

tangular plates, m.p. 205–208° dec., yield 20–30% (for cobalt).

Anal. Calcd. for $C_{48}H_{36}CoB$: C, 82.04; H, 8.03; Co, 8.39; B, 1.54. Found: C, 82.10; H, 8.17; Co, 8.19; B, 1.49.

The picrate of the π -complex was recrystallized from methyl ethyl ketone as large golden flakes, 210° dec.

Anal. Calcd. for $C_{20}H_{18}CoN_3O_7$: Co, 9.61; N, 6.85. Found: Co, 9.83; N, 6.76.

To the water layer separated from the hydrolyzed mixture, 10 g. of sodium chloride was added. The solution was extracted with chloroform until colorless. After drying with anhydrous sodium sulfate the chloroform was removed under reduced pressure leaving a deep orange-red material. This residue was dissolved in 5 ml. of methyl ethyl ketone and then was filtered. The addition of 200 ml. of ether precipitated bis-hexamethylbenzene-cobalt(I) chloride.

Repetition of this precipitation gave a highly hygroscopic, fine, orange-red powder, yield 20–30%.

Anal. Calcd. for $C_{24}H_{16}ClCo$: Cl, 8.46. Found: Cl, 8.05.

Reductive Cleavage of Bis-hexamethylbenzenecobalt-(I) Chloride with Lithium Aluminum Hydride.—The reductive cleavage of the chloride was carried out in a manner similar to that employed with bis-biphenylchromium iodide.⁴ The chloride (0.2660 g.) was decomposed with 1 g. of LiAlH in 2.51 g. of ether. After hydrolysis of the reaction mixture, the solvent was removed from ether solution leaving a white crystalline hexamethylbenzene, 0.200 g., m.p. 155–159°. This product formed a picrate, m.p. 170–173°, which was identified as hexamethylbenzene picrate by mixed melting point and infrared comparison with authentic sample; yield of hexamethylbenzene: calcd. 0.206 g., found 0.200 g. (97%).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO, TORONTO, CAN.]

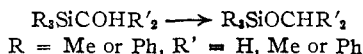
Isomerization of α -Hydroxysilanes to Silyl Ethers. III. Triphenylsilylcarbinol*

BY A. G. BROOK AND BRUNO IACHIA

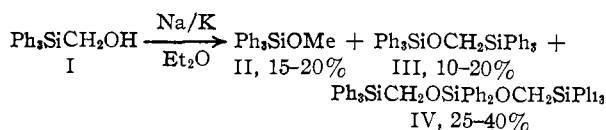
RECEIVED JULY 5, 1960

Treatment of triphenylsilylcarbinol with sodium-potassium alloy gives not only the isomeric ether triphenylmethoxysilane but also triphenylsilyloxytriphenylsilylmethane and bis-(triphenylsilylmethoxy)-diphenylsilane. The formation of these latter products is explained as a nucleophilic attack by the anion of triphenylsilylcarbinol on itself with displacement of either hydroxymethyl or phenyl groups. Triphenylsilylmethyl formate was isolated from a preparation of triphenylsilylcarbinol.

It has been shown^{1,2} previously that practically all types of aliphatic or aromatic α -silylcarbinols are rearranged readily to the isomeric silyl ethers by treatment with sodium-potassium alloy or other reagents



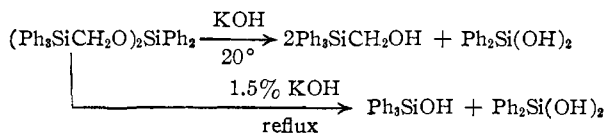
The sole exception to this general reaction appeared to be the primary alcohol triphenylsilylcarbinol (I), which reacted with sodium-potassium alloy to give an unidentified high-melting solid, but apparently none of the expected ether triphenylmethoxysilane (II). Further investigation has shown that triphenylsilylcarbinol is no exception to the general reaction since triphenylmethoxysilane now has been isolated from the reaction mixture in about 20% yield along with two other products, triphenylsilyloxytriphenylsilylmethane (III) and bis-(triphenylsilylmethoxy)-diphenylsilane (IV), and recovered carbinol.



