The mixture was stirred overnight and hydrolyzed. Removal of the ether yielded a water-like liquid which was distilled to yield 7.3 g. (68.6%) of tetraethyltin, b.p. 178.5°, $n^{20}\text{D}$ 1.4691.[14] The compound gave a positive qualitative test for tin.[13]

Run 2.—This run was carried out exactly as the first. The yield of tetraethyltin was 7.7 g. (72.6%), b.p. 177°, $n^{20}\text{D}$ 1.4691.

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[14] L. L. Gershbein and V. N. Ipatieff, This Journal, **74**, 1540 (1952), report $n^{20}\text{D}$ 1.4693 for tetraethyltin.

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Formation of Tetraphenylsilane from Reactions Involving Triphenylsilylpotassium

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It has been shown that triphenylsilylpotassium adds to unsaturated linkages such as the carbon–carbon double bond of *trans*-stilbene.[1] Studies

$$(C_6H_5)_3SiK + C_6H_5CH{=}CHC_6H_5 \longrightarrow (C_6H_5)_3SiCH(C_6H_5)CH(C_6H_5)K$$

of the extension of the addition reaction to the acetylenic linkage showed that good yields of tetraphenylsilane were obtained. Thus, the reaction of triphenylsilylpotassium with phenylacetylene gave tetraphenylsilane as the major product.[2] Similarly, tolane reacts with triphenylsilylpotassium to give tetraphenylsilane in a lower yield. The high yield of tetraphenylsilane from the phenylacetylene reaction suggested the possible significance of the acidic hydrogen although we observed tetraphenylsilane was also formed from reactions involving triphenylsilylpotassium and some other compounds.[3] We have examined the reactions of triphenylsilylpotassium with phenylcarbinols and obtained high yields of tetraphenylsilane in all cases. It was interesting to observe that triphenylsilanol also gave a high yield of tetraphenylsilane. Whether tetraphenylsilane was formed by disproportionation in these reactions is not known. The course of these reactions is being examined with compounds containing other functional groups as well as compounds containing substituted aryl groups, like the *m*-tolyl group.

Incidental to the studies of the reaction of triphenylsilylpotassium with triphenylcarbinol we observed that triphenylcarbinol does not depress the melting point of triphenylsilanol. The similarities between these two compounds rendered the separation of a mixture of them very difficult. It has been found that by treating a mixture of triphenylcarbinol and triphenylsilanol with formic acid the carbinol was reduced to triphenylmethane,[4] whereas the silanol was converted into hexaphenyldisiloxane.[5]

$$(C_6H_5)_3COH + HCOOH \longrightarrow (C_6H_5)_3CH$$

$$(C_6H_5)_3SiOH + HCOOH \longrightarrow (C_6H_5)_3SiOSi(C_6H_5)_3$$

The resulting hydrocarbon and the silicon compound were separated by recrystallization.

Experimental[6]

Reaction of Triphenylsilylpotassium with Phenylacetylene.—A triphenylsilylpotassium suspension in ether prepared from 5.2 g. (0.01 mole) of hexaphenyldisilane followed by amalgamation according to the recent directions[7] was added rapidly to 1 g. (0.01 mole) of phenylacetylene dissolved in 20 ml. of ether. There was a slight heating effect accompanied by a slight change in color during the addition. The reaction mixture was stirred at room temperature for 30 hours. At the end of this period Color Test I[8] was still positive. Water was added to the reaction mixture and the latter was stirred and filtered. There was obtained 3.5 g. of light gray solid melting at 230°. This solid was extracted with benzene and filtered hot in order to remove a trace of gray residue. The filtrate yielded 2.8 g. (83%[9]) of colorless shining crystals melting at 233–235°; a mixed melting point with an authentic sample of tetraphenylsilane showed no depression. The ether solution of the hydrolyzed mixture was separated, dried over sodium sulfate, and distilled. The oily solid residue was recrystallized from a mixed solvent of benzene and petroleum ether (b.p. 60–70°) to give 0.5 g. of triphenylsilanol (mixed m.p.) melting at 149–151°.

