DIBENZOYLSILANES AND SUBSTITUTED BENZOYLSILANES

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ABSTRACT

A number of silicon-substituted benzoylsilanes have been prepared. These all showed identical carbonyl infrared stretching wavelengths, and were all yellow, having essentially identical ultraviolet absorption spectra. Hence it is concluded that the spectral properties of benzoyl-silanes are insensitive to the nature of the groups attached to silicon, even when these could provide $d_{\pi}-p_{\pi}$ bonding.

It has previously been reported that benzoylsilanes (α -silylketones) have anomalous infrared and ultraviolet spectra, compared with their carbon analogues. Not only is the carbonyl-stretching vibration at considerably longer wavelength (6.18 μ , 1618 cm⁻¹) than in usual carbonyl compounds, but the long wavelength (carbonyl) ultraviolet absorption band falls in the visible region at about 403–417 m μ , so that all benzoylsilanes are yellow, regardless of whether phenyl or methyl groups are attached to silicon.

It seems reasonable to assume that the available d orbitals of silicon play some role in these spectral phenomena. West (2) has observed that $d_{\pi}-p_{\pi}$ bonding can occur between silicon and adjacent atoms possessing unshared electrons such as halogen and oxygen, and that as the number of groups available for such bonding increases, the strength of the $d_{\pi}-p_{\pi}$ bonds decreases. If $d_{\pi}-p_{\pi}$ bonding with the carbonyl group is associated with the spectral behavior of the acylsilanes, then if alternative and perhaps stronger $d_{\pi}-p_{\pi}$ bonding with some other group becomes possible, it might be anticipated that the spectral behavior of the ketone would revert toward that of a normal ketone. In order to see if this concept was valid attempts have been made to synthesize a number of substituted benzoylsilanes. These were of three main types: (a) hydroxy- and methoxy-benzoylsilanes, I; (b) halogenobenzylbenzoylsilanes, II; (c) dibenzoylsilanes, III.

PhCOSiPh ₂ (OR)	-	PhCOSiPh ₂ CXYPh	PhCOSiR ₂ COPh
Ι		II	III
(a) $R = H$		(a) $X = H, Y = Cl$	(a) $R = Ph$
(b) $R = Me$		(b) $X = H, Y = Br$	(b) $R = Me$
		(c) $X = Cl, Y = Br$	
		(d) $X = Y = Br$	

The synthesis of these compounds followed, in general, previously reported routes (1, 3). However, acylsilanes, with the possible exception of benzoyltriphenylsilane, are not particularly stable, hydrolyzing rapidly on exposure to air, benzaldehyde being formed. Most of the benzoylsilanes reported herein were exceptionally unstable.

The hydroxy- and methoxy-benzoylsilanes were synthesized as indicated by the following sequence of reactions:

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All of these reactions occurred readily and in good yield with the exception of the hydrolysis of dibromobenzyldiphenylmethoxysilane. Under all conditions used the methoxy group also hydrolyzed readily, giving the hydroxysilane or a mixture of the hydroxy- and methoxy-silanes, which were separated only with difficulty.

The synthesis of the dibenzoylsilanes caused particular difficulty, largely due to their instability. They and the various halobenzylbenzoylsilanes were prepared by the following routes:



Dibenzyldiphenylsilane resisted tetrabromination with N-bromosuccinimide even in refluxing tetrachlorethylene, probably because of steric hindrance, and only a tribromo derivative could be isolated. Hence hydrolysis of the tribromide to a bromoketone, followed by further halogenation, toward which the ketone was not very stable, had to be employed. Hydrolysis of this dibromoketone gave very low yields of an extremely unstable compound, which appeared to be dibenzoyldiphenylsilane (see below).