Treatment of the carbinol in ether at room temperature with 0.1 equivalent or less of sodium-potassium alloy led to the evolution of a small quantity of gas (1.5% of the total active hydrogen) and the slow formation over several hours of crystals of IV. After removal of the apparently unconsumed alloy and the crystalline precipitate,

the oily material obtained on removal of the ether was worked up by fractional crystallization giving III and recovered I or by distillation giving II. Our failure to isolate II previously probably was due to the fact that II is hydrolyzed to triphenylsilanol during chromatography on alumina.

The identity of III and IV were established both by degradation and by synthesis. Thus on treatment with cold 1.5% potassium hydroxide in ethanol-pyridine-water, III gave triphenylsilanol and triphenylsilylcarbinol and IV gave diphenylsilanediol and two equivalents of triphenylsilylcarbinol. However at reflux temperature III gave only triphenylsilanol and IV gave diphenylsilanediol and triphenylsilanol, since at higher temperatures triphenylsilylcarbinol is hydrolyzed mainly to triphenylsilanol. Syntheses of III and IV were



accomplished by treatment of either triphenylchlorosilane or diphenyldichlorosilane with triphenylsilylcarbinol using ammonia as hydrogen chloride acceptor.

Some variation in the yields of the various products in different runs was observed (see Table I). Undoubtedly part of this is associated with difficulties of separation of the products, but part may be due to variations in reaction time or in quantity of alloy used, although no clear-cut trend was observed. The fact that the reaction mixtures were not stirred continuously and that the droplets of alloy often became encrusted with crystalline product undoubtedly led to variations in yield.

* Presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960.

(1) A. G. Brook, *THIS JOURNAL*, **80**, 1886 (1958).

(2) A. G. Brook, C. M. Warner and M. E. McGriskin, *ibid.*, **81**, 981 (1959).

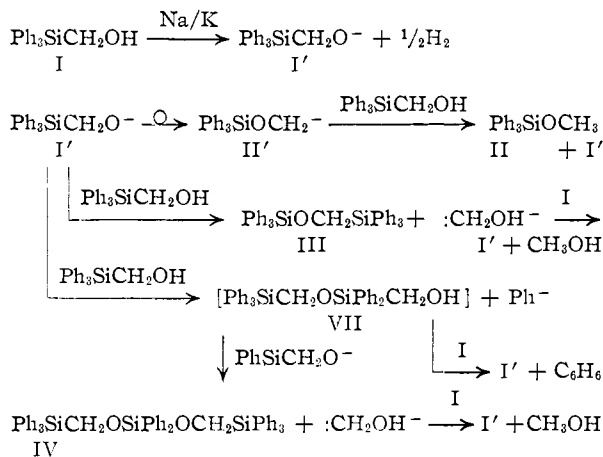
TABLE I

REACTIONS OF TRIPHENYLSILYL-CARBINOL AND RELATED COMPOUNDS^a WITH SODIUM-POTASSIUM ALLOY

Com- pound	Mole	Ml. alloy	Time, hr.	Products, % yield			
				IV	III	II	I
I	0.0034	"	0.75	34.5	3	^b	31
I	.0034	"	4.0	23.5	10.6	^b	11
I	.0034	0.025	4.0	41.3	14.9	^b	22
I	.0034	.30	4.0	26.4	14	^b	22
I	.0034	.025	4.0	32	17	^b	3
I	.0344	.05	8.0	27	24	23	^c
I	.017	.075	5.5	39	11	17	2
II	.0034	.05	4.0			68	^f
III	.0014	.05	4.0		91		
I	.0018	.05	4.0	1		74	94
II	.0018						
I	.0018	"	3.5	2	9	21 ^d	73
II	.0018	0.025	4.0		86		84
I	.0017						
III	.0009	"	3.0	11	65		46
I	.0017	0.03	4.0	1	110 ^e		72
III	.0009						

^a Amount of alloy not measured. ^b Present but not isolated pure. ^c Hexaphenyldisiloxane (9%) and diphenylsilanediol (0.3%) also isolated. ^d Recovered as triphenylsilanol. ^e 100% recovery plus 10% synthesis. ^f Hexaphenyldisiloxane (5%) also isolated. ^g I = Ph₃SiCH₂OH, II = Ph₃SiOCH₃, III = Ph₃SiOCH₂SiPh₃, IV = Ph₃SiCH₂OSiPh₂OCH₂SiPh₃.

A number of different reaction schemes can be written to account for the products of this reaction. The following, although not directly established, is supported by considerable evidence.



