

# SPECTRAL PROPERTIES OF *p*-SUBSTITUTED BENZOYLTRIPHENYLSILANES

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#### ABSTRACT

A series of p-substituted benzoylsilanes have been synthesized and their infrared and ultraviolet spectra determined. Correlations of both the infrared carbonyl stretching frequency and the  $n-\pi^*$  ultraviolet absorption with Hammett substituent constants have been found. Benzoylsilanes are generally unstable in ethanol undergoing light-catalyzed decomposition. Benzoyldiphenylphosphine was found to give spectra similar to those of benzoylsilanes.

The yellow color and general spectral properties of benzoylsilanes are of some interest since the analogous carbon compounds are colorless and since the benzoylsilanes represent the only known group of colored silicon-containing compounds in which the silicon atom is obviously acting as part of the chromophoric system (1-4). As part of our continuing investigation of the behavior of silyl ketones we were led to synthesize a number of substituted benzoyltriphenylsilanes, where substituents were present either on the para position of the benzoyl group or on the para positions of all three phenyl groups attached to silicon. All of the substituted silanes were varying shades of yellow. The infrared and ultraviolet spectral data are given in Tables I and II.

Infrared carbonyl stretching frequency				
For Ph <sub>3</sub> SiCO-X		For (Y-), SiCOPh		
X	cm <sup>-1</sup>	Y	cm <sup>-1</sup>	
H NO <sub>2</sub> Br Cl F OCH <sub>3</sub> C(CH <sub>3</sub> ) <sub>3</sub>	$1 \begin{array}{c} 1 \\ 617 \\ 1 \\ 624 \\ 1 \\ 618 \\ 1 \\ 618 \\ 1 \\ 617 \\ . 5 \\ 1 \\ 616 \\ 1 \\ 616 \end{array}$	H Cl CF3	$1\ 617 \\ 1\ 617 \\ 1\ 617 \\ 1\ 617 \\$	

TABLE I

The carbonyl infrared stretching frequency for all ketones occurred near 1 617 cm<sup>-1</sup> (6.18  $\mu$ ). An approximately linear correlation between the stretching frequency and  $\sigma$ , the Hammett substituent constant, was found for the *p*-substituted benzoyltriphenylsilanes (Fig. 1), as had been observed previously for the corresponding acetophenones (5) except that in the present case the  $\sigma^-$  value for the *p*-nitro group fitted the data better. Since the frequencies for all compounds occurred over a range of only 8 cm<sup>-1</sup> a more precise correlation could not be expected.

One difference noted between the acetophenones and the benzoylsilanes was in the slope of the  $\nu$  vs.  $\sigma$  plot; in the acetophenones the slope  $\Delta\nu/\Delta\sigma$  was 16.6, whereas in the benzoylsilanes the slope was 5.4, indicating considerably less sensitivity of the carbonyl

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FIG. 1. Infrared carbonyl stretching frequency vs. Hammett  $\sigma$  (or  $\sigma^-$ ) constant for p-substituted benzoylsilanes.

group in the latter compounds to inductive and mesomeric effects of the p-substituent. This is to be expected because of the significant degree of single bond or polar character present in the carbonyl group of these compounds. The carbonyl stretching frequencies of the tris-p-substituted phenylbenzoylsilanes occurred in the same position as the unsubstituted compound within experimental error. The insensitivity of the stretching frequency to the nature of the group attached to silicon has been observed before, triphenyl- and trimethyl-benzoylsilanes, as well as mixed methylphenylbenzoylsilanes, absorbing at the same frequency (2).

