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Photolysis of Acylsilanes in Cyclohexane and Other Solvents

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Whereas photolysis of acylsilanes in carbon tetrachloride has been shown to generate silyl radicals which yield chlorosilanes exclusively, and photolyses in alcohols yield siloxycarbenes which yield "mixed acetal" insertion products, it is shown that photolysis of acylsilanes in non-polar, non-halogenated solvents such as cyclohexane give complex mixtures of products which result primarily from the attack of silyl radicals on the carbonyl oxygen of an acylsilane, followed by conventional disproportionation or recombination reactions. Under some circumstances silyl radicals add to carbon–carbon double bonds. The structures of the products formed and the mechanism of their formation are described.

Alors que la photolyse des acylsilanes dans le tétrachlorure de carbone produit, comme il a été démontré, des radicaux "silyses" ce qui conduit exclusivement à des chlorosilanes, et que la photolyse dans des alcools conduit à des siloxycarbènes qui donnent des produits d'insertion d'acétales mixtes, il est démontré que la photolyse d'acylsilanes dans des solvants non-polaires et non halogénés comme le cyclohexane, donne des mélanges complexes de produits qui proviennent surtout de l'attaque des radicaux "silyles" sur l'oxygène du groupe carbonyle d'un acylsilane, suivi de réactions classiques de dismutation ou de recombinaison. Dans certains cas les radicaux "silyles" s'additionnent aux doubles liaisons carbone-carbone. Les structures des produits formés ainsi que le mécanisme de leur formation sont décrits. [Traduit par le journal]

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It has recently been shown that the photolysis of acylsilanes in carbon tetrachloride or similar halogenated solvents leads by a Norrish Type 1 cleavage to silyl and acyl radicals which subsequently react to give silyl chloride and the usual products from acyl radicals (1) (eq. 1). It has also

1]
$$R_3SiCOR' \xrightarrow{h\nu} R_3Si + R'CO \rightarrow$$

$$R_3SiCl + R'COCl + R'COCCl_3 + Cl_3CCCl_3$$

been shown that photolysis in polar solvents such as alcohols gives rise to mixed acetals by way of a siloxycarbene intermediate (2, 3) (eq. 2). In view

$$[2] R_{3}SiCOR' \xrightarrow{h\nu} R_{3}SiO\ddot{C}R' \xrightarrow{H} R_{3}SiO\ddot{C}R' \xrightarrow{H} OMe$$

of these extremes in behavior as the solvent was changed, it appeared of interest to photolyze acylsilanes in non-polar, non-halogenated solvents where, if silyl radicals were formed they would lack electronegative halogen atoms with which to react by abstraction, or where, if siloxycarbenes were formed, they would lack highly polar bonds such as OH into which they might insert.

Acetyltriphenylsilane clearly undergoes radical

cleavage when photolyzed in carbon tetrachloride (3) and siloxycarbene formation when photolyzed in methanol containing a trace of pyridine (2). When photolyzed in cyclohexane using a 100 W low pressure mercury flood lamp, a complex mixture of products was formed from which three major products were separated by a combination of chromatography and crystallization.

The structures assigned to these products, their vield, and details of their structure proof are shown in eq. 3. The least soluble compound had an analysis and spectroscopic data consistent with the siloxyalkene 1. The stereochemistry was not established but the isomer having *trans*-triphenylsilyl groups appears much more probable on steric grounds. Degradation of 1 gave almost 3 equiv of triphenylsilanol. Cleavage did not occur under milder conditions, and no reduction of the siloxy group to a silyl hydride occurred when the compound was refluxed with lithium aluminum hydride in ether. However, when treated with phenyllithium or *n*-butyllithium, both a tetra-substituted silane and a new compound 4, which contained both an acylsilane and a β ketosilane functionality were obtained (eq. 4). Thus 4 had $n-\pi^*$ u.v. absorption at 377 nm typical of an acylsilane (e.g. acetyltriphenylsilane λ_{max} 377 nm) and carbonyl i.r. absorption at BROOK AND DUFF: PHOTOLYSIS OF ACYLSILANES



 $\mathbf{R} = n$ -Bu, Ph

6.16 μ corresponding to the position expected for an acylsilane (acetyltriphenylsilane 6.08 μ) perturbed to longer wavelength by the expected amount by the β -silicon atom (*e.g.* Me₃CCH₂-COMe 5.82 μ , Me₃SiCH₂COCH₃ 5.89 μ). The structure of **4** was further confirmed when, on heating, it underwent the known thermal rearrangement of β -ketosilanes (4) to give the isomer **2** which was also synthesized by an alternate route (eq. 5).