Thus I on reaction with sodium-potassium alloy is converted in part to I', the anion of the carbinol. This may either rearrange to II', which yields the normal product triphenylmethoxysilane (II), or it may attack a second molecule of I, displacing either a hydroxymethyl group forming III, or displacing a phenyl group forming the species VII, which was not isolated and which is presumed to undergo further attack by I' yielding IV. Hence the formation of III and IV can be accounted for by nucleophilic attack on silicon by an alkoxide ion with displacement of either a hydroxymethyl or a phenyl anion.

Similar displacements are observable in less complex systems. Thus treatment of triphenylsilylcarbinol with hot dilute alkali (see Table II) was found to give triphenylsilanol (VI) accompanied by some diphenylsilanediol. Similarly when triphenylmethoxysilane was treated with ethoxide ion triphenylethoxysilane was the sole product isolated from attack by alkoxide ion, but when the isomeric triphenylsilylcarbinol was treated under identical conditions, besides triphenylethoxysilane which was the major product, a small amount of diphenyldiethoxysilane was obtained. These results indicate that a phenyl group is not displaced from an alkoxy-silane by alkoxide ion under these conditions, and that while displacement of phenyl from a tetra-alkyl/arylsilane does occur, the displacement of a hydroxymethyl group (probably the more electronegative group³) by alkoxide ion occurs preferentially.

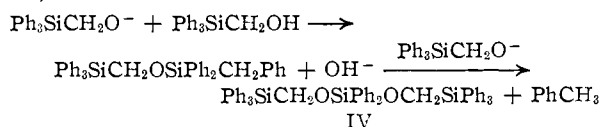
TABLE II

REACTIONS OF ORGANOSILICON COMPOUNDS^a WITH ALKALI

Com- pound	Re- agent	Conditions	Products, % yield		
			Ph ₃ SiOH	Ph ₃ Si- (OH) ₂	I
IV	^a	1 hr. reflux	83	34	
IV	^a	5 min. reflux	46	35	
IV	^a	1 min. at 20°		59	60
III	^a	5 min. reflux	52	7	
III	^a	1 min. at 20°	5		35 ^b
II	^c	1 min. at 20°	98		
I	^c	5 min. reflux	68	12	
I	^c	2 min. reflux	48	7	7
I	^c	1 min. reflux	33	5	25
I	^c	1 min. at 20°			80 ^d
VI	^e	5 min. reflux	77 ^d		
V	^e	5 min. reflux	62		^f
V	^e	1 min. at 20°			73 ^g

^a 2% potassium hydroxide in 93% ethanol plus 20% pyridine. ^b 33% of III recovered. ^c 2% potassium hydroxide in 93% ethanol. ^d Pure yield; crude yield was quantitative. ^e 2% sodium hydroxide in 93% ethanol. ^f 14% sodium formate isolated. ^g Inorganic layer not worked up. ^h I = Ph₃SiCH₂OH, II = Ph₃SiOCH₃, III = Ph₃SiOCH₂SiPh₃, IV = Ph₃SiCH₂OSiPh₂OCH₂SiPh₃, V = Ph₃SiCH₂OOCH, VI = Ph₃SiOH.

It may be questioned as to whether phenyl anion is actually being displaced in these reactions. Eaborn and Jeffrey,⁴ studying the reaction of chloromethyl-dimethylphenylsilane with ethoxide ion, found evidence not only for the displacements of chloride ion or of a chloromethyl group but, as well, for the displacement of phenyl from silicon to carbon with concurrent elimination of chloride ion to give ethoxydimethylbenzylsilane. The latter compound was not isolated since further reaction with ethoxide ion gave diethoxydimethylsilane and toluene. A similar situation could be visualized in the formation of IV, *viz.*



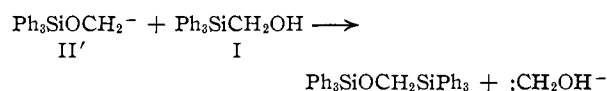
(3) H. Gilman, A. G. Brook and L. S. Miller, *THIS JOURNAL*, **75**, 4531 (1953).

(4) C. Eaborn and J. C. Jeffrey, *J. Chem. Soc.*, 137 (1957).

