed by amalgamation.

hexaphenyldisilane with sodium-potassium alloy or potassium proceeds in accordance with the following equations:

$$(C_6H_5)_3SiSi(C_6H_5)_3 \xrightarrow{K} 2\,(C_6H_5)_3SiK$$

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

The only foreign materials in this system are the excess alloy, ether, and possibly a small amount of uncleaved hexaphenyldisilane.

The cleavage reaction of hexaphenyldisilane starts promptly on stirring a mixture of the disilane with sodium-potassium alloy and then proceeds smoothly even though neither hexaphenyldisilane nor triphenylsilylpotassium dissolves appreciably in ether. Using triphenylchlorosilane as a starting material it is very difficult to tell whether the formation of triphenylsilylpotassium has taken place because the color of triphenylsilylpotassium is masked by the dark purple color formed when triphenylchlorosilane is used. On the other hand, the color resulting from the cleavage of hexaphenyldisilane can be observed without difficulty due to the white background of the disilane.

TABLE III

REACTION OF TRIPHENYLSILYLPOTASSIUM WITH PHENYL HALIDES[a]

NUMBER	MOLE OF HEXAPHENYLDISILANE USED FOR THE PREPARATION OF TRIPHENYSILYLPOTASSIUM	PHENYL HALIDE	MOLE OF PHENYL HALIDE USED	MODE OF ADDITION[b]	TIME (minutes)	YIELD OF TETRAPHENYLSILANE, %
1	0.0077	C_6H_5F	0.031	A	70 hours	12
2	.0077	C_6H_5Cl	.015	A	15	50
3	.015	C_6H_5Cl	.031	A	60	53
4	.010	C_6H_5Br	.022	A	30	55
5	.010	C_6H_5Br	.022	B	30	40
6	.010	C_6H_5Br	.022	B	30	45
7	.010	C_6H_5I	.022	A	15	63

[a] The excess sodium-potassium was removed by amalgamation procedure for all reactions. [b] The letter A indicates the addition of triphenylsilylpotassium suspension to the phenyl halide solution; the letter B indicates the reverse order of addition.

Because of the reasons mentioned above hexaphenyldisilane has been used more extensively in hitherto unpublished studies than any other compound for the preparation of triphenylsilylpotassium. The results are summarized in Table I. The results of preparations of triphenylsilylpotassium from compounds other than hexaphenyldisilane are listed in Table II.

In our studies of triphenylsilylpotassium, we have found it advantageous to remove excess sodium-potassium alloy from the suspension, by amalgamating the excess alloy with mercury. The separation of excess alloy may be important in some subsequent reactions in which the presence of excess alloy may induce secondary reactions. However, in the reactions of triphenylsilylpotassium with phenyl halides there was no marked difference in the products obtained whether the amalgamation procedure was used or not. Also, a prolonged period of amalgamation seemed undesirable. The possibility of the formation of organomercuric compounds incidental to the amalgamation procedure is being examined.

The reactions of phenyl halides with triphenylsilylpotassium are summarized in Table III. Although a strict comparison of the rates of reactions of these phenyl halides was difficult in a heterogeneous system, nevertheless, from the results of these studies it appears that the reactivity of the phenyl halides decreases in the order: iodobenzene, bromobenzene, chlorobenzene, and fluorobenzene, the last compound being far less reactive than other compounds of this series.

Among the solvents used for the preparation of triphenylsilylpotassium we found that diethyl ether is most desirable because the cleavage reaction usually goes to completion in ether, whereas a considerable amount of uncleaved hexaphenyldisilane was found when benzene or petroleum ether was used.

The preparation of triphenylsilylpotassium from hexaphenyldisilane has been extended to other aryl disilanes. For example, hexa-*p*-tolyldisilane can be cleaved the same way by sodium-potassium alloy to give tri-*p*-tolylsilylpotassium (8). The extension of this reaction to the alkyl silanes is underway (9). Rubidium and cesium also cleave hexaphenyldisilane to the corresponding triphenylsilylmetallic compounds. Triphenylchlorosilane does not react with very finely divided magnesium powder under ordinary conditions.