$$[5] \xrightarrow{Ph_{3}Si}_{CH_{2}-C-SiPh_{3}} \xrightarrow{Ph_{3}Si-O}_{CH_{2}=C-SiPh_{3}} \xrightarrow{Ph_{3}SiCl}_{CH_{2}=C-SiPh_{3}} \xrightarrow{Ph_{3}SiCl}_{CH_{2}=C-SiPh_{3}} \xrightarrow{Ph_{3}SiCl}_{CH_{2}=C-SiPh_{3}} \xrightarrow{Q}_{CH_{3}C-SiPh_{3}} \xrightarrow{Q}_{CH_{3}C-SiPh_{3}}$$

It was difficult to separate the mixture of 2 and the saturated compound 3 obtained from the original photolysis of acetyltriphenylsilane. However, when treated with dilute base, 2 was rapidly hydrolyzed to give 2 equiv of triphenylsilanol whereas 3 was relatively inert and could be isolated pure. The structure of 3 was independently confirmed by silylating the corresponding alcohol (eq. 5).

[6]
$$Ph_3SiCH(OH)Me + Ph_3SiBr \xrightarrow{C_5H_5N} Ph_3SiCH(Me)OSiPh_3$$

The above three products, which accounted for about 50% of the starting material, were the only ones from the photolysis reaction which were isolated and characterized. Other compounds were

present, and at least some of these were unstable since on standing or on chromatography, up to 30% of triphenylsilanol and small amounts (<5%) of acetyltriphenylsilane could be isolated.

Before discussing mechanisms for the formation of the above products it is pertinent to describe the results of photolysis of another acylsilane, phenylacetyltriphenylsilane, under comparable conditions. Photolysis in cyclohexane gave three readily separable products which accounted for about 90% of the starting material. The structures and details of the structure proofs are shown in eq. 7.

17] Ph₃SiCOCH₂Ph
$$\xrightarrow{h\nu}$$
 Ph₃SiO
Ph₃Si C=C Ph
5 (8-12%)
+ Ph₃SiO
Ph₃Si
Ph₃SiO
Ph₃SiO
Ph₃SiO
Ph₃SiO
Ph₃SiO
P

The structure of 5, obtained in about 8-12%yield from various runs, was supported by analytical and spectroscopic data. The geometry has been assigned purely on steric arguments. Attempts to synthesize 5 by coupling the enolate ion of phenylacetyltriphenylsilane with triphenylchlorosilane, or to degrade it, by treatment with phenyl- or *n*-butyllithium, gave complex mixtures of unidentified products. Treatment with aqueous alkali gave 2 equiv of triphenylsilanol but the expected phenylacetaldehyde was not isolated, presumably due to its further reaction under the

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alkaline conditions. However, reduction of 5 with lithium aluminum hydride in refluxing di-*n*butyl ether gave a 45% yield of triphenylsilane and a 30% yield of phenylacetyltriphenylsilane together with some recovered starting material and unidentified products (eq. 8).

[8]
$$Ph_{3}Si \rightarrow O$$

 $Ph_{3}Si \rightarrow O$
 $Ph_{3}Si \rightarrow O$
 $H \rightarrow (1) LiAlH_{4}$
 $H \rightarrow (2) H_{3}O^{+}$

 $Ph_3SiH + Ph_3SiC - CH_2Ph$

The structure of $\mathbf{6}$, isolated in about 40% yield, was assigned on the basis of analytic and spectroscopic data. The compound showed no parent ion (m/e 728) in the mass spectrum, the highest molecular weight ions being 637 (M - CH₂Ph) and 636 (M - PhCH₃). Attempts to degrade 6 with the usual reagents such as lithium aluminum hydride in refluxing *n*-butyl ether, *n*-butyllithium, hydrochloric acid in aqueous acetone, or potassium hydroxide in refluxing aqueous ethanol led to almost quantitative recovery of starting material, probably because the molecule is severely sterically crowded. However, when refluxed in aqueous alkaline diglyme, conditions so harsh that phenyl groups were cleaved from silicon, 1,3-diphenyl-2-propanol (7), the expected carbon skeleton, was isolated in good yield (eq. 9). Rational mechanisms for this degradation involving alkoxysilane cleavage, a silylcarbinol to alkoxysilane rearrangement (5), and subsequent further cleavage can be proposed for this transformation.