In the ultraviolet and visible region benzovlsilanes have two absorptions, one in the region of 260 m $\mu$  assigned as a  $\pi - \pi^*$  transition and the other occurring at about 420 m $\mu$ ascribed as an  $n-\pi^*$  transition of the carbonyl group involving interaction with the silicon d-orbitals (3, 4). The high intensity  $\pi - \pi^*$  band occurs in essentially the same position as that of its carbon analog  $\beta$ -benzpinacolone (2), while the n- $\pi^*$  transition is, of course, at much longer wavelength. Comparing the absorption data with that of the related acetophenones (6), we found, with the exception of the p-nitrobenzovlsilane, where the shift in wavelength is rather smaller, that the  $\pi$ - $\pi^*$  absorption maxima of p-substituted benzoylsilanes occurs at  $17-18 \text{ m}\mu$  longer wavelength than that of the corresponding acetophenones, suggesting that the silicon atom adjacent to the carbonyl group is not significantly involved in the  $\pi - \pi^*$  transition, and that the p-substituents are acting in their normal manner as far as their effects on the position of absorption maxima are concerned. The extinction coefficients of benzovlsilanes are, however, slightly larger than those of the corresponding acetophenones. On the other hand, the  $n-\pi^*$  absorption band of the benzoylsilanes occurs at approximately 100 m $\mu$  longer wavelength, and with a considerably greater extinction coefficient than the  $n-\pi^*$  band for the corresponding acetophenones. Unfortunately, the position of this band in acetophenones has not always been reported, but from the available data (7), the minor changes in wavelength caused by p-substituents appear to vary in the same way with both benzoylsilanes and acetophenones.

An interesting correlation between the wavelength of the most intense  $n-\pi^*$  band and  $\sigma$ , the Hammett substituent constant, was noted (Fig. 2). Although it is recognized that ultraviolet data, which involve both ground and excited states, cannot normally be

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related to Hammett substituent effects, which involve ground states only, the apparent correlation appears worthy of comment. A linear correlation of wavelength with  $\sigma$  was found for benzoyltriphenylsilane and its *p*-tert-butyl, *p*-chloro, and *p*-bromo derivatives. The *p*-nitro, *p*-fluoro, and *p*-methoxy compounds deviate significantly from this correlation: in other cases involving Hammett correlations of kinetic data, compounds with these same substituents have been observed to deviate in the same direction. Thus *p*-nitro compounds fitted the data better here, and in Eaborn's work (8) if  $\sigma^-$  values were used, and in both base-catalyzed hydrolyses of benzylsilanes (9) and in base-catalyzed isomerizations of  $\alpha$ -silylcarbinols (10), the *p*-fluoro and *p*-methoxy compounds required, as here, more negative  $\sigma$  values than those normally employed to fit the correlation. Further data seems desirable, before the significance of the correlation and the deviations from it can be assessed. We believe that this deviation is a real and significant effect and will be discussed in more detail in a future publication.

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The ultraviolet data reported in Table II were measured in cyclohexane, and in some cases, in ethanol as well. In ethanol, the solvent employed in previous studies (2), the 420 m $\mu$  band appears as one peak, with shoulders on each side, whereas in cyclohexane all the ketones showed three clearly resolved bands as well as a shoulder on the short wavelength side of the shortest wavelength band. This fine structure, previously observed with simple carbonyl compounds in nonpolar solvents (11), is presumably associated with various vibrational levels of the  $n-\pi^*$  excitation. A comparison of the data in cyclohexane and ethanol showed small changes in wavelength in ethanol than in cyclohexane (blue shift) whereas the  $\pi-\pi^*$  transition generally occurred at 1-2 m $\mu$  longer wavelength in changing to the more polar solvent (red shift). These changes follow the pattern usually observed in carbonyl compounds in changing from nonpolar to polar solvents and hence substantiate the assignment of the spectroscopic transitions as  $\pi-\pi^*$  and  $n-\pi^*$  (12).

Apart from the enhanced resolution of the  $n-\pi^*$  band an additional reason for changing the solvent from ethanol to cyclohexane was the observation that some of the ketones appeared to be unstable in ethanol; different extinction coefficients were found for new and aged solutions, and in extreme cases, the yellow color of the solutions faded rapidly to colorless. It was shown that this decomposition was light catalyzed. Thus several grams of benzoyltriphenylsilane in methanol were irradiated with a lamp rich in near ultraviolet radiation and in 1–2 h the yellow color was entirely bleached. Distillation of