EXPERIMENTAL[1]

Preparation of sodium-potassium alloy. The sodium-potassium alloy used was conveniently prepared by fusing one part of sodium with five parts of potassium in dry xylene. The following is a typical preparation which includes some special details.

To a 1-liter 3-necked T/S flask (preferably with one neck of size 34/35, to facilitate addition of the metals) was added 500 ml. of sodium-dried xylene, after the flask had been flushed with dry, oxygen-free nitrogen gas. To this was added 200 g. of potassium and 40 g. of sodium. The mixture was heated by an electric mantle until both metals melted. The molten metals were coalesced very carefully with the aid of a glass rod until a big globule was formed. The alloy was then allowed to cool to room temperature and then was transferred to a well-protected container by means of a 50-ml. pipet attached to a rubber bulb. First a thin layer of xylene was sucked into the pipet followed by the alloy and finally another thin layer of xylene was sucked into the pipet in order to protect the alloy from air and moisture. Due precautions should be exercised as the alloy is very reactive and may ignite spontaneously in air. Most of the alloy could be transferred in this manner, but there were some small droplets of alloy which were coated and could not be coalesced. This small part of the alloy was disposed of in the following way. About 300 ml. of the xylene was removed, and, while the flask was filled with nitrogen, ethanol was added slowly to the coated alloy and allowed to react with it until all of it had been destroyed. This operation must be carried out in the absence of air.

It was found that 25 x 200 mm. test tubes securely placed in a jar filled with dry soda ash were satisfactory containers, because in an upright position, the alloy was confined

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[1] Compounds melting below 250° were determined in an oil-bath with a 250°-thermometer (one degree divisions), those melting above 250° were determined in a flame-heated copper block with a 520°-thermometer (two degree divisions). All melting points are uncorrected. In all reactions involving triphenylsilylpotassium an atmosphere of nitrogen was maintained.

to a small cross section, thereby reducing coating. The alloy was always covered with dry xylene and the surface above was flushed with dry nitrogen.

Preparation of hexaphenyldisilane (7). The success of this preparation was found to depend on thorough stirring of the heterogeneous system, as shown in the following experiments.

In a 1-liter three-necked flask fitted with a condenser, a Trubore glass stirrer, and a gas-inlet tube, was placed 180 g. (0.61 mole) of triphenylchlorosilane (Dow Corning Corporation, purified grade),[2] 15 g. (0.65 g.-atom) of sodium, and 400 ml. of sodium-dried xylene. The mixture was heated by an electric mantle until the sodium melted. Then the stirring motor was started. Immediately the mixture turned dark and some bluish-violet precipitate was formed, indicating the initiation of the reaction. The reaction mixture was stirred under reflux for six hours. At the end of this period a large amount of purplish-white solid was formed. The reaction mixture was allowed to cool to room temperature and then was filtered by suction. The solid residue was added, in small portions, to a 1-liter beaker containing 500 ml. of 95% ethanol in order to destroy the small amount of excess sodium. During this operation the blue precipitate changed to a white solid. The solid residue was filtered by suction and was washed twice with 20% aqueous ethanol, once with ether,[3] and finally dried in an oven at 110° to constant weight. The yield was 145 g. (92%). The product melted at 368–370°.

In a check run of the same size a 94% yield of the product of the same purity was obtained. A sample of this product was recrystallized from tributyl phosphate to yield white needles (hexagonal under the microscope). However, the melting point after such recrystallization did not change.

It was observed that in a run using the same procedure as above, except that the blade stirrer was placed about an inch from the bottom of the reaction flask instead of directly on the bottom, only a 65% yield of hexaphenyldisilane was obtained. Large amounts of unreacted sodium and triphenylchlorosilane were left over. Apparently, part of the sodium settled down to the bottom of the flask and was covered by the hexaphenyldisilane formed.