Attempts to prepare the related dibenzoyldimethylsilane were made by an analogous route, except that tetrabromination with N-bromosuccinimide was successful. Hydrolysis with silver acetate – water gave a yellow oil which, however, decomposed to colorless products during attempted distillation, or during chromatography on silica gel or silicic acid columns. The major decomposition products isolated were benzaldehyde and/or benzoic acid, formed by hydrolysis and oxidation, and benzoin. The formation of this latter product may be explained as arising from rearrangement of the dibenzoyl compound, by a route analogous to that found for monobenzoylsilanes (4, 5), as illustrated below:

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 $(Me_2Si(OH)_2) + PhCOCHOHPh$

The ultraviolet spectra and carbonyl-stretching region of the infrared spectra for the new benzoylsilanes are reported in Table I together with the data for benzoylmethyldiphenylsilane (1) as reference compound. It is evident that in these compounds the carbonyl-stretching vibration is insensitive to the substituents attached to silicon, as was

TABLE 1				
Infrared and	ultraviolet absorpt	ion data for	benzoylsilanes	

Compound	Infrared (C=O), μ	Ultraviolet $(\pi - \pi^*)$ $\lambda_{\max}, m\mu$	Carbonyl group $\lambda_{\max}, m\mu$	
PhCOSiPh ₂ OH	6.19	257 (e, 16,900)	a	415 (e, 318)
PhCOSiPh ₂ OMe	6.19		$405 - 415^{b}$	
PhCOSiPh ₂ CHBrPh	6.18	$260 \ (\epsilon, 16, 800)$	403 (s) (ϵ , 244)	$417 (\epsilon, 292)$
PhCOSiPh ₂ CBr ₂ Ph	6.18	259 (ϵ , 18,600)	405 (s) (ϵ , 233)	416 (ϵ , 265)
PhCOSiPh ₂ CHClPh	6.18			
PhCOSiPh ₂ CBrClPh	6.18			
PhCOSiPh ₂ COPh	6.18.5.97	$258 (\epsilon, 24.100)$	405 (s) (ϵ , 233)	416 (ϵ , 244)
PhCOSiMe ₂ Ph	6.18	255 (ϵ , 13,900)	403 (s) (ϵ , 200)	415 (ϵ , 216)

NOTE: (s) = shoulder. ^aUnresolved shoulder at about 405 m μ . ^bExtinction coefficient not determined since compound contaminated with small amount of benzoyldiphenylsilanol, as shown by infrared spectrum.

observed previously (1). The ultraviolet spectra also conform closely to those found earlier for methyl- or phenyl-benzoylsilanes, with no significant change occurring in position for either the $\pi - \pi^*$ or for the long wavelength (carbonyl) band. These results indicate that if $d_{\pi} - p_{\pi}$ bonding is occurring between silicon and the adjacent oxygen or halogen atoms in these molecules, it has little effect on the silicon-carbonyl interaction which causes the anomalous spectral behavior.

The spectra of dibenzoyldiphenylsilane are worthy of comment. Since the compound was too unstable to be analyzed it is necessary to establish that impurities are not responsible for any of the prominent absorption bands. The most probable impurities, based on our experience, are benzaldehyde, benzoic acid, benzoin, and silanols. That these were not present in significant concentrations is evident from the absence of absorption bands at 2.8–3.0 μ (OH) or in the 3.7 μ (CHO) region.

The intensity of the $\pi - \pi^*$ band of the compound ($\epsilon 24,100$) relative to benzoyldiphenylmethylsilane (ϵ 13,900) indicates the presence of two benzoyl groups, although the long wavelength (carbonyl) band has an extinction coefficient little greater than that of the monobenzoylsilane. At the same time, the infrared shows two strong carbonyl bands at 5.97 and 6.18 μ . These may be due to two non-equivalent carbonyl groups, due to differences in the interaction with silicon or to conformational effects (6). Alternatively the two

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carbonyl bands may be due to equivalent carbonyl groups undergoing vibrational coupling with each other to produce two bands, as has been observed with other dicarbonyl compounds (7). It does not seem possible at this time to decide whether both carbonyl groups of dibenzoyldiphenylsilane interact identically with the silicon atom, or whether one is a typical α -silyl ketone and the other acts as a "normal" ketone type of carbonyl group.

