[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

PREPARATION AND CLEAVAGE OF SOME ORGANOSILANES CONTAINING HETEROCYCLIC GROUPS

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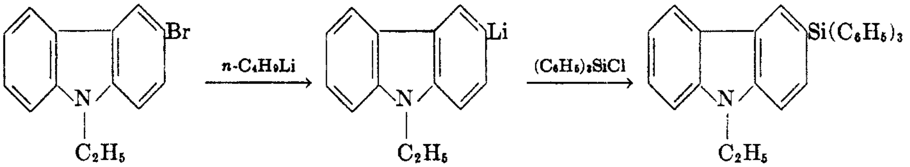
Several tetrasubstituted silanes have been reported in which silicon is attached to the following heterocycles: furan (1a), thiophene (1a, b, c, d, e, f), dibenzothiophene (1g, h), dibenzofuran (1g), quinoline (1d), and quinoxaline (1e). The object of the present investigation was to extend these syntheses to additional heterocyclic[1] systems and to study the stability of the silanes in acidic and in basic solution. The general method of synthesis follows that used previously, namely, treatment of a C-lithium derivative of a heterocycle with triphenylchlorosilane in ether solution. The organolithium compounds were prepared by treatment of either the heterocycle or its bromo derivative with *n*-butyllithium according to known procedures (2). Using these procedures the following triphenylsilanes were prepared in yields based on triphenylchlorosilane ranging from 5 to 71%: 2-benzothiazolyl-, 2-benzothienyl-, 2- and 4- [1*g*] dibenzothienyl-, 2- [1*g*] and 4- dibenzofuryl-, 5-ethyl-4-carbazolyl-, 5-ethyl-2-carbazolyl-, and 8-chloro-5-ethyl-2-carbazolyl-. By treatment of 5-ethyl-2-carbazolyllithium with the appropriate chlorosilane, the following silanes were prepared in yields based on the chlorosilane of 25 to 82%: diphenylbis(5-ethyl-2-carbazolyl)-, phenyltris(5-ethyl-2-carbazolyl)-, and tetrakis(5-ethyl-2-carbazolyl)-.

The preparation of 2-benzothiazolyltriphenylsilane was made difficult by the instability (3) of 2-benzothiazolyllithium at temperatures above −35°. Unfortunately there was no appreciable reaction with triphenylchlorosilane at this temperature. At a higher temperature of −15 to −10° only a 5% yield was obtained. This was increased to 19% by employing the more reactive compound triphenylbromosilane. Likewise, the use of this reagent increased the yield of 5-ethyl-4-carbazolyltriphenylsilane from 8 to 12%.



The interaction of trisubstituted silanes with an organolithium compound to form tetrasubstituted silanes has been reported (4), but apparently trisubstituted silanes are less reactive in some reactions than trisubstituted chlorosilanes (5). From triphenylsilane and 2-benzothiazolyllithium no 2-benzothiazolyltriphenylsilane could be isolated.

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[1] *Chemical Abstracts* numbering conventions are followed with the sole exception that the carbazole ring system is numbered in a manner analogous to the related dibenzofuran and dibenzothiophene systems.

Tetrasubstituted silanes can also be prepared (6) by treatment of an appropriate halide with triphenylsilylpotassium.

$$(C_6H_5)_3SiK + RBr \rightarrow (C_6H_5)_3SiR + KBr$$

With 2-bromodibenzothiophene and 2-bromo-5-ethylcarbazole 57% yields of the corresponding silanes were obtained. These products were identical with those obtained from the organolithium compounds and triphenylchlorosilane.

The cleavage of tetrasubstituted silanes by acids and by bases has been the subject of a number of recent investigations. Acid cleavages have been reported with hydrogen chloride in acetic acid (1g, h, 7) and with concentrated sulfuric acid (8). It has been shown (7a) that the ease of hydrogen chloride cleavage of an aryl substituent from a number of trimethylarylsilanes decreases in the order: 2-thienyl > *p*-anisyl and *p*-dimethylaminophenyl > *p*-tolyl > phenyl > *p*-chlorophenyl. This has been shown to be in essential agreement with the ease of removal of radicals from organic derivatives of mercury and lead. That is, the ease of cleavage depends on the electronegativity of the radicals as determined by the Kharasch procedure (9, 10). Benkeser has extended this work to a series of *m*- and *p*-substituted aryltrimethylsilanes, and has related the ease of cleavage