Preparation of triphenylsilylpotassium from hexaphenyldisilane and sodium-potassium alloy. In a 250-ml. three-necked flask fitted with a Trubore glass blade stirrer, a glass stopper, and a gas inlet tube was placed 5.2 g. (0.01 mole) of hexaphenyldisilane after the flask had been swept with dry, oxygen-free nitrogen. To this was added 1.3 ml. of sodium-potassium alloy,[4] followed by 5 ml. of absolute ether. The stirring motor was turned on at a slow speed. In a large number of reactions a grayish-green coloration developed immediately, indicating the starting of the cleavage reaction. The paste gradually developed a yellow color. After about 1 hour a brown paste was formed. At this time another 50 ml. of

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[2] Mr. S. H. Eidt has observed that some lots of triphenylchlorosilane contain a small amount of *p*-terphenyl.

[3] Formerly, this was washed with water in order to dissolve the sodium chloride formed (7). Later, we found that the washing was more efficient when dilute aqueous ethanol was used because water alone did not wet the hexaphenyldisilane very well and the compound tended to float. The last washing with ether seemed to be desirable because it not only speeded up the drying period, but also helped in the removal of trace amounts of organic substances which adhered to the product. Thus, after the ether washing the product became pure white, fluffy, and shining.

[4] One ml. of this alloy contains approximately 0.02 g.-atom of potassium and 0.007 g.-atom of sodium. The alloy was transferred by a 2-ml. graduated pipet. Occasionally, a film of alloy attached to the inner wall of the pipet after the delivery of the alloy to the reaction flask. This was removed easily by placing the pipet (tip down) in an ordinary test tube. A few drops of ethanol were added to the top of the pipet which was then closed immediately with the forefinger. As the ethanol flowed down it reacted with the alloy and liberated hydrogen which pushed all the alloy down into the test tube and thus was destroyed slowly and safely.

anhydrous ether was added and the resulting light brown suspension was stirred under nitrogen at room temperature for 24 hours.[5] At the end of this period the color of the reaction mixture varied from dark greenish-brown to light tan. It was observed that if too much ether was used at the beginning of the reaction it took a long time for the initiation of the reaction. On the other hand, if the alloy and hexaphenyldisilane were stirred alone in the absence of ether, the reaction mixture turned dark and sticky, probably due to some decomposition. By using about 5 ml. of ether at the beginning a prompt initiation was ensured. This has been checked many times. The second batch of ether was added in order to convert the paste to a suspension. Otherwise an appreciable amount of hexaphenyldisilane would not contact the sodium-potassium alloy in the paste. If the second batch of ether was added too soon the tan color of the paste would disappear and usually some time was required for the color to reappear, probably due to the reaction of triphenylsilylpotassium with traces of impurities in the ether. However, after one hour enough triphenylsilylpotassium had been formed so that the addition of ether did not stop the reaction.

Under normal conditions the reaction mixture after 24 hours of stirring was brownish-tan with some droplets of shining alloy suspended in it. The excess alloy could be removed by amalgamation. While the suspension was being stirred, small portions of mercury were added dropwise against a stream of nitrogen. Much heat was evolved especially when the first few drops of mercury were added. As the amalgam formed swirled around in the bottom of the flask it picked up the excess alloy so that gradually the concentration of the amalgam increased to form a solid amalgam. Therefore, more mercury was added until a viscous, semi-liquid silvery white amalgam was formed which did not change to solid in a period of half an hour. Usually, it took about 15–20 g. of mercury for the amalgamation and one to two hours seemed to be sufficient for this process.

The triphenylsilylpotassium suspension was decanted from the viscous amalgam to a nitrogen-filled dropping-funnel. The flask was rinsed once with anhydrous ether and the washing was combined with the suspension. Usually one washing was sufficient to transfer all material but the heavy, viscous amalgam to the dropping-funnel. Due to the lack of a suitable method for the analysis of the triphenylsilylpotassium suspension it was assumed that the cleavage reaction was complete. This assumption was justified since in only a few cases was any hexaphenyldisilane recovered after completion of the reaction. A test for the completion of the cleavage reaction involved the removal of a sample and its hydrolysis.[6] The appearance of white solids at the interface indicated an incomplete reaction since hexaphenyldisilane is insoluble in ether while triphenylsilanol (from the hydrolysis of triphenylsilylpotassium) is soluble. The triphenylsilylpotassium was now ready for the subsequent reactions. Color Test I (10) for the triphenylsilylpotassium was positive, the organic layer being bluish-green and the aqueous layer being violet.

