crude product gave 2.6 g. of forerun, b.p. up to 238° (0.005 mm.), followed by 7.3 g. (80%) of colorless liquid, b.p. 250–251° (0.005 mm.), n^{20}_D 1.5750, d^{20}_4 1.005. The compound volatilized between 460–470° with no sign of decomposition.

Anal. Calcd. for $C_{40}H_{52}Si_2$: C, 81.60; H, 5.91; Si, 9.53; *MR*, 192.9. Found: C, 81.60; H, 5.94; Si, 9.69, 9.52; *MR*, 193.7.

5,5-Dimethyldibenzosilole.—An ethereal solution containing 0.068 mole of methyllithium and 15.67 g. (0.068 mole) of 5-chloro-5-methyldibenzosilole was allowed to react at room temperature. Following work-up of the mixture, the crude product was crystallized from methanol to give 9.93 g. (70%) of colorless plates, m.p. 58–59°. The analytical sample melted at 60–61°.

Anal. Calcd. for $C_{14}H_{14}Si$: C, 79.93; H, 6.72. Found: C, 80.30, 80.45; H, 6.64, 6.66.

5,5-Diphenyldibenzosilole. (a) **From 5-Chloro-5-phenyldibenzosilole.**—A solution of 1.35 g. (0.0046 mole) of 5-chloro-5-phenyldibenzosilole in 25 ml. of ether was allowed to react with 0.008 mole of phenyllithium. The mixture was hydrolyzed with water. The crude product was crystallized from ethanol to give 1.1 g. (72%) of 5,5-diphenyldibenzosilole, m.p. 147–148°, which showed no depression in melting point when admixed with a sample prepared from diphenyldichlorosilane and 2,2′-biphenylenedilithium.[3]

(b) **From 5,5-Dichlorodibenzosilole.**—To 1.23 g. (0.0049 mole) of impure 5,5-dichlorodibenzosilole dissolved in 20 ml. of dry ether was added 18 ml. of a 0.87 *M* phenyllithium solution. The mixture was hydrolyzed and worked up as described previously to yield 1.21 g. (74%) of 5,5-diphenyldibenzosilole, m.p. 148–149°, identified by mixed melting point.

5-(2-Biphenylyl)-5-methyldibenzosilole.—2-Biphenylyllithium,[9] 0.0098 mole, and 2.86 g. (0.0124 mole) of 5-chloro-5-methyldibenzosilole were allowed to react at room temperature. The mixture was worked up in the usual fashion. The crude product was crystallized from ethanol to yield 2.8 g. (65%) of white needles, m.p. 115–116°.

Anal. Calcd. for $C_{25}H_{20}Si$: C, 86.22; H, 5.74. Found: C, 86.34; H, 5.83.

Infrared Absorption Spectra.—All of the infrared spectra of dibenzosilole compounds in carbon disulfide, in carbon tetrachloride or as liquids showed an absorption band at 8.9 μ which appears to be characteristic of the dibenzosilole nucleus. In addition, the 5,5-diaryldibenzosiloles exhibited a split band at 9.4 μ, while the 5,5-dialkyldibenzosiloles had only one band at 9.4 μ. The 5-alkyl-5-aryldibenzosiloles had sharp bands at 9.3 and 9.4 μ.

Acknowledgment.—This research was supported by the United States Air Force under contract AF 33(616)-3510 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright Patterson AFB, Ohio. They are also grateful to the Institute for Atomic Research, Iowa State College, and Mr. E. Miller Layton for assistance in the infrared determinations.