TABLE I

CLEAVAGES OF TETRASUBSTITUTED SILANES BY HYDROGEN CHLORIDE IN GLACIAL ACETIC ACID FOR 15 HOURS AT REFLUX TEMPERATURE

Silane	Silane, Mole	Recovered Silane, %	Products[a]
5-Ethyl-2-carbazolyltriphenyl-	0.005	0	25% Triphenylsilanol 51% 5-Ethylcarbazole
Diphenylbis(5-ethyl-2-carbazolyl)-	.005	0	75% 5-Ethylcarbazole[b]
Phenyltris(5-ethyl-2-carbazolyl)-	.0015	0	66% 5-Ethylcarbazole[b]
Tetrakis(5-ethyl-2-carbazolyl)-	.005	0	73% 5-Ethylcarbazole[b]
5-Ethyl-4-carbazolyltriphenyl-	.005	0	33% Triphenylsilanol 84% 5-Ethylcarbazole Trace of benzene[c]
2-Dibenzothienyltriphenyl-	.005	74	0
4-Dibenzothienyltriphenyl-	.005	78	0
2-Dibenzofuryltriphenyl-	.005	0	19% Triphenylsilanol 31% Dibenzofuran 8% Benzene[c]
4-Dibenzofuryltriphenyl-	.005	75	0
2-Benzothienyltriphenyl-	.005	0	7% Triphenylsilanol
2-Thienyltriphenyl-[d]	.005	0	21% Triphenylsilanol[d]
2-Benzothiazolyltriphenyl-	.0025	0	20% Triphenylsilanol 7% Benzene[c]
Triphenylchloro-	.02	—	24% Triphenylsilanol 2% Benzene[c]

[a] Unless otherwise noted no attempt was made to recover volatile products. [b] Calculated on the basis of removal of all of the 5-ethylcarbazole groups. [c] Isolated by condensation from the evolved gases. Estimated and identified as *m*-dinitrobenzene. Yield calculated on the basis of cleavage of one phenyl group. [d] Gilman and Marshall (7a) obtained 13% triphenylsilanol after a reaction time of seven hours.

to the Hammett σ-value (7c) and to the ease of electrophilic substitution of the aromatic radical (1f).

Alkaline cleavages have been studied with alkali amides or alkoxides (11), *n*-butyllithium (12), and with potassium hydroxide (13). In general it is known that tetraalkylsilanes are stable to alkali but that halogen-substituted groups and unsaturated or aromatic groups can be cleaved. It has been shown (13) that the ease of cleavage of a hydrocarbon radical from silicon is dependent on the acidity or electron-attracting properties of the corresponding hydrocarbon as determined by the procedure of Conant (14).

In the present study the earlier cleavage procedures were followed. The acid cleavages were carried out under a stream of hydrogen chloride in glacial acetic acid at reflux temperature (7a). The alkaline cleavages were carried out at 85° in a mixture of potassium hydroxide, alcohol, dioxane, and a small amount of water (13).

The results of the acid cleavages, Table I, indicate that, in general, there is extensive cleavage of the heterocyclic substituent from silicon. In connection

TABLE II

CLEAVAGE OF TETRASUBSTITUTED SILANES BY POTASSIUM HYDROXIDE AT 85°

Silane	Silane, Mole	Reagent	Time, Hours	Recovered Silane, %	Products
5-Ethyl-2-carbazolyltriphenyl-	0.001	D	24	98	0
Diphenylbis(5-ethyl-2-carbazolyl)-	.0005	C	24	93	0
Phenyltris(5-ethyl-2-carbazolyl)-	.00025	C	24	93	0
Tetrakis(5-ethyl-2-carbazolyl)-	.0005	C	24	97	0
8-Chloro-5-ethyl-2-carbazolyltriphenyl-	.002	D	1	91	0
5-Ethyl-4-carbazolyltriphenyl	.002	D	1	59	18% Triphenylsilanol 26% 5-Ethylcarbazole
5-Ethyl-4-carbazolyltriphenyl-	.0005	C	1	79	2% Triphenylsilanol
5-Ethyl-4-carbazolyltriphenyl	.0005	C	24	17	45% Triphenylsilanol 64% 5-Ethylcarbazole
2-Dibenzothienyltriphenyl	.001	D	1	93	0
4-Dibenzothienyltriphenyl	.001	D	1	11	44% Triphenylsilanol 44% Dibenzothiophene
2-Dibenzofuryltriphenyl	.001	D	1	93	0
4-Dibenzofuryltriphenyl	.001	D	1	0	73% Triphenylsilanol 48% Dibenzofuran
2-Benzothienyltriphenyl	.001	D	1	0	83% Triphenylsilanol 33% Benzothiophene[a]
2-Thienyltriphenyl	.002	D	1	0	69% Triphenylsilanol
2-Benzothiazolyltriphenyl	.001	D	1	0	73% Triphenylsilanol