Hydrolysis of triphenylsilylpotassium. The triphenylsilylpotassium suspension was prepared in accordance with the procedure described above from 2.6 g. (0.005 mole) of hexaphenyldisilane and 0.7 ml. of sodium-potassium alloy. Following the removal of excess alloy by the amalgamation procedure, water was added to the reaction mixture and the latter was then filtered to remove traces of insoluble solid. The ethereal solution was separated from the filtrate, dried over sodium sulfate, and distilled to give a somewhat oily colorless residue. This residue was recrystallized twice from petroleum ether (b.p. 60–70°) to yield 1.6 g. (58%) of triphenylsilanol (mixture m.p.) melting at 150–152°.

Effect of prolonged period of amalgamation. In the first experiment a mixture of 2.6 g. (0.005 mole) of hexaphenyldisilane and 0.8 ml. of sodium-potassium alloy was stirred in

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[5] Although the cleavage reaction might be complete in a shorter period of time the mixture was stirred for about 24 hours because of convenience.

[6] If the excess alloy has not been removed by the amalgamation procedure the hydrolysis must be carried out with extreme care due to the possible contamination of alloy in the sample. This can be done safely only in a nitrogen atmosphere.

ether for 24 hours. Then a large excess of mercury was added and the amalgamated mixture was stirred for an additional 48 hours. The resulting greenish-yellow mixture was hydrolyzed with water. The reaction products were worked up to give only 25% of triphenylsilanol and 8% of hexaphenyldisiloxane.

In the second experiment using the same amount of alloy and hexaphenyldisilane the excess alloy was removed by amalgamation. The triphenylsilylpotassium suspension was separated from the amalgam and then 10 g. of mercury was added to the triphenylsilylpotassium suspension. After 48 hours of stirring at room temperature 1.2 g. of trimethylchlorosilane was added to the reaction mixture. The resulting mixture was stirred for 10 minutes and was hydrolyzed. From the ethereal solution an oily residue was obtained. Following repeated recrystallizations only 4% of 1,1,1-triphenyl-2,2,2-trimethyldisilane was isolated from the rest of the oily products.

Preparation of triphenylsilylpotassium in benzene. A mixture of 1.3 ml. of sodium-potassium alloy, 5 ml. of sodium-dried benzene, and 5.2 g. (0.01 mole) of hexaphenyldisilane was stirred at room temperature under an atmosphere of nitrogen. After about 15 minutes a greyish-tan color formed. Another 40 ml. of benzene was added after 30 minutes. The reaction mixture was stirred for 24 hours. Trimethylchlorosilane (2.5 g.) dissolved in 10 ml. of benzene was added rapidly to the greyish-green mixture. Heat was evolved during the addition. After 15 minutes the grey mixture thus formed was treated with water. There was obtained 3.7 g. (71%) of uncleaved hexaphenyldisilane by filtration. The gummy solid from the benzene solution was recrystallized from 95% ethanol to give 1 g. (15%) of 1,1,1-triphenyl-2,2,2-trimethyldisilane (mixture m.p.) melting at 106–108°.

Preparation of triphenylsilylpotassium in petroleum ether. In an experiment using the same conditions as those described in the preceding section, except that petroleum ether (b.p. 60–70°) was used instead of benzene, 79% of hexaphenyldisilane was recovered. Only 6% of pure 1,1,1-triphenyl-2,2,2-trimethyldisilane was obtained.