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Ultraviolet spectra			
	X	Cyclohexane $(\lambda(\epsilon))$	Ethanol $(\lambda(\epsilon))$
Of Ph <sub>3</sub> SiCO-X			
	Н	$257(16\ 200)$ $388(s)(118),\ 405(222)$ $424(292),\ 440(177)$	258(15 500) 403(264), 417(300)
	$NO_2$	$266(17\ 800)$ 411(s)(132), 434(192) 448(192) 478(89)	$267(15\ 600)\ 430(215)$
	Br	271(21700) 390(s)(117), 407(216) 428(271) 448(158)	$271(21\ 300)$ $410(266),\ 421(288)$ 442(165)
	Cl	268(18400) 391(s)(117), 407.5(217) 427(273), 448(159)	*
	F	260(13700) 384(s)(119), 400(223) 4185(290), 440(188)	*
	OCH3	290(20800), 298(s)(17400) 380(s)(132), 396(246) 414(335), 434(232)	t
	C(CH <sub>3</sub> ) <sub>3</sub>	269(19800) 386(s)(120), 403(227) 421(305), 442(200).	*
Of (X-)3SiCOPh		121(000); 112(200).	
	Cl	$228.5(38\ 400),\ 257(s)(19\ 600)$ $387(s)(149),\ 403(277)$ $422(363),\ 442(330)$	259(17 400) 400(288), 411(325 425(218)
	CF3	$266(17\ 250)$ $384(s)133,\ 401(239)$ $418(s)143,\ 428(201)$	t
OF PL P COPL	CH3	263 404, 423, 446	263 405(s), 417, ‡
OI rn₂r—COrn		*	$265(12\ 000)\ 377(247),\ 390(270\ 404(175)$

TABLE II

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Abbreviation: s = shoulder. \*Spectrum not determined. †Unstable in ethanol. ‡Compound not pure so extinction coefficient unknown.

the solution gave triphenylmethoxysilane in high yield, a small amount of benzaldehyde and a much larger yield of benzaldehydedimethylacetal, identified by its infrared and nuclear magnetic resonance (n.m.r.) spectra, and physical properties.

$$\frac{h\nu}{\text{MeOH}} \text{Ph}_3\text{SiOMe} + \text{PhCH}(\text{OMe})_2$$

This decomposition occurs much more slowly, if at all, in the dark in methanol and is completely avoided in nonpolar solvents such as cyclohexane.

It has been reported in the literature that benzoyldiphenylphosphine is a yellow solid although no spectral data is reported (13). Because of the obvious analogy between benzoylsilanes and benzoylphosphines the synthesis was repeated and a yellow solid was obtained. The material could not be entirely freed of benzaldehyde, and the compound was found to be rather less stable than the original literature suggested. In air, it decomposed yielding benzoic acid and diphenylphosphonic acid. As expected the yellow (impure)

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material, freshly distilled, showed a low frequency carbonyl stretching band (1 645 cm<sup>-1</sup>) although the frequency was higher than that of benzoylsilanes, and the ultraviolet spectra showed  $\pi - \pi^*$  absorption at 265 m $\mu$ , and  $n - \pi^*$  absorption centered about 390 m $\mu$ , rather lower than that of a benzoylsilane. It seems clear in view of the similar spectra that benzoylsilanes and benzoylphosphines are closely related species subject to the same sort of group interactions.

It now seems quite clear that the abnormally low infrared carbonyl stretching frequency in benzoylsilanes is a result of significant single bond character in the carbonyl group caused by inductive release of electrons by the adjacent silicon atom. In accord with this Yates and Agolini (14) have established that benzoyltriphenylsilane is significantly more basic than benzovltriphenylmethane. Also, Brook and Pierce (3) have shown that  $\beta$ - but not  $\gamma$ -silvl ketones absorb at a lower frequency than their carbon analogs, a result consistent with inductive electron release acting through a single intervening methylene group. Thus in the ground state benzoylsilanes must have a significant negative charge associated with the carbonyl-oxygen atom. Back bonding of this charge from oxygen into the available d orbitals on silicon forming n-d  $\pi$ -bonding seems inconsistent with the basicity studies, but cannot be excluded on the present available data. As noted before, the  $\pi-\pi^*$  transition is little affected in ketones by replacement of carbon by silicon, wherease the  $n-\tau^*$  is significantly affected by this change. West has explained these effects as due to a general lowering of both the  $\pi$  and  $\pi^*$  levels, relative to the n energy level in silvl ketones (4) which implies stabilization of the excited state by contributions from structures such as

through charge delocalization from carbon into the adjacent unoccupied silicon d orbitals. At the same time, it seems probable that the n level is raised relative to the  $\pi^*$  level, by virtue of the strong inductive electron release of the adjacent silicon atom, as characterized by the infrared stretching frequency. These two effects in concert result in  $\pi - \pi^*$  transitions at about the same wavelength for ketones and benzoylsilanes, while at the same time the  $n-\pi^*$  wavelength is raised significantly. Superimposed on these two effects are the general effects of para substituents (6) which appear to influence both transitions in the same way and to about the same extent in both ketones and benzoylsilanes.