[a] Isolated and identified as the picrate, G. Komppa, *Acta Soc. Sci. Fennicae*, **23**, 1 (1897) [*Chem. Zentr.*, **68**, **II**, 270 (1897)].

with the resistance to cleavage of the 4-dibenzofuryl and 4-dibenzothienyl radicals it is to be noted that the 4-position in these heterocycles does not readily undergo electrophilic substitution.

The low yields of triphenylsilanol as compared with the yields of the heterocyclic substituents are in agreement with the previous report (7a) that cleavage of phenyl radicals from silicon also occurred. In partial confirmation of this it is noted that triphenylchlorosilane can be recovered only in 25% yield (as triphenylsilanol). In addition, benzene was isolated in several instances.

Under alkaline conditions, Table II, dibenzofuryl, dibenzothienyl, and carbazolyl substituents are resistant to cleavage when attached to silicon in the 2- position, but are cleaved when attached in the 4- position. The acidity of the 4- positions in each of these heterocycles has been demonstrated by metalation studies. In addition, the relative ease of cleavage: 4-dibenzofuryl > 4-dibenzothienyl > 4- carbazolyl, is the same as the relative ease of metalation (15) of these heterocycles. The 2-benzothienyl, 2-thienyl, and 2-benzothiazolyl substituents are also readily cleaved. Again this is in agreement with the marked ease with which these heterocycles can be metalated (3b) in the 2- position. These observations are in accord with the earlier conclusion (13) that the ease of alkaline cleavage of a substituent depends on the acidity of the related hydrocarbon.

It is apparent that the relative ease of cleavage of heterocyclic substituents from silicon is not the same under acidic and under basic conditions. While the present work is inconclusive, it does suggest that the ease of acidic and of basic cleavages are to some extent opposite.

EXPERIMENTAL[2]

2-Bromo-5-ethylcarbazole.[3] A solution was prepared from 19.5 g. (0.1 mole) of 5-ethylcarbazole, 300 ml. of glacial acetic acid, 8.0 g. (0.067 mole) of potassium bromide, and 15 ml. of water. This was kept at 25 to 35° by a cooling bath while 12.5 g. (0.075 mole) of finely powdered potassium bromate was added portionwise during 30 minutes. The resulting mixture was stirred for three hours at 25° and then filtered to give 15.9 g. (58%) of a solid, melting at 79.5–81.5°. One recrystallization from ethanol gave 11.0 g. of crystals melting at 82.5–84.5°.

5-Ethyl-2-carbazolylsilanes. 5-Ethyl-2-carbazolyllithium[4] was prepared by interaction of 11.0 g. (0.04 mole) of 5-ethyl-2-bromocarbazole in 50 ml. of benzene and 0.04 mole of *n*-butyllithium[5] in 28 ml. of ethyl ether for 3 hours at 25°. This halogen-metal interconversion was

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[2] All melting points are uncorrected. All operations involving organometallic compounds were carried out under an atmosphere of dry oxygen-free nitrogen, in sodium-dried solvents. All directions involving ethanol refer to the absolute solvent.

[3] This preparation has been reported previously but in scant detail (16a, b).

[4] Gilman and Spatz (17) carried out this halogen-metal interconversion at reflux temperature for one hour. On carbonation they obtained a 71% yield of the carboxylic acid.

[5] The preparation of *n*-butyllithium, Gilman, Beel, Brannen, Bullock, Dunn, and Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949), has been modified by Mr. K. Oita of this laboratory. By employing a lower reaction temperature of −35 ± 5° for one hour followed by a two hour period at 0°, 89 to 94% yields were obtained.

The titer of *n*-butyllithium was determined by the double titration method of Gilman and Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

assumed to be quantitative in the calculations of the molar quantities used in the following preparations.