Reactions of triphenylsilylpotassium with organic halides. The procedures for the reactions of triphenylsilylpotassium with benzyl chloride and *o*-bromotoluene were essentially the same. This involved the addition of the amalgamated triphenylsilylpotassium suspension to the organic halide in ether. The reaction mixture was stirred for the length of time indicated in Table I. Then the reaction mixture was hydrolyzed by slow addition of water and filtered to remove any insoluble solid. The organic layer was worked up in the conventional manner and recrystallized from the solvents indicated in the Table. In the experiment with *p*-iodotoluene, the organic halide was added to the triphenylsilylpotassium suspension containing the excess alloy and worked up as usual.

Preparation of triphenylsilyltriphenyltin. A triphenylsilylpotassium suspension prepared by the procedure described above from 0.01 mole of hexaphenyldisilane was, after amalgamation, added rapidly to 7.7 g. (0.02 mole) of triphenyltin chloride suspended in 50 ml. of anhydrous ether. Some heat was evolved during the addition and the tan color of the reaction mixture faded away slowly. Color Test I (10) at the end of 2 hours was positive, at the end of 4 hours weakly positive, and at the end of 6 hours negative. At this time the white mixture was hydrolyzed and filtered. The insoluble solid residue was dried at 110° to give 10.5 g. (86%) of crude product melting at 280–286°. Recrystallization was effected by dissolving the crude product in dioxane-benzene (1:1), which after hot filtration was cooled slowly to room temperature. There was obtained 9.2 g. (76%) of fine, colorless, shiny crystals. The melting point depended somewhat on the rate of heating. When a sample was heated slowly it melted at 288°. When it was heated fairly rapidly it melted at 296–298° to a clear liquid. On further heating the liquid turned yellow and became more and more turbid with the separation of a gray solid. This indicates that triphenylsilyltriphenyltin is not stable above its melting point. A mixture melting point of this sample with the triphenylsilyltriphenyltin prepared by the reaction of triphenyltin-lithium and triphenylchlorosilane (11) was not depressed.

Preparation of triphenylsilylpotassium from triphenylethoxysilane. A mixture of 3.0 g. (0.01 mole) of triphenylethoxysilane, 1.2 ml. of sodium-potassium alloy, and 100 ml. of anhydrous ether was stirred at room temperature for 18 hours to give a dark suspension. Then 3.5 g. (0.022 mole) of bromobenzene in 15 ml. of ether was added rapidly to the reaction mixture, and the latter was stirred for 15 minutes. Dilute hydrochloric acid was added carefully to destroy the excess alloy. From the hydrolyzed mixture 1.6 g. (48%) of solid melting from 218–231° was obtained by filtration. After 2 recrystallizations from benzene, 0.8 g. (24%) of colorless crystals melting at 233–235° was obtained; a mixture melting point with an authentic sample of tetraphenylsilane showed no depression.

Preparation of triphenylsilylpotassium from triphenylchlorosilane. The use of triphenylchlorosilane for the preparation of triphenylsilylpotassium was studied in more detail because it is commercially available. In all reactions using triphenylchlorosilane the excess alloy was not removed. The mixture containing triphenylchlorosilane and sodium-potassium alloy was stirred in ether under a nitrogen atmosphere. First, the alloy was broken up into small droplets coated with a gray material. After several hours of vigorous stirring a brown color gradually developed from the dark mixture, indicating that an appreciable amount of triphenylsilylpotassium had been formed. The reaction mixture was stirred for the period of time indicated in Table II. An ethereal solution of trimethylchlorosilane was then added and stirred for an additional 15 to 30 minutes. The reaction mixture was then hydrolyzed. The layers were filtered to remove any white insoluble hexaphenyldisilane, which usually collected at the ether-water interface, and the ether layer was separated, dried with sodium sulfate, and distilled. The crude product thus separated was recrystallized from 95% ethanol. The results are summarized in Table II. The isolation of hexaphenyldisilane suggests that the disilane may be an intermediate product in this reaction.

In run No. 6, instead of adding trimethylchlorosilane, triethylchlorosilane was used. The reaction product was worked up in the same way to give 60% of pure 1,1,1-triphenyl-2,2,2-triethyldisilane.