 $\dot{\sum}_{i=0}^{0^+}$ 

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The new ketones employed in this study were all prepared from the appropriately substituted benzylsilane by dibromination with N-bromosuccinimide followed by hydrolysis in aqueous organic solvent mixtures employing either silver acetate (1) or silver trifluoroacetate (3), the latter effecting hydrolysis much more rapidly. The triphenylbenzylsilanes were prepared by one of several general routes; viz. (a) coupling of a p-substituted benzyl Grignard reagent with triphenylchlorosilane (X = p-tert-butyl, p-methoxy), (b) reaction of a p-substituted benzyltrichlorosilane with silicon tetra-chloride, followed by coupling of the benzyltrichlorosilane with 3 mole equivalents of phenyl Grignard reagent (X = p-fluoro, p-chloro), (c) bromination of benzyltrichlorosilane, followed by coupling with phenyl Grignard reagent (X = p-bromo), (d) nitration of benzyltriphenylsilane (X = p-nitro). The properties of these compounds and of their intermediates are given in Table III.

The tris-p-substituted phenylbenzylsilanes were synthesized by similar routes; viz. (a) coupling of the appropriately tris-p-substituted phenylchloro- or bromo-silane with

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#### TABLE III

		1 11 1		4 4 .4
A Substituted ber	71/11/0000	ricilanes and	thorr	derivatives
$\nu$ -oubstituted bei		and and	LIICII	utire aures

$96 \\ 85 \\ 94 \\ 54 \\ 91 \\ 28 \\ 77$	$133-135^{a}$ $144-146^{b}$ $116-117^{c}$ $155-156^{c}$ $148-149^{g}$
$85 \\ 94 \\ 54 \\ 91 \\ 28 \\ 77$	$144-146^{b}$ $116-117^{c}$ $155-156^{c}$ $148-149^{g}$
$94 \\ 54 \\ 91 \\ 28 \\ 77$	$116-117^{\circ}$ $155-156^{\circ}$ $148-149^{\circ}$
$54 \\ 91 \\ 28 \\ 77$	$155-156^{\circ}$ $148-149^{\circ}$
$91 \\ 28 \\ 77$	148-1490
$\frac{28}{77}$	
77	$114.5 - 116.5^{n}$
<u>.</u> .	$112 - 120^{2}$
72	155-1571
86	$207 - 208^{k}$
80	$107 - 108^{t}$
44	$131.5 - 132.5^{m}$
3	$106 - 108^{n}$
83	$111 - 112^{n}$
83	134.5–135.5°
89	93–95 <sup>p</sup>
79	98-99ª
76	$107 - 108^{r}$
83	$116 - 118^{s}$
89	125 - 126'
92	138.5–139.5*
78	151–152°
; H. 5.36; N, 3. 2.6; H. 4.39; N, 3.78. 5.3.60. 7. 3.48. Found: C, 78.7 77.8; H. 5.47. 1; H, 7.32. , 62.0; H. 4.90.	56. 3.07. ; H, 5.81.
	28 77 72 86 80 44 3 83 83 89 79 76 83 89 92 78 78 78 5.6; H, 4.39; N, 3.78. 5.3; A.48. Found: C, 78.7 77.8; H, 5.47.

benzyl magnesium chloride (X = p-Me<sub>2</sub>N, p-Me, p-Cl,), or (b) of the methoxysilane with benzyl magnesium chloride  $(X = p - CF_3)$ , (c) coupling of benzyltrichlorosilane with 3 equivalents of the appropriate p-substituted phenyl Grignard reagent (X = p-Me). The benzylsilanes were converted in the ordinary way to the ketones. In the case of tri-p-tolylbenzylsilane bromination probably occurred both on the methylene hydrogens and also on the methyl group. The dibromide isolated was crystallized to give an apparently pure product which analyzed correctly, but hydrolysis gave a yellow oil with the characteristic spectrum of a benzoylsilane but which was contaminated with unhydrolyzable bromine-containing material and acetate esters from which it could not be separated by crystallization or chromatography. Properties of the compounds are given in Table IV.