5-Ethyl-2-carbazolyltriphenylsilane. A. Using triphenylchlorosilane. A solution of 10.7 g. (0.036 mole) of triphenylchlorosilane in 900 ml. of ethyl ether was added at 25° with cooling to a solution containing 0.04 mole of 5-ethyl-2-carbazolyllithium. After 15 minutes Color Test I (18) was negative. After hydrolysis with ice and sulfuric acid, filtration gave 13.7 g. (75%) of a solid melting at 216–219°. Recrystallization from ethanol-benzene (2:1) gave 11.6 g. (64%) of crystals melting at 218–220°. The analytical sample melted at 218.5–220°.

Anal.[6] Calc'd for $C_{32}H_{27}NSi$: C, 84.70; H, 6.00; N, 3.09, Si, 6.2.
Found: C, 84.73, 84.89; H, 6.02, 6.00; N, 3.17, 3.22; Si, 6.2, 6.2.

B. Using triphenylsilylpotassium. Triphenylsilylpotassium (6), prepared from 5.2 g. (0.01 mole) of hexaphenyldisilane, was added cautiously to a stirred solution of 5.48 g. (0.02 mole) of 2-bromo-5-ethylcarbazole in 30 ml. of ethyl ether. During the addition vigorous refluxing occurred. After 30 minutes Color Test I was very weak. Hydrolysis with ice and dilute hydrochloric acid gave 5.66 g. (63%) of a solid melting at 211–215°. Recrystallization gave 5.14 g. (57%) of tan crystals melting at 213–217°. A mixture melting point with the product from procedure A was not depressed.

Diphenylbis(5-ethyl-2-carbazolyl)silane. A solution of 8.3 g. (0.033 mole) of diphenyldichlorosilane in 25 ml. of ethyl ether was added at 25° with cooling to a solution containing 0.07 mole of 5-ethyl-2-carbazolyllithium. After 60 minutes Color Test I was negative. Hydrolysis with ice and dilute sulfuric acid followed by filtration gave 18.6 g. of a solid melting at 196–240°. Repeated recrystallizations from ethanol-benzene (2:1) and from ethanol-chloroform (2:1) gave 14.6 g. (77%) of crystals melting at 233–235°.

Anal. Calc'd for $C_{40}H_{34}N_2Si$: Si, 4.9. Found: Si, 4.8, 4.8.

Phenyltris(5-ethyl-2-carbazolyl)silane. A solution of 4.9 g. (0.023 mole) of phenyltrichlorosilane in 25 ml. of ethyl ether was added at 25° with cooling to a solution containing 0.08 mole of 5-ethyl-2-carbazolyllithium. After eleven hours Color Test I was negative. Subsequent to hydrolysis with ice and very dilute sulfuric acid, filtration gave 14.0 g. (88%) of a solid melting at 279–282°. Repeated recrystallizations from benzene-ethanol, chloroform-ethanol, and dioxane-ethanol gave 3.9 g. (25%) of a powder melting at 292–294°.

Anal. Calc'd for $C_{48}H_{41}N_3Si$: Si, 4.1. Found: Si, 4.0, 3.9.

Tetrakis(5-ethyl-2-carbazolyl)silane. A solution of 3.7 g. (0.022 mole) of silicon tetrachloride in 25 ml. of ether was added at 25° with cooling to a solution containing 0.13 mole of 5-ethyl-2-carbazolyllithium. The mixture was kept at 25° for 12 hours and then stirred under reflux for three hours. After hydrolysis with ice and dilute sulfuric acid, filtration gave 15.6 g. (88%) of a solid melting at 328–339°. One recrystallization from chloroform-ethanol gave 14.6 g. (82%), m.p. 335–337°.

Anal. Calc'd for $C_{56}H_{48}N_4Si$: Si, 3.5. Found: Si, 3.4, 3.4.

8-Chloro-5-ethyl-2-carbazolyltriphenylsilane. A solution of 15.4 g. (0.05 mole) of 8-chloro-2-bromo-5-ethylcarbazole (16a) in 85 ml. of benzene was kept at 0 to 2° while 32 ml. of an ethyl ether solution containing 0.05 mole of *n*-butyllithium was added during ten minutes. After one hour at this temperature and 30 minutes at 10°, Color Test II-A (19) was negative. The solution was kept at 10° while a solution of 13.5 g. (0.046 mole) of triphenylchlorosilane in 90 ml. of ethyl ether was added during 30 minutes. After 30 minutes Color Test I was negative. The mixture was hydrolyzed with ice and aqueous ammonium chloride. The ether phase was separated, washed with water, dried with sodium sulfate and vacuum-concentrated. The resulting oil was diluted with 34 ml. of warm benzene. Addition of 120 ml. of ethanol gave 16.5 g. (74%) of crystals melting at 165–167°. One recrystallization from ethanol-benzene gave 15.8 g. (71%), m.p. 166–168°.