Preparation of triphenylsilylpotassium from tetraphenylsilane. A mixture of 3.4 g. (0.01 mole) of tetraphenylsilane and 2 ml. of sodium-potassium alloy in 50 ml. of ether was stirred for 24 hours at room temperature. Mercury was added cautiously to the dark brown mixture to amalgamate the excess alloy. The suspension was decanted from the amalgam into a dropping-funnel, and added to 11.8 g. (0.04 mole) of triphenylchlorosilane dissolved in ether. Some heat was evolved, and the color of the reaction mixture became light gray rapidly. After 20 minutes of stirring water was added, and the reaction mixture was filtered to separate 7.5 g. of insoluble residue. This was boiled with benzene, cooled, and filtered to give 4.3 g. (83%) of solid melting at 350–355°. One recrystallization from dioxane gave 3.6 g. (70%) of hexaphenyldisilane (mixture m.p.) melting at 360–362°. From the ethereal solution there was obtained 2.1 g. (0.008 mole) of triphenylsilanol (mixture m.p.) melting at 149–150°. This may be the hydrolysis product of either or both triphenylchlorosilane and triphenylsilylpotassium.

Preparation of triphenylsilylpotassium from 1,1,1-triphenyl-2,2,2-trimethyldisilane. A mixture of 2.0 g. (0.006 mole) of 1,1,1-triphenyl-2,2,2-trimethyldisilane, 1.5 ml. of sodium-potassium alloy, and 100 ml. of ether was stirred at room temperature. A yellow color developed immediately, on stirring the reaction mixture, and a large amount of yellow precipitate was formed in the next 2 hours. After 21 hours of stirring a solution containing 1.4 g. (0.009 mole) of bromobenzene dissolved in 20 ml. of ether was added rapidly to the reaction mixture, which then became a light tan suspension, with evolution of heat. Fifteen minutes later water was added to destroy the unused alloy. The mixture was filtered to give 1.2 g. (60%) of solid melting at 230–232°. One recrystallization from benzene raised the melting point to 233–234°; a mixture m.p. with tetraphenylsilane showed no depression. The yield of the pure product was 1.0 g. (50%). The ethereal solution was separated and distilled to leave a small amount of brown liquid containing some white solid. The solid was filtered and washed with a small amount of petroleum ether (b.p. 60–70°) and filtered again to give 0.2 g. of solid melting at 217–226°. This was recrystallized and shown to be impure tetraphenylsilane by a mixture melting point.

Later,this experiment was repeated (9) in a larger size run. There were obtained tetraphenylsilane and phenyltrimethylsilane as the products. The latter product seemed to indicate that trimethylsilylpotassium was also formed.

Reaction of triphenylsilylpotassium with fluorobenzene. An amalgamated triphenylsilylpotassium suspension prepared from 4.0 g. (0.0077 mole) of hexaphenyldisilane by the procedure described above was added rapidly to 1.5 g. (0.016 mole) of fluorobenzene dissolved in 25 ml. of ether. No color change occurred and no heat was evolved during the addition. Six hours later there still appeared to be no apparent change. Another 1.5 g. of fluorobenzene was added to the reaction mixture and it was stirred at room temperature for 70 hours. At the end of this period Color Test I (10) was still strongly positive. Water was added to the reaction mixture. Some heat was evolved while the mixture turned bright yellow and then gradually gave way to a gray suspension. The hydrolyzed mixture was filtered to separate 0.1 g. (3%) of impure hexaphenyldisilane melting at 350–356°. The ethereal solution was separated from the filtrate, dried over sodium sulfate, filtered, and distilled. The oily residue solidified on standing. The solid was washed with a small amount of cold petroleum ether (b.p. 60–70°) and filtered in order to remove the oily material. The solid residue was boiled with ethanol and filtered hot to separate 0.6 g. (12%) of colorless crystals melting at 231–233°; a mixture melting point with tetraphenylsilane showed no depression. Ethanol was distilled from the filtrate. The residue was recrystallized from petroleum ether (b.p. 60–70°) to give 1.3 g. (31%) of triphenylsilanol (mixture m.p.) melting at 149–151°.