## EXPERIMENTAL

All reactions involving organometallic reagents were carried out under an atmosphere of nitrogen. Infrared spectra were obtained on a Perkin-Elmer 221 instrument run at very slow speed using carbon tetrachloride as solvent and are probably accurate to  $1-2 \text{ cm}^{-1}$ . Ultraviolet spectra were determined in ethanol on a Beckmann DK 1 instrument or in cyclohexane on a Perkin-Elmer 350 instrument.

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### TABLE IV

## Tris(p-substituted phenyl)benzylsilanes and their derivatives

Compound	Reagents	Yield (%)	Melting point (°C)		
p-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiCH <sub>2</sub> Ph p-ClC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiCH <sub>2</sub> Ph p-ClC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiCH <sub>2</sub> Ph p-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiCH <sub>2</sub> Ph p-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiCH <sub>2</sub> Ph p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiCH <sub>2</sub> Ph p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiCBr <sub>2</sub> Ph p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> SiCPr <sub>2</sub> Ph	$\begin{array}{l} (p \cdot Me_2NC_6H_4)_3SiCl^a + PhCH_2MgCl \\ (p \cdot ClC_6H_4)_3SiBr^e + PhCH_2MgCl \\ NBS^e; AgOOCCF_3 \\ (p \cdot CF_3C_6H_4)_3SiOMe^e + PhCH_2MgCl \\ NBS^e; AgOOCCF_3 \\ PhCH_2SiCl_3 + p \cdot CH_3C_6H_4Li \\ (p \cdot CH_3C_6H_4)_3SiCl + PhCH_2MgCl \\ (p \cdot CH_3C_6H_4)_3SiBr^k + PhCH_2MgCl \\ NBS^e \\ NBS^e \\ AgOAc \end{array}$	$     \begin{array}{r}       11 \\       44 \\       62 \\       53 \\       63 \\       97 \\       58 \\       94 \\       62 \\       62     \end{array} $	$\begin{array}{c} 163-165^{b} \\ 148-150^{d} \\ 111-111.5^{f} \\ 138.5-140^{h} \\ 79-80^{i} \\ 102-103.5^{j} \\ 102-103.5^{j} \\ 102-103.5^{j} \\ 131-134^{m} \\ \text{Oil}^{n} \end{array}$		
PCH3C6H4/3SICOFII       AgOAC       OII*         Recrystallization solvent given in parenthesis prior to analytical data.       *See reference 17.       b(EtOH-benzene) Calcd. for C11H2SIN3: C, 77.6; H, 7.70; N, 8.80, Found: C, 77.5; H, 8.04; N, 8.93.         eFrom tris-p-chlorophenylsilane (18) and NBS, m.p. 86-91° crude.       d(EtOH) Calcd. for C224H2SIC1: C, 66.1; H, 4.22. Found: C, 65.5; H, 3.99.         eIntermediate dibromide not isolated.       /(EtOH) Calcd. for C224H1SIOF1: C, 64.2; H, 3.66. Found: C, 64.7; H, 3.48.       gSee Experimental.         *(Hexane) Calcd. for C224H1SIOF2: C, 60.6; H, 3.45. Found: C, 61.0; H, 3.45.       *(Pentane) Calcd. for C224H2SIF9: C, 60.6; H, 3.45. Found: C, 59.4; H, 3.01. Found: C, 59.4; H, 3.48.       ;(EtOH) Calcd. for C224H2SIF9: C, 65.7; H, 7.19. Found: C, 59.4; H, 3.48.         *(EtOH) Calcd. for C24H2SIF9: C, 65.7; H, 7.19. Found: C, 59.4; H, 3.48.       ;(EtOH) Calcd. for C24H2SIF9: C, 61.1; H, 4.76; Found: C, 61.6; H, 4.90.         *(EtOH-benzene) Calcd. for C24H2SIF2: C, 61.1; H, 4.76; Found: C, 61.6; H, 4.90.       *(EtOH-benzene) Calcd. for C24H2SIF2: C, 61.1; H, 4.76; Found: C, 61.6; H, 4.90.					

## Reagents

p-Bromobenzyltrichlorosilane was prepared by bromination of benzyltrichlorosilane (15).

*p*-Fluorobenzyltrichlorosilane, b.p. 56° at 0.13 mm, was prepared in 56% yield by reaction of silicon tetrachloride in 1:5 ether-hexane at 0° with the Grignard reagent of *p*-fluorobenzyl bromide in ether. Anal. Calcd. for C7H<sub>6</sub>SiCl<sub>3</sub>F: Cl (titratable), 43.5. Found: Cl, 43.5.