EXPERIMENTAL

All reactions involving organometallics were carried out under a dry oxygen-free nitrogen atmosphere. Infrared spectra were taken in CCl₄ on a Beckman IR5 instrument calibrated against polystyrene; ultraviolet spectra were taken in ethanol.

A. Benzyldiphenylchlorosilane and its Derivatives

Benzyldiphenylchlorosilane

To 104 g (0.41 mole) of diphenyldichlorosilane in 250 ml of ether was added dropwise 0.41 mole of 1.65 N benzylmagnesium chloride. After the mixture had been stirred overnight a negative Gilman color test I (8) was obtained. To the suspension was added 1 l. of petroleum ether (b.p. 60–70°) and the mixture was filtered. After removal of the solvents the material was distilled at 190–194° at 0.6 mm to give 85 g (67%) of benzyldiphenylchlorosilane, n_D^{25} 1.6078 Anal. Calc. for $C_{19}H_{17}$ SiCl: Si, 9.07. Found: Si, 9.12.

α, α -Dibromobenzyldiphenylchlorosilane

To 20.0 g (0.65 mole) of benzyldiphenylchlorosilane in 150 ml of carbon tetrachloride was added 25.0 g (0.14 mole) of N-bromosuccinimide and a few small lumps of benzoyl peroxide. The mixture was refluxed for 16 hours, cooled, and the succinimide filtered off. Evaporation of the filtrate to dryness gave a yellow oil which was crystallized twice from hexane to give 15.75 g (52%) of α, α -dibromobenzyldiphenylchlorosilane, m.p. 79–81°. Anal. Calc. for C₁₉H₁₆SiClBr₂: C, 48.8; H, 3.22. Found: C, 48.8; H, 3.29.

Benzoyldiphenylsilanol

To 5.0 g (0.0107 mole) of dibromobenzyldiphenylchlorosilane in 50 ml acetone and 7 ml of water was added at 0° (ice-water bath) 7.1 g (0.032 mole) of silver trifluoroacetate in 110 ml of benzene. A pale yellow color and grey precipitate formed immediately. The ice bath was removed once addition was complete and the mixture was stirred for 2 hours. The silver bromide was filtered off, about 1 l. of water was added, and the mixture was extracted with benzene. The benzene layers were back-extracted with water, dilute sodium bicarbonate, and then water. After the benzene layer was dried over sodium sulphate the solvents were removed under reduced pressure to yield a yellow oil, which was recrystallized from hexane-cyclohexane to give 2.13 g (65%) of bright yellow benzoyldiphenylsilanol, m.p. 97–99°. Anal. Calc. for C₁₉H₁₆SiO₂: C, 75.0; H, 5.28. Found: C, 74.5; H, 5.22. The solid became a sticky mass in a few days with a strong odor of benzaldehyde.

Benzyldiphenylmethoxysilane

To 15 g (0.048 mole) of benzyldiphenylchlorosilane in 80 ml of methanol was added 5 ml of pyridine. The reaction mixture became hot. After 15 minutes the reaction mixture was drowned in water and extracted with benzene. The dried benzene layer on distillation gave 10 g (70%) of benzyldiphenylmethoxysilane, b.p. 159–161° at 0.28 mm, n_D^{25} 1.5932.

Benzyldiphenylsilanol

To 1 l. of ice and water containing 5 ml of conc. ammonium hydroxide was added slowly with vigorous stirring 10 g (0.032 mole) of benzyldiphenylchlorosilane in 100 ml of ether. After 0.5 hour the ether layer was removed, dried over sodium sulphate, and the solvent removed under reduced pressure to give 9.4 g of a white solid, m.p. 46–49°. Recrystallization from petroleum ether (b.p. 60–70°) gave 7.2 g (77%) of benzyldiphenylsilanol, m.p. 51.5–53°. Anal. Calc. for $C_{19}H_{18}SiO$: C, 78.5; H, 6.23. Found: C, 78.4; H, 6.22.