Ames, Iowa

[Contribution from the Department of Chemistry, University of Toronto]

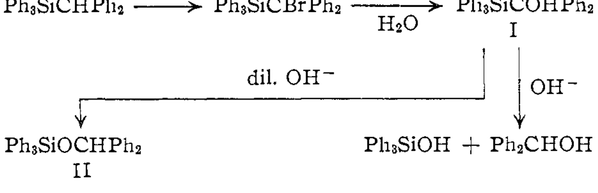
Isomerism of Some α-Hydroxysilanes to Silyl Ethers

By A. G. Brook

Received December 20, 1957

Triphenylsilyldiphenylcarbinol (I), prepared from benzhydryltriphenylsilane *via* the bromide, was found to rearrange to the isomeric ether benzhydryloxytriphenylsilane (II) in refluxing pyridine, or when treated with catalytic amounts of sodium hydroxide, sodium or sodium–potassium alloy or with sodium hydride at room temperature. The possible rearrangement of other similar α-silylcarbinols was investigated, but only diphenylcarbinols appear to rearrange under these conditions. When Compound I was treated with excess phenyllithium only tetraphenylsilane and benzhydrol were isolated.

In connection with an investigation of the reaction of triphenylsilylmetallics with benzophenone, to be reported in a forthcoming paper, it became necessary to prepare triphenylsilyldiphenylcarbinol (I). This compound, prepared from α-bromobenzhydryltriphenylsilane by treatment with aqueous silver acetate, was found to be extremely sensitive to alkali. While brief refluxing in dilute alcoholic aqueous sodium hydroxide caused complete hydrolysis to triphenylsilanol and benzhydrol, when the compound was treated briefly at room temperature with extremely dilute alkali (about 0.01 *M* for 1 minute) it was converted into the isomeric ether benzhydryloxytriphenylsilane (II) in high yield.



$$\begin{tikzcd}
Ph_3SiCHPh_2 \arrow[r, "NBS"] & Ph_3SiCBrPh_2 \arrow[r, "AgOAc", "H_2O"'] & \underset{\text{I}}{Ph_3SiCOHPh_2} \arrow[d, "OH^-"] \arrow[dll, "dil.\ OH^-"'] \\
\underset{\text{II}}{Ph_3SiOCHPh_2} & & Ph_3SiOH + Ph_2CHOH
\end{tikzcd}$$

Subsequently it was found that compound I was converted to II more conveniently by refluxing briefly in pyridine where a practically quantitative yield was obtained, or by treating I in ether with catalytic amounts of sodium or sodium–potassium alloy or with an excess of sodium hydride.

Undoubtedly the ether II is an intermediate in the hydrolysis of I to triphenylsilanol and benzhydrol, since compound I may be converted to II under conditions where no hydrolysis occurs, although II itself is hydrolyzed readily to triphenylsilanol and benzhydrol with dilute alkali.

The generality of this reaction was studied by investigating related carbinols. Methyldiphenylsilyldiphenylcarbinol (III) readily was converted by refluxing pyridine to benzhydryloxymethyldiphenylsilane (IV) in good yield, and in view of the similar behavior of methyldiphenylsilyl- and dimethylphenylsilyl derivatives[1] it seems probable that dimethylphenylsilyldiphenylcarbinol could be similarly isomerized.

$$\underset{\text{III}}{MePh_2SiCOHPh_2} \qquad \underset{\text{IV}}{MePh_2SiOCHPh_2}$$

However, triphenylsilyldimethylcarbinol, prepared from triphenylsilyllithium and acetone, could not be rearranged either with refluxing pyridine or when treated with sodium–potassium alloy.

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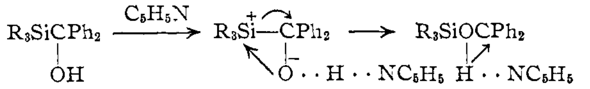
[1] We are indebted to Dr. Henry Gilman, Iowa State College, for unpublished information about these compounds.

Similarly the primary carbinol triphenylsilylmethanol[2] was not isomerized by refluxing pyridine or quinoline. Based on these rather limited studies, it appears that under these conditions only diphenylcarbinols are isomerized readily.