In the present case such a rearrangement evidently does not occur. Approximately 90–95% of the phenyl groups eliminated have been accounted for by gas chromatography as benzene, and no toluene could be detected. In addition, about 70% of the hydroxymethyl groups eliminated were accounted for as methanol.

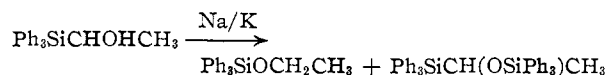
The mechanistic scheme proposed is consistent with the observations that only catalytic quantities of alloy are consumed and that only a trace of hydrogen is evolved, since the reactions once started are self-sustaining, the ion I' common to each step being regenerated. It is likely that each product of the reaction is formed independently of the others and that one product is not the precursor of another. Thus mixed runs of I and II with alloy led to lower yields of III and IV than in the absence of II and mixed runs of I and III gave only a few per cent. of IV where normally 25–40% was obtained.

The species II' could conceivably be the nucleophile involved in the formation of some of the products. Thus attack of II' on I can give rise to III



but the same species could not give rise to IV but instead would form an isomer $\text{Ph}_3\text{SiOCH}_2\text{-SiPh}_2\text{CH}_2\text{OSiPh}_3$, which was not encountered. Hence while II' cannot be excluded as an intermediate, the evidence seems to favor I' as the actual intermediate.

The isolation of a compound like III from this reaction finds an analogy in a previously reported arrangement where 1-triphenylsilylethanol was found to form not only the expected triphenylethoxysilane but, as well, small amounts of 1-triphenylsilyl-1-triphenylsilyloxyethane.² However, other



α -silylcarbinols were not found to give rise to analogous products. It is significant that these more complex products are formed in those cases where minimum steric effects between attacking anion and organosilicon compound would exist, although the nucleophilicity of the anions or other factors may be involved.

Triphenylsilylcarbinol, the starting material for these reactions, was prepared by reaction of formaldehyde with triphenylsilyllithium.⁵ In one preparation, in which the formaldehyde was added more rapidly than normally, a new compound, triphenylsilylmethyl formate (V) $\text{Ph}_3\text{SiCH}_2\text{OOCH}$, was isolated along with the triphenylsilylcarbinol. Its identity was established by alkaline hydrolysis at room temperature which gave triphenylsilylcarbinol and sodium formate. The compound presumably was formed by a Tishchenko type of reaction.⁶

(5) H. Gilman and T. C. Wu, *THIS JOURNAL*, **76**, 2502 (1954).

(6) W. Tishchenko, *Zhur. Fiz. Khim.*, **38**, 355 (1966); J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 262.

Experimental⁷

The details of typical reactions of triphenylsilylcarbinol and other compounds with sodium-potassium alloy are summarized in Table I and the details of workup of a single representative run are included here. Similarly, details of the hydrolysis of the several reaction products are summarized in Table II and only representative examples are described in detail.

Rearrangement of Triphenylsilylcarbinol.—To a solution of 10 g. (0.034 mole) of triphenylsilylcarbinol in 220 ml. of dry diethyl ether was added 0.05 ml. (approx. 0.0013 g. atom) of 1:5 sodium-potassium alloy. A small amount of gas was evolved slowly over the first half-hour. Crystals began to separate slowly from the solution, and a crust formed on the surface of the alloy, which was removed occasionally by vigorous shaking. After 4 hr. no further crystals appeared to be formed, and the unconsumed alloy was removed mechanically. The mixture was filtered and the crystalline residue was washed with ether. This crude bis-(triphenylsilylmethoxy)-diphenylsilane (IV), 2.31 g. (27%), melted from 199–201°. Recrystallization from ethanol raised the melting point to 202–203.5° and a mixed melting point with authentic IV was not depressed.

Anal. Calcd. for $\text{C}_{50}\text{H}_{44}\text{Si}_3\text{O}_2$: C, 78.9; H, 5.84; Si, 11.0; mol. wt., 760. Found: C, 79.1; H, 5.78; Si, 10.7; mol. wt. (Rast, in borneol), 715, 680.

The ether layer obtained at this point was worked up in several ways depending on which products were to be isolated.