In another experiment involving the same quantities of reactants the phenylacetylene was added to the triphenylsilylpotassium suspension. After 22 hours of stirring at room temperature the reaction mixture was carbonated with Dry Ice–ether slurry. Following the attainment of room temperature the carbonation mixture was hydrolyzed with dilute hydrochloric acid. There was separated 3.1 g. of light gray solid melting from 228–234°. This was recrystallized twice from benzene to yield 1.6 g. (48%[9]) of tetraphenylsilane. Some impure tetraphenylsilane was recovered from the mother liquor. The ethereal solution from the hydrolysis mixture was extracted with dilute alkali. Some white solid was separated upon the acidification of the alkaline extract. This was dissolved in ether from which 0.8 g. of light brown solid residue was obtained by evaporation. This solid was recrystallized from benzene to give colorless shining prisms melting at 134–136°; a mixed melting point with phenylpropiolic acid showed no depression. The purified acid weighed 0.5 g. (34%).

Reaction of Triphenylsilylpotassium with Tolane.—One and eight-tenths grams (0.01 mole) of tolane in 30 ml. of ether was added to 0.02 mole of a triphenylsilylpotassium suspension in ether without amalgamation over a period of 5 minutes. No appreciable amount of heat was evolved while the reaction mixture became very dark brown during the period of addition. The resulting mixture was stirred at room temperature for 24 hours. The black mixture thus formed was hydrolyzed with water and filtered by suction. There was collected 1.6 g. of solid melting to a turbid mass at 190°. This was recrystallized from benzene. The first crop separated as a fine white powder melting from 325–340°. Evaporation of the mother liquor to a small volume yielded 0.7 g. of colorless crystals melting from 225–230°. One recrystallization from benzene gave 0.5 g. (15%[9]) of tetraphenylsilane (mixed m.p.) melting at 233–235°. Evaporation of the ethereal solution from the hydrolysis mixture resulted in a glue-like residue. Attempts to purify it by crystallization and by chromatographic separation were unsuccessful.

Reaction of Triphenylsilylpotassium with Triphenylcarbinol.—A triphenylsilylpotassium suspension was prepared by cleaving 5.2 g. (0.01 mole) of hexaphenyldisilane with sodium–potassium alloy in ether. The excess alloy was removed by amalgamation and the triphenylsilylpotassium

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[1] H. Gilman and T. C. Wu, This Journal, **75**, 234 (1953).

[2] From one reaction between phenylacetylene and triphenylsilylpotassium, followed by carbonation, there was isolated phenylpropiolic acid as well as tetraphenylsilane.

[3] For example, reaction of triphenylsilylpotassium with diphenyl sulfoxide also gives tetraphenylsilane.

[4] A. Kovache, *Ann. chim.*, **10**, 184 (1918).

[5] Unpublished studies by H. W. Melvin.

[6] All melting points are uncorrected.

[7] H. Gilman and T. C. Wu, *J. Org. Chem.*, in press; H. Gilman and T. C. Wu, This Journal, **73**, 4031 (1951); H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman and S. H. Eidt, *ibid.*, **74**, 561 (1952).

[8] H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

[9] The percentage yield was calculated on the assumption that from an initial mole of hexaphenyldisilane there is obtained 1 mole of tetraphenylsilane.