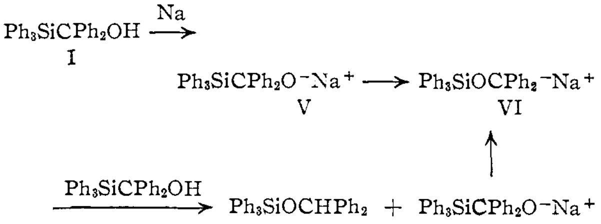
It seems evident that these rearrangements occur by nucleophilic attack of the oxygen of the hydroxyl group on the α-silicon atom in a manner similar to that described for the thermal rearrangement of silanecarboxylate esters,[3] and that the base (OH^- or pyridine) is required to promote the necessary electron density on the oxygen atom: it was found impossible to cause rearrangement by prolonged refluxing in xylene.



$$R_3Si\underset{\displaystyle OH}{\underset{|}{C}}Ph_2 \xrightarrow{C_5H_5N} R_3\overset{+}{Si}{-}\underset{\displaystyle \overset{-}{O}\cdot\cdot H\cdot\cdot NC_5H_5}{\underset{|}{C}}Ph_2 \longrightarrow R_3SiO\underset{\displaystyle H\cdot\cdot NC_5H_5}{\underset{|}{C}}Ph_2$$

Rearrangements of an electronegative atom or group from carbon to silicon are not new, but those previously observed have generally been catalyzed by reagents such as sulfuric acid and aluminum chloride,[4] and not by bases or metals as in the present case.

In view of the fact that sodium or sodium–potassium alloy are also able to cause rearrangement, it appears that the salt V of the carbinol I also rearranges readily. Thus when the carbinol, in anhydrous ether, was treated with a catalytic amount of sodium over two hours, or with a small amount of sodium–potassium alloy for three minutes, the ether layer yielded benzhydryloxytriphenylsilane almost quantitatively, simply by removal of the ether under reduced pressure. Evidently no significant quantity of the salt V was formed since no hydrogen appeared to be evolved, and the metal did not dissolve or change significantly in appearance. These results can best be explained by a sort of chain-transfer process, illustrated below, in which a trace of salt V is formed, which subsequently rearranges, presumably on the metal surface, to compound VI which could not be detected by the Color Test I[5] for organometallic reagents. Hence VI must react with more carbinol on or near the metal surface to produce benzhydryloxytriphenylsilane and additional salt, which repeats the cycle.



$$\underset{\text{I}}{Ph_3SiCPh_2OH} \xrightarrow{Na} \underset{\text{V}}{Ph_3SiCPh_2O^-Na^+} \longrightarrow \underset{\text{VI}}{Ph_3SiOCPh_2{}^-Na^+}$$

$$\xrightarrow{Ph_3SiCPh_2OH} Ph_3SiOCHPh_2 + Ph_3SiCPh_2O^-Na^+$$

The only other explanation which seems possible for this unusual rearrangement catalyzed by metals is that traces of hydroxide were introduced with the metals into the reaction mixture: all possible precautions were taken to avoid this possibility. Similar results were obtained when the carbinol was treated with excess sodium hydride: again the yield of benzhydryloxytriphenylsilane was shown to be independent of whether or not the reaction mixture was hydrolyzed with water prior to isolation of the product.

When triphenylsilyldiphenylcarbinol was treated with excess phenyllithium an intense blue color reminiscent of benzophenone ketyl was produced. This color gradually faded over some hours, and when the reaction mixture was hydrolyzed and worked up the products isolated were tetraphenylsilane and benzhydrol. These products are explained by attack of phenyllithium on the silicon atom of the carbinol or its salt to form tetraphenylsilane accompanied by the elimination of the elements of benzophenone ketyl, which on hydrolysis forms benzhydrol and benzophenone.[6]

In this connection it is interesting that triphenylsilyldiphenylcarbinol is not formed by the action of phenylmagnesium bromide or phenyllithium on ethyl triphenylsilanecarboxylate. Tetraphenylsilane, obtained in low yield, was the only product isolated from the reaction with phenyllithium, and only recovered ester was obtained from the reaction with Grignard reagent. No intense benzophenone ketyl color was observed which suggests that addition to the carbonyl group does not occur and that the tetraphenylsilane was formed by attack of phenyllithium on the silicon atom of the carbinol.