$$[9] \xrightarrow{\text{Ph}_3\text{SiO}} C \xrightarrow{\text{CH}_2\text{Ph}} \xrightarrow{\text{OH}^-} \text{PhCH}_2\text{CHOHCH}_2\text{Ph}$$

Further evidence for the structure of **6** was obtained by finding that it rapidly and quantitatively thermally isomerized to the disiloxane **8** at 200° (eq. 10). This appears to be a new variant of a previously recognized type of 1,2-rearrangement reaction involving silicon-oxygen bond formation and silicon-carbon bond breaking (5, 6). The structure of **8**, based on analytical and spectroscopic data, was confirmed by its hydrolysis using refluxing aqueous alkaline diglyme solution to the known 1,2,3-triphenylpropane (**9**).

The third product from the photolysis of phenylacetyltriphenylsilane was the well-known benzyltriphenylsilane.



Mechanism of the Photolyses in Cyclohexane

The products from the photolysis of acetyl- and phenylacetyltriphenylsilane are readily explained on the basis of the formation of triphenylsilyl radicals which subsequently attack the most electronegative atom in the system, namely the oxygen of an unreacted acylsilane molecule, to form a new radical species which subsequently undergoes normal (dark) radical reactions.

For acetyltriphenylsilane, a reasonable reaction path is shown in Scheme 1.

The conversion of 2 to 1 by addition of triphenylsilyl radical to the alkene 2 is not unexpected since it is known that triphenylsilyl radicals will add to alkenes (7, 8). When 2 equiv of 2 were photolyzed with any acylsilane which yielded triphenylsilyl radicals on photolysis (*e.g.* $Ph_3SiCOCH_2Ph$, *vide infra*) it was found that significant yields (20%) of 1 could be isolated, a finding consistent with the alkene 2 reacting with the silyl radicals.

The products from the photolysis of phenylacetyltriphenylsilane can be explained by the following reaction pathways (Scheme 2) where again silyl radical adds to carbonyl oxygen, followed either by loss of a hydrogen atom or addition of a benzyl radical.

Two details of this mechanism require clarification. One question concerns the initial mode of cleavage of the acylsilane, which could have occurred to give silvl and phenylacetyl radicals (path a), the latter of which subsequently (and totally) decarbonylated, or which could have occurred to give silylacyl and benzyl radicals (path b), the former of which decarbonylated. No products containing a carbonyl group are found among the products of photolysis of phenylacetyltriphenylsilane in cyclohexane, or in carbon tetrachloride, where in the latter case the products are found to be triphenylchlorosilane and benzyltriphenylsilane, together with bibenzyl, trichloroethylbenzene, and hexachloroethane, each a product reasonably derived from silyl and benzyl

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 $\frac{h\nu}{(a)} \quad \text{Ph}_{3}\text{Si} \cdot + \cdot \text{COCH}_{2}\text{Ph} \rightarrow \text{PhCH}_{2} \cdot + \text{COCH}_{2}\text{Ph}$ Ph₃SiCOCH₂Ph $Ph_3SiCO + \cdot CH_2Ph \rightarrow Ph_3Si \cdot$ Ph₃SiCH₂Ph + CO PhaSiO Ph₃Si• + Ph₃SiCOCH₂Ph Ph₃Si PhCH₂• Ph₃SiO Ph₃SiO CH₂Ph Ph₃Si CH₂Ph Ph₃Si 5 6

SCHEME 2. Photolysis of phenylacetyltriphenylsilane.

radicals. The known stability of benzyl radical suggests that decarbonylation of phenylacetyl radical might occur easily; nothing is known about triphenylsilylacyl radicals to date.

The second question is how the observed benzyltriphenylsilane is formed. Formally, it could arise by combination of triphenylsilyl and benzyl radicals. However, it is to be noted that almost the same yields of benzyltriphenylsilane are obtained by photolysis of the acylsilane in any of cyclohexane, carbon tetrachloride, or methanol. Since silvl radicals have been shown previously to be very reactive toward carbon tetrachloride it is not clear why they should sur-

benzyl radicals, nor why, if formed in methanol, their behavior should not be strongly influenced by the rather different nature of this solvent so that at least a different amount of benzylsilane would be formed. To date all acylsilanes except phenylacetyltriphenylsilane, when photolyzed in methanol, have yielded almost no products of radical reactions, but instead yielded products derived from siloxycarbenes. These various observations are rationalized by the proposal that the major source of benzyltriphenylsilane is from a separate concerted intramolecular extrusion of CO from phenylacetyltriphenylsilane (i.e. reaction within and relatively independent of the vive in this solvent to be able to combine with solvent cage), rather than from the coupling of

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free silyl and benzyl radicals, which species are the sources of the other products observed as noted.