Reaction of triphenylsilylpotassium with chlorobenzene. A triphenylsilylpotassium suspension prepared from 8.0 g. (0.015 mole) of hexaphenyldisilane by the usual procedure was, after amalgamation, added rapidly to 3.5 g. (0.031 mole) of chlorobenzene dissolved in 30 ml. of ether. Some heat was evolved during the addition. After 1 hour of stirring the reaction mixture was poured into a Dry Ice-ether slurry so as to see if any carbonation product could be obtained. Following the attainment of room temperature, the carbonation mixture was acidified with dilute hydrochloric acid and filtered. The ethereal solution was separated and extracted three times with dilute aqueous alkaline solution. However, no organic acid separated upon the acidification of the alkaline extract. The ether-insoluble solid from the reaction mixture was filtered and dried to give 7.6 g. of white solid melting at 230° to form a turbid liquid. The crude product was digested with benzene and filtered hot. The insoluble solid was recrystallized from dioxane to give 0.8 g. (10%) of hexaphenyldisilane melting at 362°. The benzene solution was evaporated to a small volume and cooled to give 5.6 g. (53%) of colorless crystals melting at 230–232°; a mixture melting point with tetraphenylsilane was not depressed.

In a second reaction the above experiment was repeated but the chlorobenzene was allowed to react with triphenylsilylpotassium for only 15 minutes. From this run a 60% crude and 50% pure yield of tetraphenylsilane was obtained in addition to the recovery of 5% of hexaphenyldisilane.

Reaction of triphenylsilylpotassium with bromobenzene. In run No. 4 of Table III the procedure was essentially the same as that for chlorobenzene described in the previous section, except that the reaction mixture was hydrolyzed without carbonation. The reaction product was worked up as usual and recrystallized from benzene. The results are given in Table III.

In run No. 5, instead of adding the triphenylsilylpotassium suspension to bromobenzene, the reverse order of addition was carried out. In working up the reaction products a 29% yield of hexaphenyldisilane was isolated in addition to the main product tetraphenylsilane. Reaction No. 6 was a repeat run of No. 5 under similar conditions where a 15% yield of hexaphenyldisilane was obtained. Although it is not certain whether the hexaphenyldisilane isolated was uncleaved material from the preparation of triphenylsilylpotassium, or was a reaction by-product, it seems unlikely that all the hexaphenyldisilane recovered is starting material. Comparison of the results of run No. 5 and No. 6 shows that under approximately the same conditions the results obtained in different runs may not be the same. In a heterogeneous system the reaction is complicated by many factors which might interfere with the rate of reaction as well as the yield of the products.

Reaction of triphenylsilylpotassium with iodobenzene. A triphenylsilylpotassium suspension was prepared from 0.01 mole of hexaphenyldisilane and the excess alloy was removed by amalgamation. It was added, over a period of 5 minutes, to 4.5 g. (0.022 mole) of iodobenzene dissolved in 50 ml. of ether. Some heat was evolved and the reaction mixture became light gray rapidly. Color Test I (10) 5 minutes after the addition was complete was weakly positive, and at the end of 10 minutes was negative. Fifteen minutes after the addition, water was added to the reaction mixture. The latter was filtered to separate 5.8 g. (86%) of a white solid melting at 228° to form a slightly turbid liquid which became clear at 235°. The crude product was recrystallized from benzene to give 4.2 g. (63%) of colorless crystals melting at 233–235°; a mixture melting point with tetraphenylsilane was the same. The ethereal solution was evaporated to give 1.8 g. of light brown gummy solid. Two recrystallizations from a mixture of benzene and petroleum ether (b.p. 60–70°) yielded 0.2 g. (4%) of hexaphenyldisiloxane (mixture melting point) melting at 227–228°.

Attempted reaction of hexaphenyldisilane with magnesium powder. A mixture of 2.6 g. of hexaphenyldisilane, 0.5 g. of magnesium powder (Golwynne Chemicals Corporation, 70% of the powder passes through 325 mesh), and 30 ml. of ether was stirred at room temperature for 24 hours. The unused magnesium was destroyed with dilute hydrochloric acid. The solid residue was washed with water, then with ethanol, and dried. The recovered hexaphenyldisilane (mixture m.p.) melting at 368° weighed 2.4 g. (92%).