(a) **Fractional Crystallization.**—Removal of the ether under reduced pressure gave an oily solid which was crystallized from 1:10 ethanol-petroleum ether (b.p. 60–70°). Solid, as ball-shaped lumps and powder, was obtained which was separated mechanically to give (from a 1.0-g. run) 0.14 g. (14.5%) of triphenylsilyoxytriphenylsilylmethane (III), m.p. 130–132°, and 0.06 g. (7%) of IV, m.p. 194–199°. Addition of warm petroleum ether to the mother liquor gave after workup a total of 0.22 g. (22%) of recovered triphenylsilylcarbinol, m.p. 113–117°, identified by mixed melting point, and 0.21 g. of non-crystallizable oil.

The III obtained above was recrystallized from ethanol to m.p. 131–131.5° and was identified by mixed melting point with an authentic sample.

Anal. Calcd. for $\text{C}_{37}\text{H}_{32}\text{Si}_2\text{O}$: Si, 10.23. Found: Si, 10.24.

The infrared spectra of all compounds were consistent with the proposed structures.

(b) **Distillation.**—The oil remaining (6.89 g.) after removal of the ether from the ether filtrate of a 10-g. run was distilled at reduced pressure to give 2.31 g. (23%) of crude triphenylmethoxysilane, b.p. 102–136° (0.08 mm.), and 4.37 g. of residual material. The triphenylmethoxysilane (II) was redistilled at 125–130° (0.35 mm.) to give some slightly impure material as oil; 0.47 g. of crystalline triphenylmethoxysilane, m.p. 52–55°, identified by mixed melting point; and 0.02 g. (0.2%) of diphenylsilanediol, m.p. 162–166°.

From the residue of the original distillation there was obtained by fractional crystallization 2.24 g. (23%) of III, m.p. 126–129°; 0.81 g. (8%) of hexaphenyldisiloxane, m.p. 220–223°, identified by mixed melting point; and 0.81 g. of oil.

(c) **Chromatography.**—The oil (3.01 g.) obtained by removal of the ether from the ether filtrate of a 5-g. run was dissolved in petroleum ether (b.p. 60–70°) and added to a column of alumina which was eluted with petroleum ether, benzene, ether and finally ethanol. The products obtained and the eluent were: IV, 0.08 g. (1.8%), petroleum ether (b.p. 60–70°) in addition to 1.64 g. (38%) removed from the ether layer by filtration; III, 0.54 g. (11.5%), petroleum ether; triphenylsilylcarbinol, 0.1 g. (2%), benzene; and triphenylsilanol, 0.80 g. (17%), ether and ethanol.

(d) **Gas Chromatography.**—Most of the ether was distilled from the ether filtrate of a 10-g. run. Part of this crude concentrate was then crudely distilled with a pot temperature of about 100° at about 0.1 mm. pressure into two consecutive traps maintained at about –80°. Samples of this distillate as well as the crude concentrate

(7) All reactions involving organometallics or sodium-potassium alloy were carried out in a dry, oxygen-free nitrogen atmosphere.

then were chromatographed semi-quantitatively in the usual manner. Besides ether, only methanol (about 0.0042 mole, 69%, based on probable product distribution) and benzene (about 0.0034 mole, 94%, based on IV isolated) were detected. No toluene could be detected. From this run 2.75 g. (31.5%) of IV was obtained.

(e) **Measurement of Hydrogen Evolution.**—A rough measurement of the hydrogen evolved when 1.0 g. of triphenylsilylcarbinol in 20 ml. of ether was treated with a few drops of sodium-potassium alloy was made by connecting the reaction vessel to a mercury-filled gas buret. Because of the volatile nature of the solvent large corrections were necessary which were determined by carrying out the measurements over equivalent time intervals (4 hr.) in the absence of alloy. From two identical runs 0.58 and 0.59 ml. of hydrogen (S.T.P.) were evolved corresponding to about 1.5% of the theoretical active hydrogen.

Identification of Bis-(triphenylsilyl-methoxy)-diphenylsilane (IV). A. **Synthesis.**—To 0.5 g. (0.0017 mole) of triphenylsilylcarbinol in 35 ml. of dry benzene was added 0.22 g. (0.00086 mole) of redistilled diphenyldichlorosilane. The mixture was vigorously stirred in an ice-bath as anhydrous ammonia was passed through at a rapid rate for a total of 30 min. The mixture was drowned in dilute acid which dissolved the precipitated material. The organic layer was washed with dilute acid and water and, after drying over anhydrous sodium sulfate, was evaporated to dryness at reduced pressure. The resulting yellow oily solid was recrystallized from a mixture of petroleum ether (b.p. 60–70°), ethanol, benzene and chloroform to give a total of 0.1 g. (15%) of IV, m.p. 202–203.5°, identical with the IV obtained from the rearrangement reaction. Also isolated was 0.21 g. (42%) of recovered triphenylsilylcarbinol, m.p. 112–116°, and 0.01 g. (5%) of diphenylsilanediol, m.p. 162–165°.