Experimental[7]

Bromobenzhydryltriphenylsilane.—A solution of 21.3 g. (0.05 mole) of benzhydryltriphenylsilane[8] in 250 ml. of carbon tetrachloride was refluxed overnight with 8.9 g. (0.05 mole) of N-bromosuccinimide and a trace of benzoyl peroxide. After cooling, 4.95 g. (100%) of crude succinimide, m.p. 122–126°, was filtered off. After removal of the solvent under reduced pressure the residue was recrystallized from benzene–petroleum ether (b.p. 90–100°) to yield 20.1 g. (80%) of pure, white, bromobenzhydryltriphenylsilane, m.p. 198.5–200°. An additional 3.97 g. (16%) of less pure material, m.p. 180–188°, was isolated from the mother liquors.

Anal. Calcd. for $C_{31}H_{25}SiBr$: Si, 5.55; Br, 15.8. Found: Si, 5.54; Br (as AgBr), 15.8.

Triphenylsilyldiphenylcarbinol (II).—To 5.0 g. (0.0099 mole) of the above bromide dissolved with warming in a solution of 100 ml. of acetone, 25 ml. of benzene and 20 ml. of water was added 1.8 g. (0.0108 mole) of silver acetate. The suspension was stirred at room temperature for 18 hours in the dark. The silver bromide was filtered off and washed with acetone and the pale yellow filtrate was evaporated to dryness. Recrystallization of the residue from benzene–petroleum ether (b.p. 90–100°) gave two crops of white solid weighing 2.43 g., m.p. 146–153°. Recrystallization from petroleum ether (b.p. 90–100°) raised the melting point to 156–159°, and further recrystallization failed to sharpen the melting point of this triphenylsilyldiphenylcarbinol.

Anal. Calcd. for $C_{31}H_{26}OSi$: C, 84.46; H, 5.93; Si, 6.35. Found: C, 84.59; H, 5.97; Si, 6.28.

If the substitution of bromine was carried out using excess freshly prepared moist silver oxide, from which all traces of free alkali had been washed, considerable rearrangement and decomposition occurred. Thus treatment of 5.0 g. (0.0099 mole) of the bromide in acetone–benzene–water as above with about 3 g. of moist silver oxide over 16

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

(3) A. G. Brook and R. J. Mauris, *ibid.*, **79**, 971 (1957).

(4) F. C. Whitmore and L. H. Sommer, *ibid.*, **68**, 481, 486 (1946).

(5) H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

(6) H. Gilman, "Organic Chemistry, An Advanced Treatise," Vol. 1, 2nd ed., J. Wiley and Sons, Inc., New York, N. Y., 1943, p. 613.

(7) Experiments involving organometallic reagents were carried out in a dry oxygen-free nitrogen atmosphere. Melting points are corrected.

(8) H. Gilman, A. G. Brook and L. S. Miller, THIS JOURNAL, **75**, 3757 (1953).

hours gave on fractional crystallization of the reaction products 0.95 g. (35%) of triphenylsilanol, m.p. 150–152°, and a total of 1.91 g. (44%) of benzhydryloxytriphenylsilane (III), m.p. 80–81°, both compounds identified by mixed melting points with authentic specimens. No attempt was made to isolate the benzhydrol which must also have been present.

Reactions of Triphenylsilyldiphenylcarbinol. A. With Pyridine.—A solution of 0.2 g. (0.00045 mole) of triphenylsilyldiphenylcarbinol in 5 ml. of pyridine was refluxed for 15 minutes. The pyridine was removed under reduced pressure and the resulting oil was crystallized by scratching. This benzhydryloxytriphenylsilane melted from 79–82°, and was identified by mixed melting point with an authentic specimen. Recrystallization from ethanol yielded 0.16 g. (80%) of purified compound, m.p. 82–84°.