Attempted reaction of triphenylchlorosilane with magnesium powder. A few drops of a solution containing 3.0 g. (0.01 mole) of triphenylchlorosilane in 40 ml. of ether was added to 0.5 g. of magnesium powder suspended in 10 ml. of ether. There was no reaction after stirring for 4 hours. The rest of the chloride solution was added to the reaction mixture and it was stirred at room temperature for 24 hours. One gram of trimethylchlorosilane was added to the reaction mixture in order to see if any 1,1,1-triphenyl-2,2,2-trimethyldisilane could be isolated. After two hours the reaction mixture was hydrolyzed with dilute hydrochloric acid. From the ethereal solution there was obtained 2.7 g. (96%) of triphenylsilanol (mixture m.p.) melting at 150–152°.

Reaction of hexaphenyldisilane with rubidium. A mixture of 1.05 g. (0.012 g.-atom) of rubidium, 25 ml. of sodium-dried di-*n*-butyl ether, and 2.6 g. (0.005 mole) of hexaphenyldisilane was heated at 90° (bath temperature). After about 1 hour a light brown color began to form. On further stirring the mixture became deeper brown. After 30 hours of stirring 2.2 g. (0.02 mole) of trimethylchlorosilane in 30 ml. of ether was added rapidly to the triphenylsilylrubidium suspension. The resulting light grey suspension was stirred 45 minutes and then allowed to stand overnight. Water was then added carefully to destroy the unreacted rubidium and the hydrolyzed mixture was filtered to separate 0.3 g. (12%) of light grey solid melted at 360–362°. A mixture melting point with hexaphenyldisilane showed no depression. The ethereal solution was evaporated and yielded 2.5 g. (75%) of colorless solid melting at 95–100°. This was recrystallized twice from 95% ethanol to give 1.6 g. (48%) of pure 1,1,1-triphenyl-2,2,2-trimethyldisilane (mixture m.p.) melting at 107–108°.

Reaction of hexaphenyldisilane with cesium. A mixture of 1.0 g. (0.008 g.-atom) of cesium, 1.5 g. (0.0029 mole) of hexaphenyldisilane, and 3 ml. of ether was stirred at room temperature. After about 1 minute a faint greyish-green coloration appeared in the reaction mixture. After ½ hour, 10 ml. of ether was added. Gradually a dark brown suspension was formed. After 24 hours of stirring 1.3 g. (0.012 mole) of trimethylchlorosilane dissolved in a small amount of ether was added to the triphenylsilylcesium formed. Some heat was evolved, and the reaction mixture became light tan in color. After 30 minutes of stirring, water was added to the reaction mixture. Two liquid layers were formed. From the ethereal solution an oily residue was obtained after evaporation of the ether. Attempts to purify the residue by crystallization were unsuccessful due to the formation of an oil. The solvents were removed and the residue was washed with cold ethanol and filtered to give 1.0 g.

(52%) of crude product melting at 85–92°. This was recrystallized three times from small amounts of 95% ethanol to yield 0.5 g. (26%) of pure product, 1,1,1-triphenyl-2,2,2-trimethyldisilane (mixture m.p.) melting at 107–108°.

SUMMARY

Various methods for the preparation and the manipulation of the significantly useful triphenylsilylpotassium are described. The advantages of using the combination of hexaphenyldisilane with sodium-potassium alloy are discussed.

The reaction of phenyl halides with triphenylsilylpotassium showed that the order of decreasing activity is: iodobenzene, bromobenzene, chlorobenzene, and fluorobenzene. Reactions of triphenylsilylpotassium with other organic halides including those containing silicon and tin are also described.

An amalgamation procedure for the removal of sodium-potassium alloy from the triphenylsilylpotassium suspension after its preparation is described.

Directions are given for the preparation of triphenylsilylrubidium and for triphenylsilylcesium.

AMES, IOWA

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