The p-fluorobenzyl bromide was prepared in 63% yield by treatment of p-fluorotoluene with 1 equivalent of N-bromosuccinimide in CCl4, b.p. 29.3-31° at 0.035 mm, nD22 1.5480. p-Chlorobenzyltrichlorosilane was similarly prepared from the Grignard reagent of p-chlorobenzylchloride and silicon tetrachloride in 64%yield, b.p. 80° at 0.10 mm.

Anal. Calcd. for C7H6SiCl4: Cl (titratable), 40.4. Found: Cl, 41.3.

#### Tri-(p-trifluoromethylphenyl)-methoxysilane

A solution of p-trifluoromethylphenylmagnesium bromide, prepared from 60.8 g (0.27 mole) of p-bromobenzotrifluoride and 6.55 g (0.27 g-atom) of magnesium in 250 ml of dry ether, was added over 1 h to 10.0 g (0.074 mole) of trichlorosilane in 50 ml of dry ether. There was immediate evolution of heat. After 4 h reflux, the reaction mixture was cooled and drowned in ice water and dilute acid, and was ether extracted. Bubbles of gas were evolved during the extraction. The organic phase was dried over anhydrous sodium sulfate and then distilled to give 18.3 g of product, b.p. 136–146° at 0.15 mm. The infrared spectrum had a strong band at 2.7  $\mu$  (SiO–H) but no band at 4.7  $\mu$  (Si–H). Crystallization from methanol gave 18.8 g (51.5%) of tri-(p-trifluoromethylphenyl)-methoxysilane, m.p. 123°, which was raised to  $130-131^{\circ}$  by further recrystallization. Evidently, the silanol reacted with the methanol since the product had no SiO-H peak at 2.7  $\mu$  but a new peak at 3.5  $\mu$  (CH<sub>3</sub>O) had appeared.

Anal. Calcd. for C22H15SiOF: C, 53.4; H, 3.06. Found: C, 53.4; H, 3.16.

#### Synthesis of Benzyl- and Benzoyl-silanes

Typical procedures for the synthesis of the benzyl- and benzoyl-silanes are described below.

Method A. Coupling of p-Methoxybenzylmagnesium Chloride with Triphenylchlorosilane

To 11.8 g (0.040 mole) of triphenylchlorosilane in 150 ml of tetrahydrofuran was added over 45 min 160 ml of 0.25 N p-methoxybenzylmagnesium chloride (0.04 mole) prepared by the method of Van Campen et al. (19) except that tetrahydrofuran was employed as solvent. The reaction was refluxed for 1 h and then stirred overnight. After hydrolysis with dilute acid the organic phase was water washed, dried, and evaporated to dryness. Addition of ethanol gave 12.2 g (80%) of p-methoxybenzyltriphenylsilane, m.p. 107-108° after recrystallization from 1:1 ethanol-hexane.

## Method B

To 2.73 g (0.011 mole) of p-fluorobenzyltrichlorosilane in ether was added slowly at 0° 3 equivalents of phenyllithium in ether. A negative color test was obtained at the end of the addition. After hydrolysis with

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dilute acid and work-up 3.30 g (79%) of *p*-fluorobenzyltriphenylsilane was obtained, m.p. 98–99° after recrystallization from absolute ethanol.

Method C. Nitration of Benzyltriphenylsilane

To a solution of 15.2 g (0.043 mole) of benzyltriphenylsilane in 150 ml of acetic anhydride was added over 45 min 5 g of red fuming nitric acid, specific gravity 1.59. The reaction became warm. After cooling to room temperature the reaction was poured into ice water and concentrated ammonium hydroxide. The crude product was filtered and crystallized from 1:1 ethanol – ethyl acetate to yield 9.40 g (55%) of *o*-nitrobenzyltriphenylsilane, m.p. 155–156°. This material was shown to be the ortho-nitro compound as follows.\* A mixture of 4.0 g (0.01 mole) of the nitro compound, m.p. 155–156°, in 50 ml of a solution prepared from 1 volume of 50% aqueous sodium hydroxide and 7 volumes of ethanol was refluxed for 30 h. After addition of water and ether extraction, the dried ether layers were concentrated and then distilled to yield 1.0 g (73%) of *o*-nitrotoluene, b.p. 50° at 1 mm, identified by the identity of its infrared and n.m.r. spectra with those of an authentic sample. The filtrate from which the ortho-nitro compound was isolated was evaporated to dryness leaving an oil which crystallized from absolute ethanol to give 4.75 g (28%) of *p*-nitrobenzyltriphenylsilane, m.p. 105–115°. Several recrystallizations raised the m.p. to 114.5–116.5°.