B. **With Sodium Hydroxide.**—To 0.2 g. (0.00045 mole) of triphenylsilyldiphenylcarbinol dissolved in 10 ml. of ethanol by brief refluxing was added, after the solution had reached room temperature, 1.0 ml. of 0.097 *M* (0.000097 mole) sodium hydroxide. The solution was shaken for 1 minute and then was drowned in 40 ml. of dilute hydrochloric acid. The suspension was extracted with ether, the ether layer was dried, and the ether removed under reduced pressure. The resulting oil crystallized when seeded with benzhydryloxytriphenylsilane and melted from 78–83°. Recrystallization from ethanol yielded 0.17 g. (85%) of pure compound, m.p. 84–85°, identified by mixed melting point with an authentic specimen.

However, when a solution of 0.2 g. (0.00045 mole) of the carbinol in 10 ml. of ethanol and 1 ml. of 10% aqueous sodium hydroxide was refluxed for 3 minutes, and the reaction mixture was drowned in water, acidified, and worked up as usual, it yielded 0.11 g. (89%) of triphenylsilanol, m.p. 149–151°, and 0.06 g. (72%) of benzhydrol, m.p. 66–68°, both compounds identified by mixed melting points with authentic specimens.

C. **With Silver Oxide.**—A mixture of 0.75 g. (0.0017 mole) of the carbinol, 7 ml. of benzene, 30 ml. of acetone, 5 ml. of water and about 1 g. of freshly prepared, thoroughly washed, silver oxide was stirred overnight. The reaction mixture yielded 0.07 g. (15%) of triphenylsilanol, m.p. 149–151°, and 0.51 g. of sticky solid which after recrystallization from petroleum ether (b.p. 60–70°) gave 0.42 g. (56%) of benzhydryloxytriphenylsilane, m.p. 81–83°. The compounds were identified by mixed melting points with authentic specimens.

D. **With Sodium and Sodium-Potassium Alloy.**—To 0.5 g. (0.00113 mole) of the carbinol in 9 ml. of ether, specially dried over sodium-potassium alloy (1:5) for 24 hours, was added approximately 0.002 g. (0.0001 mole) of freshly cut sodium. The suspension was swirled occasionally over 1 hour to dissolve the carbinol. Over the two-hour period of the reaction no gas evolution was observed, nor did the appearance of the sodium change. A positive Color Test I[5] could not be obtained. The lump of sodium was removed and the ether evaporated under reduced pressure to yield an oil which crystallized on scratching and melted from 75–81°. Recrystallization from ethanol gave 0.48 g. (96%) of pure benzhydryloxytriphenylsilane, m.p. 83–84°, which did not depress the melting point of an authentic sample.

As a blank run a duplicate experiment was carried out except that no sodium was added. Workup gave 0.47 g. (94%) of recovered triphenylsilyldiphenylcarbinol, m.p. 157–159°, identified by mixed melting point.

Similar results were obtained using sodium-potassium alloy. A drop of the alloy was added to the above system and over 3 minutes the surface of the alloy became slightly purplish although no hydrogen appeared to be evolved. After 3 minutes the ether layer was removed from the alloy and worked up to yield 95% of benzhydryloxytriphenylsilane, m.p. 82–84°, identified by mixed melting point.

E. **With Sodium Hydride.**—To 1.0 g. (0.00226 mole) of triphenylsilyldiphenylcarbinol in 25 ml. of anhydrous ether was added 0.054 g. (0.0022 mole) of sodium hydride.[9] Slow gas evolution ceased after 1 hour although all the hydride had not dissolved. A second 0.05-g. quantity of sodium hydride was added and bubbling occurred for an additional hour. The clear ether layer, which gave a negative Color Test I, was decanted from the insoluble residue into 200 ml. of dilute cold hydrochloric acid. The ether layer after drying yielded 0.90 g. (90%) of benzhydryloxytriphenylsilane, m.p. 82–84°, identified by mixed melting point.