α, α -Dibromobenzyldiphenylmethoxysilane

(a) From dibromobenzyldiphenylchlorosilane.—To 5.0 g (0.011 mole) of the dibromobenzyl compound in 15 ml of methanol and 25 ml of benzene was added 0.9 ml (0.012 mole) of pyridine. After 18 hours the reaction was drowned in water and ether-extracted. The combined organic layers were dried with sodium sulphate, and removal of the solvents under reduced pressure gave 4.02 g (81%) of α,α -dibromobenzyldiphenylmethoxysilane, m.p. 79–82°, which on recrystallization from hexane had m.p. 80–82°. Anal. Calc. for C₂₀H₁₈SiOBr₂: C, 52.0; H, 3.91. Found: C, 52.7; H, 3.91.

(b) From Benzyldiphenylmethoxysilane.—A solution of 3.0 g (0.01 mole) of benzyldiphenylmethoxysilane in 50 ml of carbon tetrachloride was refluxed 5.5 hours with 3.56 g (0.02 mole) of N-bromosuccinimide and a few small lumps of benzoyl peroxide. On cooling and filtering of the succinimide, the filtrate was evaporated to dryness to yield a viscous oil. Crystallization from hexane gave 3.48 g (72%) of α, α -dibromobenzyldiphenylmethoxysilane, m.p. 79–81°, identified by mixed melting point with the material described above. Their infrared spectra were identical.

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Attempted Preparation of Benzoyldiphenylmethoxysilane

To 4.62 g (0.01 mole) of α, α -dibromobenzyldiphenylmethoxysilane in 100 ml of acetone and 50 ml of benzene was added 3.4 g (0.02 mole) of silver acetate and 5 ml of water. The mixture was stirred overnight in the dark. The yellow solution was filtered from the silver bromide, drowned in water, and extracted into ether. Removal of the ether gave an oily yellow solid whose infrared spectrum showed the presence of strong Si—OMe absorption at 9.2 μ and only very weak OH absorption in the 2.7–2.8 μ region. The carbonyl absorption occurred at 6.19 µ. Attempts to purify the material by crystallization from hexane or by chromatography on alumina failed, and the odor of benzaldehyde soon became apparent. Subsequent repetitions of this experiment, with changes in solvent or of time of hydrolysis, failed to yield pure benzoyldiphenylmethoxysilane. When the silver acetate was replaced by silver trifluoroacetate, the major product was benzoyldiphenylsilanol, m.p. 97-99°, identified by mixed melting point.

B. Dibenzyldiphenylsilane and its Derivatives.

The polyhalogenated derivatives of this compound, most of which served as precursors for the preparations of ketones through hydrolysis with silver acetate, were prepared by conventional methods such as are described in Section A. Hence only a few typical preparations will be described in detail-the properties of the various additional compounds are summarized in Table II.

TABLE II			
Organosilicon compounds			

Compound	M.p., °C	Yield, %
PhCH ₂ SiPh ₂ CHClPh	159 decomp.	26^{a}
PhCBr ₂ SiPh ₂ CHClPh	140 decomp.	86 ^b
PhCOSiPh ₂ CHClPh	100–101	62 ^c
PhCOSiPh ₂ CBrClPh	118–120	47 ^d

^aIndicated are solvents of recrystallization and analysis, petro-leum ether (b.p. 60-70°) – CCl₄. ^bEtOH. Calc. for C₂₆H₂₁SiBr₂Cl: Si, 5.04. Found: Si, 4.99. ^cEtOH-EtOAc. Calc. for C₂₆H₂₂SiClO: C, 75.6; H, 5.17. Found: C, 74.7; H, 5.13. ^dEtOH-EtOAc. Calc. for C₂₆H₂₀SiBrClO: Si, 5.70. Found: Si, 5.60.