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[6] Silicon analyses were performed by the procedure of Gilman, Hofferth, Melvin, and Dunn, *J. Am. Chem. Soc.*, **72**, 5767 (1950). A qualitative silicon test, Gilman, Ingham, and Gorsich, *J. Am. Chem. Soc.*, **76**, 918 (1954), was positive.

Anal. Calc'd for $C_{32}H_{26}ClNSi$: Si, 5.8. Found: Si, 5.7, 5.8.

5-Ethyl-4-carbazolyltriphenylsilane. A stirred solution of 300 ml. of ether, 29.3 g. (0.15 mole) of 5-ethylcarbazole, and 0.155 mole of *n*-butyllithium was refluxed for 20 hours. An additional 0.10 mole of *n*-butyllithium was added and the refluxing was continued for a further 24 hours. Color Test II-A was negative. The resulting solution of 5-ethyl-4-carbazolyllithium (16b) was filtered and then treated with a solution of 54.2 g. (0.16 mole) of triphenylbromosilane (20) in 650 ml. of ether. After the solution had refluxed for 24 hours, Color Test I was very faint. The solution was hydrolyzed with ice and aqueous ammonium chloride. The ether phase was dried over sodium sulfate and vacuum-concentrated to a thick syrup. This was diluted with 250 ml. of petroleum ether (b.p. 60–70°) and allowed to stand several hours. Filtration gave 23.6 g. of a solid melting at 133–137°. This solid was freed of triphenylsilanol by digestion with 200 ml. of warm ethanol. Filtration gave 9.6 g. of a residue which melted at 184–192°. Crystallization from a mixture of 20 ml. of benzene and 100 ml. of ethanol gave 8.2 g. (12%) of crystals, melting at 195–197°. The analytical sample melted at 197–198°.

Anal. Calc'd for $C_{32}H_{27}NSi$: Si, 6.2. Found: Si, 6.1, 6.2.

When the procedure was repeated using triphenylchlorosilane an 8% yield of material melting at 196–197.5° was obtained. A mixture melting point with the preceding sample was not depressed.

2-Dibenzothienyltriphenylsilane.[7] *A. From triphenylchlorosilane.* A suspension of 26.3 g. (0.01 mole) of 2-bromodibenzothiophene in 300 ml. of ethyl ether was stirred at 5° while 73 ml. of an ether solution containing 0.1 mole of *n*-butyllithium was added rapidly. The suspension dissolved at once. After four minutes there was added a solution of 29.4 g. (0.1 mole) of triphenylchlorosilane in 210 ml. of ethyl ether, and the mixture was allowed to come to room temperature. After 12 hours Color Test I was negative. Hydrolysis with ice and aqueous ammonium chloride gave 22.9 g. (52%) of a solid melting at 153–155°. An analytical sample after repeated recrystallizations from ethanol-benzene melted at 153–154°.

Anal. Calc'd for $C_{30}H_{22}SSi$: Si, 6.35. Found: Si, 6.4, 6.4.

B. From triphenylsilylpotassium. A suspension of triphenylsilylpotassium prepared from 5.2 g. (0.01 mole) hexaphenyldisilane was added during five minutes to a stirred suspension of 5.26 g. (0.02 mole) of 2-bromodibenzothiophene in 30 ml. of ether. After 15 minutes the vigorous reaction had subsided and Color Test I was negative. Working up as in procedure A gave 5.09 g. (57%) of a tan-colored solid melting at 148–151°. Repeated recrystallization gave crystals melting at 153–155°, both alone and on admixture with the product from procedure *A*.