Alternatively 0.76 g. (0.00172 mole) of triphenylsilyldiphenylcarbinol in 15 ml. of anhydrous benzene was treated with 0.12 g. (0.0050 mole) of sodium hydride. After 1 hour the benzene layer was decanted from insoluble material and evaporated to dryness. Recrystallization of the residue from petroleum ether (b.p. 60–70°) yielded 0.62 g. (82%) of benzhydryloxytriphenylsilane, m.p. 81–82°.

F. **With Phenyllithium.**—To a solution of 0.8 g. (0.0018 mole) of triphenylsilyldiphenylcarbinol in 15 ml. of anhydrous ether was added 5 ml. of 0.865 *M* phenyllithium (0.0043 mole). The solution turned deep blue, reminiscent of benzophenone ketyl, and then the color slowly faded to wine-red. A positive Color Test I[5] was obtained at this stage. White needles were deposited slowly over 4 days and then after filtering off the solid the reaction mixture was drowned in water and worked up. From the ether layer was obtained 0.09 g. (15%) of tetraphenylsilane, m.p. 227–229°, and 0.14 g. (42%) of benzhydrol, m.p. 65–67°, both compounds identified by mixed melting point. Recrystallization of the white needles originally filtered off from benzene gave an additional 0.28 g. (46%) of tetraphenylsilane, m.p. 232–234°.

Benzhydrylmethyldiphenylsilane.—To 95 ml. of 0.94 *M* butyllithium[10] (0.089 mole) of diethyl ether was added 12.6 g. (0.075 mole) of diphenylmethane. After stirring for 20 hours at room temperature 16.4 g. (0.071 mole) of methyldiphenylchlorosilane (b.p. 140–145° at 25 mm.) in 100 ml. of dry benzene was added. Heat was evolved and near the end of the addition the reaction mixture became pale yellow and a white precipitate formed. The mixture was refluxed for 1 hour at which time Color Test I was negative. The reaction mixture was worked up as usual to yield a very viscous oil which failed to crystallize on standing. It was therefore distilled and after a forerun of 5.4 g. of impure diphenylmethane, b.p. 100–128° (0.6 mm.), a very viscous colorless liquid weighing 13.8 g. (51%), b.p. 170–180° (0.6 mm.) distilled. After 6 days this benzhydrylmethyldiphenylsilane crystallized, and after recrystallization from ethanol melted at 102–103°.

Anal. Calcd. for $C_{26}H_{24}Si$: C, 85.7; H, 6.59; Si, 7.69. Found: C, 85.8; H, 6.38; Si, 7.50.

Bromobenzhydrylmethyldiphenylsilane.—A suspension of 4.5 g. (0.0124 mole) of benzhydrylmethyldiphenylsilane, 2.4 g. (0.0135 mole) of N-bromosuccinimide and 50 ml. of carbon tetrachloride was refluxed for 16 hours. After cooling 1.24 g. (100%) of crude succinimide, m.p. 122–125°, was filtered off. The filtrate was evaporated to dryness and the resulting white solid was recrystallized from carbon tetrachloride to yield 4.67 g. (87%) of bromobenzhydrylmethyldiphenylsilane, m.p. 80–82°.

Anal. Calcd. for $C_{25}H_{23}SiBr$: Si, 6.33; Br, 18.1. Found: Si, 6.14; Br (as AgBr), 17.7.

Methyldiphenylsilyldiphenylcarbinol.—To 4.67 g. (0.0105 mole) of bromobenzhydrylmethyldiphenylsilane dissolved in a homogeneous solution of 100 ml. of acetone, 23 ml. of benzene and 18 ml. of water was added 1.8 g. (0.0108 mole) of silver acetate. The suspension was stirred in the dark for 16 hours and then 1.94 g. (0.0103 mole, 98%) of silver bromide was filtered off and washed with acetone. Evaporation of the combined filtrates left a white solid which was recrystallized from petroleum ether (b.p. 90–100°) and a trace of benzene to yield 3.16 g. (80%) of methyldiphenylsilyldiphenylcarbinol, m.p. 123–130°. Recrystallization from ethanol gave 2.52 g. (64%) of product, m.p. 127.5–128°.