α, α, α' -Tribromodibenzyldiphenylsilane

Dibenzyldiphenylsilane was prepared from diphenyldichlorosilane and benzylmagnesium chloride in 61% yield, m.p. 60.5-61°, reported (9) 61°. A mixture of 36.4 g (0.1 mole) of dibenzyldiphenylsilane and 80 g (0.45 mole) of N-bromosuccinimide in 300 ml of carbon tetrachloride was refluxed for 44 hours with occasional small additions of benzoyl peroxide. After cooling and removal of 51.8 g (91%) of succinimide, the filtrate was concentrated under vacuum. Addition of petroleum ether gave 47 g (79%) of α, α, α' -tribromobenzyldiphenylsilane, m.p. 129-130°, which after several recrystallizations melted at 145-149°.

Attempts to further brominate the tribromide with N-bromosuccinimide in carbon tetrachloride, in tetrachloroethylene, or in a mixture of these solvents, over various time intervals, gave mainly recovered tribromide, and no tetrabromide could be isolated.

$Benzoyl-\alpha$ -bromobenzyldiphenylsilane

A mixture of 15 g (0.025 mole) of α, α, α' -tribromodibenzyldiphenylsilane and 14.9 g (0.089 mole) of silver acetate in 150 ml of ethanol, 120 ml of acetone, and 60 ml of water was stirred in the dark for 41 hours. The silver bromide was filtered off, water was added to the filtrate, and the material was extracted with ether several times. The ether layers, after being dried over sodium sulphate, were concentrated under reduced pressure, and the resulting yellow oil was crystallized from ethanol – ethyl acetate to give 5.1 g (64%) of yellow benzoyl-α-bromobenzyldiphenylsilane, m.p. 90-92°. Anal. Calc. for C₂₆H₂₁SiOBr: C, 68.4; H, 4.60. Found: 68.4, H, 4.67.

α, α, α' -Tribromo- α' -chlorodibenzyldiphenylsilane

A solution of 6.18 g (0.011 mole) of α, α, α' -tribromodibenzyldiphenylsilane and 1.62 g (0.012 mole) of sulphuryl chloride in 50 ml of chlorobenzene was refluxed for 2.5 hours with a trace of added benzoyl peroxide. Red fumes, presumably bromine, were evolved during the reaction. The solvent was removed under reduced pressure and the resulting oil was crystallized from ethyl acetate – ethanol to give 4.17 g (58%) of α,α,α' -tribromo- α' -chlorodibenzyldiphenylsilane, m.p. 125–140°, which on recrystallization melted at 125–127°. The crystals turned orange-brown on standing. Anal. Calc. for C₂₈H₂₀SiBr₃Cl: Si, 4.42. Found: Si, 4.47, 4.59.

α, α -Dibromobenzylbenzoyldiphenylsilane

A solution of 0.68 g (0.0015 mole) of α -bromobenzylbenzoyldiphenylsilane in 10 ml of carbon tetrachloride and 0.23 g (0.0013 mole) of N-bromosuccinimide was refluxed for 1 hour with a trace of benzoyl peroxide. After removal of the succinimide and the solvent the yellow oil was chromatographed on a 6-in. silica gel column, and eluted with benzene. The yellow eluate, after removal of the solvent and crystallization from

ethyl acetate – ethanol – petroleum ether (b.p. 40–60°), gave 0.35 g (44%) of yellow α, α -dibromobenzylbenzoyldiphenylsilane, m.p. 107-109°. After 5 days marked decomposition had occurred, although the product was stored in sealed containers. Similar runs on a larger scale gave yields from 0-45%-in general better yields were obtained from smaller runs. Anal. Calc. for C26H20SiBr2O: C, 58.2; H, 3.76. Found: C, 59.6; H. 3.95.