4-Dibenzothienyltriphenylsilane.[8] Three hundred ml. of an ethyl ether solution containing 27.6 g. (0.15 mole) of dibenzothiophene and 0.15 of *n*-butyllithium was refluxed for three hours. A solution of 39 g. (0.133 mole) of triphenylchlorosilane in 400 ml. of ethyl ether was added at 25°. After two hours Color Test I was negative. Hydrolysis with ice and aqueous ammonium chloride gave 25.2 g. (42%) of a solid melting at 178–184°. Three recrystallizations from chloroform-ethanol and one from ethyl acetate gave 6.5 g. (11%), m.p. 196–198°.

2-Benzothienyltriphenylsilane. 2-Benzothienyllithium (21) was prepared by interaction of 2.01 g. (0.015 mole) of benzothiophene and 0.016 mole of *n*-butyllithium in 15 ml. of ethyl ether for 90 minutes at −20 to −15°. A suspension of 4.41 g. (0.015 mole) of triphenylchlorosilane in 10 ml. of ether was added rapidly. The temperature was allowed to rise to 25° during 90 minutes. After an additional 90 minutes at 25° Color Test I was negative. Hydrolysis with ice and dilute sulfuric acid gave 5.27 g. (90%) of a powder melting at 134–143°. Two recrystallizations from benzene-ethanol gave 4.18 g. (71%), m.p. 148–149°.

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[7] This procedure is related to the preparation of 2-trimethylsilyldibenzothiophene (1h).

[8] A similar procedure (1g) was employed with triphenylethoxysilane to prepare 4-dibenzothienyltriphenylsilane, m.p. 193–194° in 7% yield, and 2-dibenzofuryltriphenylsilane, m.p. 124–125° in 9% yield.

Anal. Calc'd for $C_{26}H_{20}SSi$: Si, 7.2. Found: Si, 7.2, 7.3.

2-Dibenzofuryltriphenylsilane (22). A solution of 24.7 g. (0.1 mole) of 2-bromodibenzofuran in 200 ml. of benzene and 0.105 mole of *n*-butyllithium in 90 ml. of ethyl ether was refluxed for 25 minutes. The resulting solution of 2-dibenzofuryllithium (22) was treated at 25° with a solution of 29.4 g. (0.1 mole) of triphenylchlorosilane dissolved in 310 ml. of ethyl ether. After 15 minutes Color Test I was negative. The mixture was hydrolyzed with ice and aqueous ammonium chloride. The ether phase was separated, washed with water, dried with magnesium sulfate, and vacuum-concentrated to give a viscous oil. The oil was treated with 25 ml. of hot benzene and 100 ml. of ethanol to give 25.0 g. (59%) of crystals which melted at 113–120°. One recrystallization from benzene-ethanol and two recrystallizations from chloroform-ethanol gave 18.4 g. (43%) of crystals which melted at 137.5–138.5°.

Anal. Calc'd for $C_{30}H_{22}OSi$: Si, 6.6. Found: Si, 6.7, 6.6.

4-Dibenzofuryltriphenylsilane. 4-Dibenzofuryllithium (15) was prepared by refluxing for 17 hours a solution of 25.2 g. (0.15 mole) of dibenzofuran and 0.16 mole of *n*-butyllithium in 200 ml. of ethyl ether. There was then added during 40 minutes at 25°, a solution of 41.2 g. (0.14 mole) of triphenylchlorosilane in 250 ml. of ethyl ether. The reaction mixture was maintained at room temperature for four hours and at reflux temperature for two hours. Hydrolysis with ice and aqueous ammonium chloride gave 41.0 g. (69%) of a solid that melted at 147–153°. One crystallization from benzene-ethanol gave 37.9 g. (63%) of crystals that melted at 152–154°. An analytical sample melted at 153–154°.

Anal. Calc'd for $C_{30}H_{22}OSi$: Si, 6.6. Found: Si, 6.6, 6.6.

2-Benzothiazolyltriphenylsilane. 2-Benzothiazolyllithium (3) was prepared by maintaining a solution of 0.05 mole of *n*-butyllithium in 155 ml. of ethyl ether at −65 to −55° while a solution of 6.8 g. (0.05 mole) of benzothiazole in 20 ml. of ethyl ether was added during 15 minutes. After this pale yellow solution had stood five minutes there was added, during 15 minutes at −45°, a solution of 17.0 g. (0.05 mole) of triphenylbromosilane in 200 ml. of ethyl ether. The temperature was allowed to rise to −13° during four hours and then was maintained at −13 to −10° for four additional hours. The clear dark amber solution gave a negative Color Test I. The solution was treated with ice and aqueous ammonium chloride. The ether phase was separated, washed with water, dried over sodium sulfate and vacuum-concentrated. The semi-solid residue was extracted with 300 ml. of boiling petroleum ether (b.p. 60–70°). This extract was vacuum-concentrated and then treated with 15 ml. of benzene and 50 ml. of ethanol. After two days at 0°, filtration gave 5.43 g. of a yellow solid, m.p. 130–142°. Two recrystallizations from a mixture of 6 ml. of benzene and 15 ml. of ethanol gave 3.71 g. (19%) of yellow crystals melting at 139–141°. An analytical sample was decolorized by dissolution in benzene and passage through an activated alumina column. Two additional recrystallizations from benzene-ethanol gave crystals that melted at 141–142°.