Anal. Calcd. for $C_{26}H_{24}SiO$: C, 82.1; H, 6.32; Si, 7.37. Found: C, 82.0; H, 6.63; Si, 7.49.

Reactions of Methyldiphenylsilyldiphenylcarbinol. A. With Pyridine.—A solution of 0.5 g. (0.00132 mole) of the carbinol in 5 ml. of dry pyridine was refluxed for 5 minutes. The pyridine was removed under reduced pressure and the resulting oil crystallized on scratching. Recrystallization from petroleum ether (b.p. 60–70°) gave 0.34 g. (68%) of benzhydryloxymethyldiphenylsilane, m.p. 72.0–72.7°,

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[9] Metal Hydrides, Inc., Beverly, Mass.

[10] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, This Journal, **71**, 1499 (1949).

which was identified by mixed melting point with an authentic specimen.[11]

No appreciable isomerization occurred if the carbinol was refluxed with 2 mole equivalents of pyridine in benzene for 1 hour since most of the carbinol was recovered unchanged.

B. **With Sodium Hydroxide.**—To 0.2 g. (0.00053 mole) of the carbinol in 10 ml. of ethanol was added 0.04 ml. of 10% aqueous sodium hydroxide. The solution after 2 minutes at room temperature was raised to boiling over 1 minute, and then drowned in dilute hydrochloric acid and ice. The reaction was worked up as usual to yield a small amount of oil, which after several days yielded 0.02 g. (20%) of needles, m.p. 65–66°, shown to be benzhydrol since the mixed melting point with an authentic specimen was not depressed. No attempt was made to isolate the methyldiphenylcarbinol probably present, since it is a liquid at room temperature.

Triphenylsilyldimethylcarbinol.—To 18 ml. of 0.46 *N* triphenylsilyllithium (0.0086 mole) in tetrahydrofuran was added excess acetone. Color Test I was immediately negative. The reaction mixture was hydrolyzed with dilute acid and the ether extracts, after drying, were evaporated to dryness under reduced pressure. The resultant solid was recrystallized from petroleum ether (b.p. 90–100°) to yield 1.25 g. (45%) of triphenylsilyldimethylcarbinol, m.p. 150–153°. Recrystallization from ethanol raised the melting point to 155–156°. Gilman and Lichtenwalter (unpublished research) report m.p. 158–159°.

When 0.3 g. of this material was refluxed for 6 hours in anhydrous pyridine, 0.23 g. (77%) of the material was recovered unchanged, m.p. 155–156°. After 0.1 g. of the carbinol in 10 ml. of dry ether was treated for 1.5 hours with a drop of sodium–potassium alloy, removal of the ether led to the recovery of the starting material in 87% yield.

Attempted Isomerization of Triphenylsilylmethanol.—A solution of 0.2 g. (0.00069 mole) of triphenylsilylmethanol[2] in 5 ml. of pyridine was refluxed for 18 hours. The pyridine was removed under reduced pressure and the resulting solid melted at 108–112°, and did not depress the mixed melting point with the starting material. Recrystallization from ethanol gave 0.15 g. (75%) recovery of pure starting material, m.p. 116–117°.

When 0.3 g. (0.00103 mole) of the material was refluxed in 5 ml. of quinoline for 1 hour the solution turned dark brown. The reaction mixture was drowned in excess dilute hydrochloric acid which was ether-extracted. Removal of the ether and recrystallization of the residue from ethanol led to the recovery of 0.16 g. (53%) of triphenylsilylmethanol, m.p. 115–117°, identified by mixed melting point with an authentic specimen.

Attempted Preparation of Triphenylsilyldiphenylcarbinol from Ethyl Triphenylsilanecarboxylate.—To 2.0 g. (0.006 mole) of ethyl triphenylsilanecarboxylate[8] in 25 ml. of anhydrous ether was added over 45 minutes 40 ml. of 0.5 *N* (0.02 mole) of phenylmagnesium bromide. After 1.5 hours a negative Color Test I was obtained and the reaction mixture was drowned in dilute acid. Workup of the ether layer in the usual manner led to the recovery of 0.73 g. (37%) of the ester, m.p. 96–98°, identified by mixed melting point.