Dibenzoyldiphenylsilane

A solution of 0.3 g (0.0005 mole) of dibromobenzylbenzoyldiphenylsilane in 3 ml of acetone, 12 ml of ethanol, 5 ml of benzene, and 0.2 ml of water was stirred in the dark for 7 hours with 0.3 g (0.0018 mole) of silver acetate. The silver salts were filtered off and the yellow filtrate was added to ether, washed with water, and dried with sodium sulphate; the ether was then removed under vacuum and the yellow oil was chromatographed on an 8-in. silica gel column, using benzene as eluant. Two yellow bands appeared on the column, the first eluted giving a positive test for halogen. This was isolated and shown to be recovered dibromobenzylbenzoyldiphenylsilane, 0.25 g (83%) after crystallization from petroleum ether (b.p. 60-70°), m.p. 107-109°. The second yellow fraction eluted was an oil which failed to crystallize when treated with a variety of solvents. It gave a negative test for halogen, and identification as dibenzoyldiphenylsilane, 0.02 g (9%), is based on the infrared and ultraviolet spectra (see discussion section). The compound decomposed rapidly on standing, even in a nitrogen atmosphere, liberating the odor of benzaldehyde.

Runs similar to the above, but without the use of acetone during the "hydrolysis", gave after chromatography on silicic acid dibenzoyldiphenylsilane in yields up to 40%.

Dibenzyldimethylsilane

To a solution of 26.4 g (0.20 mole) of dimethyldichlorosilane in 400 ml of toluene was added 0.41 mole of benzylmagnesium chloride in 300 ml of ether. The ether was distilled off and the mixture was refluxed at 100° for 21 hours. After filtration of the magnesium salts the solvents were removed under reduced pressure and the resulting oil was crystallized from ethanol to give 47 g (96%) of dibenzyldimethylsilane, m.p. 56-58°. Anal. Calc. for C₁₆H₂₀Si: C, 79.93; H, 8.39. Found: C, 80.21; H, 8.23.

$\alpha, \alpha, \alpha', \alpha'$ -Tetrabromodibenzyldimethylsilane

Bromination of 10 g (0.042 mole) of dibenzyldimethylsilane in 150 ml of carbon tetrachloride with 30 g (0.17 mole) of N-bromosuccinimide at reflux with an added trace of benzoyl peroxide over 6 hours gave, after removal of the succinimide and solvents, and crystallization from ethyl acetate, 21.8 g (94%) of $\alpha, \alpha, \alpha', \alpha'$ tetrabromodibenzyldimethylsilane, m.p. 122-125°. Anal. Calc. for C16H16SiBr4: C, 34.54; H, 2.90. Found: C, 34.90; H, 3.16.

Hydrolysis of Tetrabromodibenzyldimethylsilane

A solution of 5.0 g (0.009 mole) of the above tetrabromide in 20 ml ethanol, 30 ml of benzene, and 1 ml of water was treated with 6.01 g (0.036 mole) of silver acetate. An immediate exothermic reaction occurred, a dark precipitate formed, and the solution became yellow. The mixture was stirred for 3 hours in the dark. The silver salts, 6.6 g (98%), were filtered off, ether was added, and the ether layer was washed with water and dried over sodium sulphate; the ether was removed to give 2.8 g of yellow oil.

Attempts to crystallize the oil, which smelt strongly of benzaldehyde, from a variety of solvents failed. Attempted distillation at 0.06 mm failed when the material decomposed, turning black at 125°. If the oil was left in contact with air, it decomposed, turning black and forming solid from which benzoin, m.p. 134-136°, identified by mixed melting point, could be isolated in 25% yield.

Attempts to purify the oil by chromatography on silica gel, silicic acid, or alumina also failed. While two vellow bands were separated on the column, only one yellow band (benzoyldibromobenzyldimethylsilane?), which contained halogen and smelled strongly of benzaldehyde, could be eluted; the second faded to colorless on the column before it could be eluted.

Attempted hydrolysis using silver nitrate instead of silver acetate gave essentially quantitative yields of silver bromide, but only pale yellow oils, together with up to 70% yields of benzoic acid, m.p. 120-121°, could be obtained, indicating that considerable hydrolysis and oxidation had occurred.

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