Anal.[9] Calc'd for $C_{25}H_{19}NSSi$: Si, 7.1. Found: Si, 7.2, 7.3.

In the preparation of this compound triphenylchlorosilane can be substituted for triphenylbromosilane. However, the yield is decreased to 5% of impure material, m.p. 133–140°.

An attempted preparation using 2-benzothiazolyllithium and an equivalent amount of tripyenylsilane at −28 to −23° for 12 hours gave none of the desired product. Triphenylsilane was recovered in 57% yield.

Hydrogen chloride cleavage procedure. The procedure used for the experiments in Table I is illustrated with 5-ethyl-2-carbazolyltriphenylsilane. Hydrogen chloride was dried with sulfuric acid and bubbled through a refluxing solution of 2.27 g. (0.005 mole) of the silane in 25 ml. of glacial (99.5%) acetic acid at a rate of several ml. per minute for 15 hours. The excess solvent was removed under a vacuum at a bath temperature below 60°. The gummy residue was extracted with a total of 60 ml. of 90% aqueous methanol (13). Vacuum-concentration of the methanol extracts gave a mixture of triphenylsilanol and 5-ethylcarbazole. Treatment of this mixture with 10 ml. of petroleum ether (b.p. 60–70°) left a residue of 0.34 g. (25%) of triphenylsilanol which melted at 150.5–152°. Evaporation of the petroleum ether

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[9] Microdetermination of silicon, Gilman and Miller, *J. Am. Chem. Soc.*, **73**, 968 (1951).

and vacuum sublimation of the residue gave 0.50 g. (51%) of 5-ethylcarbazole melting at 66–69°. Both products were identified by mixture melting points with authentic samples.

Potassium hydroxide cleavage procedures. According to the reported procedures (13) (Table II), reagent C was prepared from 1.7 g. of potassium hydroxide, 5.4 ml. of water, 75 ml. of absolute ethanol, and 300 ml. of purified dioxane. Reagent D was prepared from 20 g. of potassium hydroxide, 10 ml. of water, 200 ml. of ethanol, and 200 ml. of dioxane. Titration with acid showed that reagents C and D were 0.064 and 0.69 *M* respectively in potassium hydroxide. A solution of 0.91 g. (0.002 mole) of 5-ethyl-4-carbazolyltriphenylsilane in 50 ml. of reagent D was maintained at 85° in a closed flask for one hour. The solution was cooled and poured into 200 g. of ice and a slight excess of hydrochloric acid. Filtration gave a mixture of solids. This was extracted with a total of 100 ml. of 90% aqueous methanol to leave a residue of unchanged ethylcarbazolyltriphenylsilane. After one recrystallization from benzene-ethanol it weighed 0.54 g. (59%) and melted at 196–197°. The methanol extracts yielded 0.10 g. (26%) of 5-ethylcarbazole, melting at 67–69° and 0.10 g. (18%) of triphenylsilanol, melting at 151–153°. All products were identified by mixture melting points with authentic samples. Reagent C was used with the more insoluble silanes. Solutions were prepared from 100 ml. of reagent C and 0.0005 mole of the silane. With tetrakis(5-ethyl-2-carbazolyl)silane a homogeneous solution was obtained by first dissolving the silane in dioxane and then adding a sufficient amount of a potassium hydroxide-ethanol-water solution to give the equivalent of reagent C.

SUMMARY

Several tetrasubstituted phenylsilanes have been prepared in which silicon is attached to the heterocycles: carbazole, dibenzofuran, dibenzothiophene, benzothiophene, and benzothiazole. A qualitative study of the ease of cleavage of these silanes by acids and by bases has been made.

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