When only one mole equivalent of Grignard reagent was added to 2.0 g. (0.0062 mole) of methyl triphenylsilanecarboxylate and the mixture was stirred for 24 hours prior to workup, a total of 1.76 g. (88%) of the ester, m.p. 107–109°, was recovered and identified.

When 0.0175 mole of phenyllithium was added to 2.0 g. (0.006 mole) of ethyl triphenylsilanecarboxylate, the first few drops of reagent produced a red color and the reaction mixture became warm. A solid precipitated during the next 7 hours stirring, although a positive Color Test I was still obtained after this time. The reaction mixture was drowned in dilute acid and worked up as usual to yield a total of 1.20 g. (60%) of tetraphenylsilane, m.p. 232–234°, identified by mixed melting point.

Hydrolysis of Benzhydryloxytriphenylsilane.—A solution of 0.2 g. (0.00045 mole) of the compound in 15 ml. of ethanol was treated at room temperature with 1 ml. of 10% aqueous sodium hydroxide for 10 minutes. The reaction mixture was drowned in dilute acid and then worked up to yield 0.06 g. (48%) of triphenylsilanol, m.p. 150–152°, and 0.06 g. (30%) of recovered benzhydryloxytriphenylsilane, m.p. 82–84°.

When the time and amount of alkali were each reduced to one-half the above amounts, only recovered starting material was obtained. Under identical conditions, triphenylsilyldiphenylcarbinol was isomerized to benzhydryloxytriphenylsilane, but apparently no hydrolysis occurred since no triphenylsilanol was isolated.

Acknowledgment.—The author is indebted to Dr. Henry Gilman for valuable discussions concerning this research and to the National Research Council of Canada for a grant in support of part of this work.

TORONTO, CANADA

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[11] We are indebted to Dr. Henry Gilman for a sample of this material, which as received had m.p. 63–64°. The mixed melting point with the above material was 69–70°. Recrystallization of the Gilman sample from ethanol raised the melting point to 71.5–72.7°. On being informed, Gilman recrystallized his sample but the melting point remained 63–64°. Infrared spectra of our material and Gilman's original and recrystallized material in KBr pellets were practically indistinguishable. This phenomenon is evidently a case of polymorphism, of which the polymorph, m.p. 72.0–72.7°, is evidently the stable form.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF FLORIDA]

Fluorocarbon Nitrogen Compounds. II.[1] The Synthesis and Properties of Perfluorodimethylglycine, $(CF_3)_2NCF_2COOH$[2]

BY JOHN A. YOUNG AND RICHARD D. DRESDNER

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A perfluoroamino acid, $(CF_3)_2NCF_2COOH$, has been synthesized by the electrochemical process from both the methyl ester and N,N-dimethylamide of dimethylglycine. Cleavage and cyclization products have been identified as $(CF_3)_2NCOF$, $(CF_3)_3N$, $(CF_3)_2NCFOCF_2N(CF_3)CF_2$ and probably $CF_3NCF_2CF_2OCF_2$. The nitrogen atom is not basic and the free acid resembles non-nitrogen containing fluorocarbon acids in its chemistry, except that the silver salt is unstable in aqueous solution. The preparation of various derivatives is described.

Although certain derivatives of perfluorodimethylcarbamic acid are available through the electrochemical process,[1] their use in the synthetic chemistry of nitrogen-containing fluorocarbons is severely limited by instability. This paper reports the synthesis of a stable nitrogen-containing fluorocarbon acid, perfluorodimethylglycine.

Preferred starting materials for the electrochemical preparation of fluorocarbon acids are the organic acid fluoride or chloride. Since, however,

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[1] For the previous paper in this series, see J. A. Young, T. C. Simmons and F. W. Hoffmann, THIS JOURNAL, **78**, 5637 (1956).

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