B. **Hydrolysis.**—To a solution of 0.3 g. (0.00039 mole) of IV in 25 ml. of dry pyridine was added 48 ml. of 2% potassium hydroxide in 93% ethanol. After mixing, the solution was immediately drowned in dilute acid and was extracted with ether. The ether washings were washed with dilute acid and then were dried and evaporated to dryness. The oily solid was treated with hot petroleum ether (b.p. 60–70°) and 0.05 g. (59%) of crude diphenylsilanediol, m.p. 147–151°, was filtered off. Recrystallization from benzene raised the melting point to 162–166° and the mixed melting point with an authentic sample was not depressed. From the petroleum ether solution was isolated a total of 0.14 g. (61%) of triphenylsilylcarbinol, m.p. 108–117°, which on recrystallization from ethanol melted at 116–117.5° and did not depress the mixed melting point with an authentic sample. Other hydrolyses are reported in Table II.

Identification of Triphenylsilyloxytriphenylsilylmethane (III). A. **Synthesis.**—To 2.65 g. (0.0091 mole) of triphenylsilylcarbinol in 45 ml. of benzene was added 2.68 g. (0.0091 mole) of triphenylchlorosilane. The solution was vigorously stirred in an ice-bath for 30 min. while dry ammonia was passed through rapidly. After drowning the reaction mixture in dilute acid and drying the organic layer, evaporation to dryness gave an oily solid which was recrystallized from ethanol-benzene to give 3.27 g. (65%) of III, m.p. 130–130.5°. Recrystallization from petroleum ether (b.p. 60–70°) raised the melting point to 130.5–131°. In addition 0.74 g. (28%) of triphenylsilylcarbinol, m.p. 105–113°, was recovered. The III isolated was identical with that obtained by the rearrangement reaction, as indicated by mixed melting point and infrared spectra.

B. **Hydrolysis.**—To 0.75 g. (0.0014 mole) of III in 10 ml. of pyridine was added 50 ml. of 2% potassium hydroxide in 93% ethanol. The solution was immediately drowned in dilute acid and was ether-extracted. Workup as above gave 0.14 g. (35.5%) of triphenylsilylcarbinol, m.p. 116–119°; 0.04 g. (5%) of triphenylsilanol, m.p. 150–152°; and 0.25 g. (33%) of recovered III, m.p. 132–133°; all compounds identified by mixed melting point and infrared spectra.

If the solution was refluxed for 1 min. prior to acidification, 71% of triphenylsilanol was the only product isolated, indicating that the triphenylsilylcarbinol had been hydrolyzed to triphenylsilanol under these conditions.

Synthesis of Triphenylsilylcarbinol.—Triphenylsilylcarbinol was prepared essentially as described by Gilman

and Wu⁶ except that triphenylsilyllithium in tetrahydrofuran was employed with dry formaldehyde. A crude yield of 83% was obtained, m.p. 114–117°, and after recrystallization from 1:10 ethanol-petroleum ether (b.p. 60–70°) pure material (66%), m.p. 116–117°, was obtained.

On one occasion the formaldehyde was generated at 180–200° instead of the usual 160–170° from paraformaldehyde, resulting in a very rapid addition of formaldehyde to the triphenylsilyllithium. Workup as usual followed by recrystallization from petroleum ether (b.p. 60–70°) and then ethanol-petroleum ether gave, from a run starting with 25 g. of hexaphenyldisilane, 6.0 g. (20%) of triphenylsilylmethyl formate, m.p. 113–116.5°. Additional further recrystallizations from petroleum ether eventually raised the melting point to 121.5–122.5°. Also isolated was 4.97 g. (18%) of triphenylsilylcarbinol, m.p. 119–121°.

Anal. Calcd. for C₂₀H₁₈O₂Si: C, 75.4; H, 5.70; Si, 8.82. Found: C, 75.8; H, 5.78; Si, 8.69, 8.86.