The photolyses of acetyltriphenylsilane using the di- and trichloroethylenes as solvents were briefly investigated. When photolyzed in *cis*dichloroethylene, acetyltriphenylsilane gave a large amount of oligomerized solvent and a 34%yield of *trans*-2-triphenylsilylchloroethylene (10). Using *trans*-dichloroethylene, the same product was obtained in 45% yield. The *trans* geometry was assigned based on strong i.r. absorption at 10.52μ , characteristic of a *trans*-disubstituted ethylene, and by the magnitude of the AB coupling constant of 15 Hz consistent with this geometry.

When photolyzed in trichloroethylene, acetyl chloride, triphenylchlorosilane, and 2,2-dichloro-vinyltriphenylsilane (11) were isolated.

Both the above reactions are consistent with the cleavage of the acylsilane to radicals where the silyl radical either added to the double bond of the solvent, the new radical then losing a halogen atom, or where the silyl and acetyl radicals abstracted halogen from the solvent (Scheme 3).



SCHEME 3. Photolysis of acetyltriphenylsilane in chloroethylenes.

The preceding data clearly demonstrate the pronounced tendency of photolytically generated silyl radicals either to abstract a highly electronegative atom (halogen) from the solvent, or to add to unsaturation (C=O or C=C) when halogen is not available for abstraction. The driving force for either process is obviously the stability achieved through the strong Si-X or Si-O bonds that are formed in this process.

Experimental

All photolyses were carried out using a 100 W PAR 38 clear mercury flood lamp, ASA code H34-4GS, which has

energy maxima at 366, 405, and 436 nm, closely matching the n- π^* absorption maxima of acetylsilanes which occur at about 360-380 nm. Irradiations were carried out in Pyrex flasks positioned 8-12 in. from the lamp. Solutions were flushed with nitrogen prior to irradiation to remove oxygen, and photolyses were carried out with a slight positive pressure of thoroughly dried pure nitrogen gas.

I.r. spectra were obtained on a Perkin-Elmer 237B grating spectrometer; n.m.r. spectra on Varian A60 or T60 spectrometers; u.v. spectra on a Bausch & Lomb Spectronic 505 spectrometer; mass spectra on an AEI 902 spectrometer; g.l.c. on a Varian Aerograph Series 200 dual column gas chromatograph with thermal conductivity detection. Analyses were by A. B. Gygli, Toronto, Ontario.

The Photolyses of Acetyltriphenylsilane in Cyclohexane

A solution of 3.00 g (0.0099 mol) of acetyltriphenylsilane in 75 ml of cyclohexane (dried by distillation from lithium aluminum hydride) was stirred and irradiated until all acylsilane was gone $(8\frac{3}{4}h)$.

A similar irradiation of 15.00 g of the acylsilane in 250 ml of cyclohexane required 25 h irradiation for consumption of the acylsilane; 4 g in 60 ml of solvent required $12\frac{1}{2}$ h.

A thick, faintly yellow oil, obviously a mixture, was obtained upon removal of solvent under reduced pressure. Three products giving rise to (a) a singlet at δ 6 p.p.m., (b) two doublets (J = 1.8 Hz) at 5.15 and 4.68 p.p.m., and (c) a quartet (J = 7.5 Hz) at 4.53 p.p.m. were identified by methods described below. Other unidentified absorption in the region 2.2–1.0 p.p.m. was observed.

The product from the photolysis of 3 g of acetyltriphenylsilane in cyclohexane was chromatographed on silica gel. Elution with 1:3 benzene – carbon tetrachloride gave 1.39 g of oil.

Further elution of the column with benzene gave about 0.15 g (4%) of starting material and 0.89 g of slightly yellow solid which was recrystallized from carbon tetrachloride – petroleum ether (60–70°) to give 0.77 g (28%) of pure triphenylsilanol, m.p. 155–156°, mixed m.p. 155–156°.