p-(N-Acetylamino)-benzyltriphenylsilane.—A suspension of 3.75 g (0.0075 mole) of p-nitrobenzyltriphenylsilane in 120 ml of glacial acetic acid and 20 ml of acetic anhydride was shaken under 30 p.s.i. of hydrogen in the presence of PtO<sub>2</sub> for 24 h. Work-up gave 3.35 g of crude water-insoluble product which after recrystallization from methanol gave white p-(N-acetylamino)-benzyltriphenylsilane, m.p. 207–208°. Attempted reduction under the same conditions but using glacial acetic acid or ethanol as solvents failed.

#### Halogenation of Benzylsilanes

### p-tert-Butyl- $\alpha \alpha$ -dibromobenzyltriphenylsilane

A mixture of 12.2 g (0.030 mole) of *p*-tert-butyl benzyltriphenylsilane, 10.7 g (0.060 mole) of N-bromosuccinimide and 200 ml of carbon tetrachloride was refluxed for 3 h. A trace of benzoyl peroxide was added to initiate the reaction. On cooling 6.7 g (107%) of succinimide was filtered off, the filtrate was evaporated to dryness under reduced pressure, and the residue on crystallization from ethanol-petroleum ether (90–100°) gave 14.95 g (92%) of product, m.p. 138.5–139.5°.

Other benzylsilanes were similarly halogenated. o-Nitrobenzyltriphenylsilane gave only a monobromide even when refluxed for prolonged periods, presumably due to steric hindrance.

## Hydrolysis of $\alpha \alpha$ -Dibromobenzylsilanes

Hydrolyses with silver acetate or silver trifluoroacetate were carried out in benzene-acetone-water or ethanol-water media according to previously described techniques (1, 3). Silver trifluoroacetate, prepared by reaction of trifluoroacetic acid with a slurry of silver oxide in benzene, appeared to react more rapidly with dibromides than did silver acetate.

#### Light-catalyzed Decomposition of Benzoyltriphenylsilane

A solution of 2.5 g (0.0069 mole) of benzoyltriphenylsilane in 50 ml of dry reagent grade methanol was exposed for 4 h to radiation from a General Electric "Bonus Line Mercury Reflector Spot" lamp, by which time the solution was entirely colorless. The excess methanol was removed under reduced pressure, and the residue (a mushy solid below room temperature) was distilled. Two main fractions were obtained. (a) Benzaldehyde dimethylacetal, 0.5 g (48%), b.p. 82° at 14 mm, n.m.r. 3.21  $\delta$ , singlet (CH<sub>3</sub>—O), 5.35  $\delta$ , singlet (C—H), and 7.2-7.6  $\delta$ , multiplet (C—H aromatic), areas 5.7:1:5.5 (calcd. 6:1:5). The materialw as slightly contaminated with benzaldehyde, as judged by odor, and the presence of weak infrared absorption peaks at 3.65 and 5.85  $\mu$  (CH + C=O). (b) Triphenylmethoxysilane, 1.7 g (85%), b.p. 165–175° at 0.5 mm, m.p. 56–57°, identified by mixed melting point with an authentic sample.

#### **Benzoyldiphenylphosphine**

The compound was prepared as described in the literature (13) and the yellow product was twice distilled to give a 20% yield of material, m.p.  $71-80^{\circ}$ , b.p.  $162-164^{\circ}$  at 0.12 mm. An odor of benzaldehyde was noted after distillation, and was observable in the infrared spectrum as bands at 3.65 and 5.85  $\mu$ . When air was bubbled through 0.65 g of benzoyldiphenylphosphine in carbon tetrachloride for 15 min, 0.35 g (71%) of white solid, shown by mixed melting point to be diphenylphosphonic acid, m.p. 185°, precipitated. The filtrate was evaporated to dryness and was recrystallized from boiling water to yield 0.10 g (37%) of benzoic acid, m.p. 118-120°, identified by mixed melting point.

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