Hydrolysis of Triphenylsilylmethyl Formate.—A solution of 1.0 g. (0.0032 mole) of triphenylsilylmethyl formate from above in 70 ml. of 2% sodium hydroxide in 95% ethanol was refluxed for 5 min. and then drowned in dilute acid. Workup of the ether extracts gave 0.49 g. (62%) of triphenylsilanol, m.p. 150–152°, identified by mixed melting point.

The inorganic layer was concentrated to dryness and the solid remaining was refluxed with absolute ethanol. The ethanol solution gave a positive test for formic acid.⁸ From the ethanol solution crystallized 0.03 g. (14%) of sodium formate, m.p. 255–260°, whose mixed melting point with authentic sodium formate was not depressed.

Hydrolysis of Triphenylmethoxysilane on Alumina.—Triphenylmethoxysilane (1.0 g., 0.0034 mole) in petroleum ether (b.p. 60–70°) was chromatographed on alumina in exactly the same manner as the reaction mixture from the rearrangement of triphenylsilylcarbinol had been worked up. No products were recovered from the petroleum ether eluent but from the benzene, ether and ethanol eluents a total of 0.89 g. (94%) of triphenylsilanol, m.p. 150–152°, was obtained.

Attempted Thermal Rearrangement of Triphenylsilylcarbinol.—Since triphenylmethoxysilane was only isolated directly from the reaction of triphenylsilylcarbinol by distillation of the reaction mixture, the following run was carried out to ascertain whether triphenylmethoxysilane might be formed thermally from triphenylsilylcarbinol. Triphenylsilylcarbinol was distilled at 170–175° (0.05 mm.), a higher temperature than that at which triphenylmethoxysilane had been isolated. The material solidified to melt at 116.5–118°, mixed melting point with triphenylsilylcarbinol 118–119°. An infrared spectrum showed no Si-O peak indicating the presence of little if any triphenylmethoxysilane.

Reaction of Triphenylsilylcarbinol and Triphenylmethoxysilane with Sodium Ethoxide.—To 2.0-g. (0.0069 mole) solutions of triphenylsilylcarbinol and triphenylmethoxysilane in 10 ml. of ethanol was added 10 ml. of a solution of 0.35 g. of sodium in 20 ml. of ethanol. Each mixture was heated to boiling and then allowed to cool to room temperature over 40 min. The solutions were then drowned in dilute acid and were ether extracted.

Removal of the ether from the triphenylmethoxysilane run left white crystals. Treatment with 10 ml. of cold petroleum ether (b.p. 60–70°) left 0.21 g. (10%) of insoluble triphenylsilanol, m.p. 149–152°, identified by mixed melting point. The petroleum ether solution gave 1.65 g. (79%) of pure triphenylethoxysilane, m.p. 63–65°, identified by mixed melting point.

Removal of the ether from the triphenylsilylcarbinol run gave an oily solid. Similar treatment with petroleum ether left 0.13 g. of a mixture of triphenylsilanol and diphenylsilanediol, separated by hot petroleum ether into 0.04 g. of triphenylsilanol, m.p. 150–152°, and 0.08 g. of diphenylsilanediol, m.p. 160–166°, both identified by mixed melting point and infrared spectrum. Workup of the petroleum ether layer gave 1.23 g. (59%) of pure triphenylethoxysilane, m.p. 63–65°, and a few drops of oil which

(8) F. Feigl, "Spot Tests," Elsevier Publishing Co., New York, N. Y., 1954, Vol. II, p. 245.

on the basis of their infrared spectra appeared to be diphenyldiethoxysilane. There was insufficient material to distil so a few drops of the liquid were refluxed briefly with excess alcoholic alkali and were worked up to give 0.06 g. (4%) of diphenylsilanediol, m.p. 160–165°.

The isolation of traces of triphenylsilanol and diphenyl-

silanediol directly from the reaction suggests that traces of water were present.

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[CONTRIBUTION FROM ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALA.]