suspension was transferred to another flask filled with nitrogen. To this there was added 2.6 g. (0.01 mole) of triphenylcarbinol dissolved in 50 ml. of ether. Very little heat was evolved during the addition while the reaction mixture became slightly deeper in color. After 48 hours of stirring at room temperature Color Test I[8] was still positive. Water was added to the mixture and it was filtered to separate 1.8 g. of cream-colored solid melting from 230–235°. This crude product was dissolved in hot benzene and filtered to remove a trace of gray specks. From the filtrate there was obtained 1.6 g. (48%[9]) of pure tetraphenylsilane (mixed m.p.) melting at 234–235°. The ethereal solution from the hydrolysis mixture was separated and dried over sodium sulfate. Evaporation of the solvent left 5.5 g. of a colorless solid residue melting from 145–151°. This was dissolved in hot petroleum ether (b.p. 60–70°) and allowed to cool. The first fraction of 0.2 g. of white solid melting at 225° was shown to be impure tetraphenylsilane after recrystallization. The petroleum ether solution was concentrated to give 2.7 g. of colorless crystals melting at 149–151°. It was suspected that this material might be a mixture of triphenylcarbinol and triphenylsilanol. A prepared mixture of about equal parts of triphenylcarbinol (m.p. 160–162°) and triphenylsilanol (m.p. 150–151°) melted at 151–153°. After some preliminary studies the reaction products were separated in the following manner.

The mixture of reaction products was refluxed in formic acid (Baker and Adamson, 98–100%) for 15 hours. Some colorless crystals were formed. The resulting mixture was diluted with 4 volumes of water and filtered. The solid residue (2.3 g.) was dissolved in petroleum ether (b.p. 60–70°) to give 0.5 g. of lustrous plates melting at 227–229°; a mixed melting point with hexaphenyldisiloxane showed no depression. This quantity corresponded to 10% of triphenylsilanol (presumably from the hydrolysis of excess triphenylsilylpotassium) originally present in the mixture of triphenylcarbinol and triphenylsilanol. The mother liquor after the removal of hexaphenyldisiloxane was evaporated to yield 1.6 g. of white crystals melting at 90–92°; a mixed melting point with an authentic sample of triphenylmethane was not depressed. The amount of triphenylmethane thus obtained was equivalent to 66% recovery of the triphenylcarbinol.

Reaction of Triphenylsilylpotassium with Benzohydrol.—The procedure used in this reaction was exactly the same as that described in the previous section except that 0.01 mole of benzohydrol was used instead of triphenylcarbinol. Following hydrolysis there was obtained, by filtration, 3.0 g. of crude tetraphenylsilane. This was purified as described above and 2.7 g. (80%[9]) of pure tetraphenylsilane (mixed m.p.) was isolated. From the ethereal solution 2.8 g. of white solid melting at 67–69° was obtained by recrystallization. Analyses of this product showed that it contained 3.0–3.5% of silicon. Melting point studies also pointed out that the presence of triphenylsilanol does not depress appreciably the melting point of benzohydrol. However, no attempt was made to separate this mixture.

Reaction of Triphenylsilylpotassium with Benzyl Alcohol.—Using exactly the same procedure described in the reaction with triphenylcarbinol except that 0.01 mole of benzyl alcohol was used instead of triphenylcarbinol, there was obtained 2.6 g. of crude and 2.3 g. (68%[9]) of pure tetraphenylsilane (mixed m.p.) melting at 234–235°. The ethereal solution was worked up as usual to give 1.0 g. (18%) of triphenylsilanol (mixed m.p.). Evaporation of the mother liquor resulted in an oil.

Reaction of Triphenylsilylpotassium with Triphenylsilanol.—The procedure used in this reaction was also the same as that for the triphenylcarbinol except that 0.01 mole of triphenylsilanol was used instead of triphenylcarbinol. Following hydrolysis there was obtained 3.2 g. of an insoluble solid melting at 232–235°. Recrystallization of this crude product gave 2.9 g. (86%[9]) of tetraphenylsilane (mixed m.p.) melting at 234–235°. The solid obtained from the ethereal solution was recrystallized twice from petroleum ether (b.p. 60–70°) to yield 3.2 g. of pure triphenylsilanol (mixed m.p.) melting at 150–151°. It was believed that part of the triphenylsilanol was the starting material and the rest came from the hydrolysis of triphenylsilylpotassium.