Amine Boranes. V. The Preparation of Trimethylamine Alkylboranes and 2-Alkylborobenzimidazolines¹

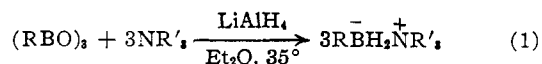
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A series of trialkylboroxines were reduced with lithium aluminum hydride in diethyl ether solution and in the presence of trimethylamine. Trimethylamine alkylboranes were obtained in up to 65% yield without alkyl group rearrangement. Trimethylamine alkylboranes were converted to the corresponding 2-alkylborobenzimidazolines by treatment with *o*-phenylenediamine in benzene solution at the reflux temperature. Primary, secondary and tertiary alkyl-, as well as cycloalkyl- and aralkylboroxines, were employed.

Recently, amine boranes have found some importance as intermediates in organoborane synthesis. A noteworthy example is the successful hydroboration of olefins with such materials as pyridine borane² and trimethylamine borane.^{3,4} The presence of boron-hydrogen bonds in amine boranes suggests many interesting protolysis reactions from which new, or at least rare, families of substituted boranes could be derived. In the past such reactions usually employed the trialkylborane, the alkyl-substituted diboranes or diborane as starting materials. Organic substituents on boron generally were limited to the methyl and ethyl groups. It was therefore desirable to develop a convenient synthesis of trialkylamine alkylboranes and to determine their usefulness as synthetic intermediates.

A promising approach to the synthesis of trialkylamine alkylboranes was suggested by the facile reduction of arylboronic⁵ and diarylborinic⁶ esters to the corresponding trialkylamine and pyridine aryl- and diarylboranes. This was accomplished by the use of lithium aluminum hydride and the proper amine in diethyl ether solution and at low temperatures. In one instance,⁵ triphenylboroxine was employed successfully as a starting material in such a reduction. This fact, coupled with the availability of a series of trialkylboroxines,⁷ suggested this route to trialkylamine alkylboranes. As previously reported,¹ this is the method of choice and it may be applied to alkylboroxines which bear primary, secondary and tertiary alkyl groups or cycloalkyl groups. Equation 1 illustrates this reaction.



R = primary, secondary and tertiary alkyl and cycloalkyl

(1) Presented previously as a Communication to the Editor, M. F. Hawthorne, *J. Am. Chem. Soc.*, **81**, 5836 (1959).

(2) M. F. Hawthorne, *J. Org. Chem.*, **23**, 1788 (1958).

(3) R. Köster, *Angew. Chem.*, **69**, 684 (1957).

(4) E. C. Ashby, *J. Am. Chem. Soc.*, **81**, 4791 (1959).

(5) M. F. Hawthorne, *ibid.*, **80**, 4291 (1958).

(6) M. F. Hawthorne, *ibid.*, **80**, 4294 (1958).

(7) P. A. McCusker, E. C. Ashby and H. S. Makowski, *ibid.*, **79**, 1179 (1957).

All reductions of alkylboroxines with lithium aluminum hydride were carried out by the slow addition of the boroxine to a solution of lithium aluminum hydride in diethyl ether which contained a 70% excess of trimethylamine. A reaction temperature of 35° was chosen and the reductions were carried out under nitrogen to exclude water. The quantity of lithium aluminum hydride employed was critical with respect to the mechanics of product workup. The best results were obtained with a 3:1 mole ratio of lithium aluminum hydride to alkylboroxine. Although trimethylamine alkylboranes are quite stable toward hydrolysis, wet samples slowly evolve hydrogen and crystalline alkylboronic acid separates on standing. For this reason the quantity of water added during work-up was limited to four moles per mole of lithium aluminum hydride employed in the reduction. With these precautions, yields of 40–65% invariably were obtained. The crude products obtained by the evaporation of solvent were reasonably pure. Additional purification was achieved for characterization purposes by distillation in a molecular still at 30–50° or by rapid distillation with spinning-band column at reduced pressure. As will be seen in the following papers of this series, the crude products were employed as synthetic intermediates without additional purification.

With but few known exceptions, trimethylamine alkylboranes are liquids at room temperature and below. They exhibit two strong B–H stretching bands and two shoulders between 4.25–4.55 μ in the infrared. Trimethylamine alkylboranes also absorbed strongly at 11.90 μ in the infrared.

Silver ion and iodine reacted rapidly with trimethylamine alkylboranes and produced silver metal and iodide ion, respectively. Water and ethanol were essentially inert toward the B–H hydrogen present. Strong proton donors such as hydrochloric and trifluoroacetic acid gave rapid hydrogen evolution in accordance with eq. 2. This latter reaction was utilized as a criterion of product purity.