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16α-Methoxy-5-pregnen-3β-ol-20-one

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Recently Mattox[1] reported the isolation of 16α-methoxy-5-pregnen-3β-ol-20-one acetate obtained by the action of methanolic hydrogen chloride on 5,16-pregnadien-3β-ol-20-one followed by acetylation of the product. Fukushima and Gallagher[2] isolated the same substance after saponifying pregnadienolone acetate in methanol and acetylating the crude product. Since we had previously isolated the unacetylated 16α-methoxy-5-pregnen-3β-ol-20-one by use of the Freudenberg[3] conditions, we are giving our results on this work.

During our studies on the acid hydrolysis of cortisone acetate, we isolated a product for which one possible structure was a 16,21-dimethoxypregnetrione.[1,4] In order to investigate whether the addition of methanol to the Δ^{16}-20-keto system would proceed by acid catalysis, we treated pregnadienolone in methanol with acetyl chloride and obtained a product having an *E*-value of 72 at 239 mμ, corresponding to the presence of about 25% of the original α,β-unsaturated ketone. The major product, 16α-methoxy-5-pregnen-3β-ol-20-one was separated by chromatography in about 35% yield, and was found to be identical with that obtained upon treatment of pregnadienolone acetate with methanolic alkali.

Treatment of the methoxypregnenolone with boiling acetic anhydride did not split out methanol, but only gave the known 3-acetate.[2] Cleavage was successful, however, when acetic anhydride catalyzed with hydrochloric acid was used, and it was possible to isolate 5,16-pregnadien-3β-ol-20-one acetate from the mixture.

Experimental[5]

16α-Methoxy-5-pregnen-3β-ol-20-one from 5,16-Pregnadien-3β-ol-20-one.—5,16-Pregnadien-3β-ol-20-one (2.0 g.) was dissolved in 160 ml. of abs. methanol and cautiously treated with 4 ml. of acetyl chloride (equiv. to 1% HCl). The mixture was allowed to stand 18 hours at room temperature. A solution of 5 g. of sodium acetate in 500 ml. of water was added and the precipitate which formed was collected by suction and washed with water. It weighed 2.1 g., m.p. 125–128°, *E* 72 (239 mμ in 95% ethanol).

One gram of the material was dissolved in benzene and chromatographed on 25 g. of Florisil as follows (100 ml. fractions):

Fraction	Eluant	Wt., mg.	M.p., °C.	$E^{1\%}_{1\,\mathrm{cm}}$	Product
1–4	Hexane	Neg.			
5–14	3:1 Hexane–C_6H_6	235	180–195	200	Pregnadienolone
15–22	1:1 Hexane–C_6H_5	50	150–180	150	Mixture
23–37	Benzene	360	144–154	22	16-Methoxy-pregnenolone
38–48	1% MeOH in C_6H_5	320	Oil		

Upon crystallization from methanol, fractions 23–37 gave 16α-methoxy-5-pregnen-3β-ol-20-one, m.p. 151–153°, $[\alpha]^{25}\mathrm{D}$ −23.9° (EtOH). *Anal.* Calcd. for $C_{22}H_{34}O_3$: C, 76.26; H, 9.89. Found: C, 76.51; H, 10.00. The ratio to re-

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[1] V. R. Mattox, THIS JOURNAL, **74**, 4340 (1952).

[2] D. K. Fukushima and T. F. Gallagher, *ibid.*, **73**, 196 (1951).

[3] K. Freudenberg and W. Jakob, *Ber.*, **74**, 1001 (1941).

[4] D. Gould and E. B. Hershberg, in press.

[5] All melting points are corrected. $E^{1\%}_{1\,\mathrm{cm}} = (l/cd) \log I_0/I$; $\epsilon = \mathrm{M.W.} \times E/10$. Analyses and optical data obtained by the Microanalytical Department of these laboratories.