The 1.39 g of oil obtained by chromatography above was dissolved in 20 ml of benzene, methanol was added, and on standing overnight 0.43 g of white crystals, m.p. 177–183°, were obtained. Recrystallization from the same solvent mixture, and then from carbon tetrachloride – heptane gave 0.26 g (9.6%) of pure 1-triphenylsiloxy-1,2-bis(triphenylsilyl)ethylene (1), m.p. 180–181°: m/e (relative abundance, proposed origin) 818 (1, M), 741 (3, M – Ph), 559 (5, M – Ph₃Si), 457 (33, Ph₃SiOSiPh₂), 259 (100, Ph₃Si); i.r. (CCl₄), 7.0, 9.0 (SiPh), 9.2 μ (Si–O–C); n.m.r. (internal TMS, CDCl₃) δ 6.00 (1H, s, C=CH), 6.6–7.5 p.p.m. (45H, m, aryl).

Anal. Calcd. for $C_{56}H_{46}OSi_3$: C, 82.10; H, 5.66; Si, 10.28. Found: C, 82.16; H, 5.60; Si, 10.35.

Hydrolysis of 1 in Aqueous Alkaline Dioxane

A solution of 0.25 g of 1 in 6 ml of dioxane was treated with 1.5 ml of 12% aqueous potassium hydroxide at room temperature for 1 h. Work-up with dilute hydrochloric acid gave a solid which was recrystallized from petroleum ether (90–100°) to give 0.22 g (88%) of triphenylsilanol, m.p. 140–155°. Recrystallization from carbon tetrachloride – pentane gave 0.20 g (79%) of material, m.p. 155-156°, identified by mixed m.p. with the authentic material.

Lithium aluminum hydride in refluxing di-*n*-butyl ether or hydrochloric acid in refluxing aqueous acetone had little or no effect on **1**.

Treatment of 1 with Phenyllithium; Triphenylsilylacetyltriphenylsilane (4)

A solution of 1.00 g (0.00122 mol) of 1 in dry benzene was treated with 3.75 ml (0.0030 mol) of freshly-prepared phenyllithium in ether-benzene solution. Upon being refluxed for $2\frac{1}{2}$ h the solution turned deep red and gave a white precipitate. Work-up with saturated aqueous ammonium chloride (β -ketosilanes are acid-sensitive) gave a solid which upon crystallization from carbon tetrachloride gave 0.31 g (76%) of tetraphenylsilane. This was recrystallized from carbon tetrachloride to give 0.26 g (65%) of the pure compound, m.p. 240–241°.

The residual product, an oil, was dissolved in hexane and gave, in three crops, 0.78 g of solid consisting largely of triphenylsilylacetyltriphenylsilane (4) which melted over a wide range. Recrystallization from methylene chloride – methanol gave 0.43 g (64%) of material, m.p. 140–153°, and recrystallization from methylene chloride – pentane gave m.p. 154–158°. Subsequent recrystallization failed to sharpen the m.p.; the large range is attributed to the ready thermal decomposition of 4.

Similar treatment of 1 with *n*-butyllithium gave *n*-butyltriphenylsilane (60%) and 4 (40%); i.r. (CCl₄) 6.16 (C=O), 7.0, 9.0 μ (Si-Ph); n.m.r. (CDCl₃) δ 3.42 (2H, s, CH₂), 7.2-7.4 p.p.m. (32H (30 required), m, aryl); u.v. (λ_{max} , (ϵ), C₆H₁₂), 338 nm (sh, 83), 350 (sh, 160), 362 (275), 376.5 (380), 391.5 (295).

Anal. Calcd. for $C_{33}H_{32}OSi_2$: C, 81.38; H, 5.75. Found: C, 80.32; H, 6.05.

The unsatisfactory elemental analysis obtained for 4 was probably a result of trapped solvent in the crystals. However, in this case heating the compound up to its melting point to remove solvent resulted in partial rearrangement to a new compound.

Thermal Rearrangement of **4** to 1-Triphenylsiloxy-1triphenylsilylethylene (**2**)

A sample of 0.100 g of 4 was heated under nitrogen at 160° for 30 min. The n.m.r. and i.r. spectra of the resulting glass were identical to those of an authentic sample of 1-triphenylsiloxy-1-triphenylsilylethylene (2), the preparation of which is described below. Crystallization from methylene chloride – methanol gave 0.071 g (71%) of crystalline 2, m.p. 115–118°.

Synthesis of 1-Triphenylsiloxy-1-triphenylsilylethylene (2)

To a well-stirred suspension of 3.9 g (0.10 mol) of sodium amide in 100 ml of dry benzene under nitrogen, was added 16.1 g (0.100 mol) of bis(trimethylsilyl)amine to give a suspension of sodium bis(trimethylsilyl) amide.

To the suspension containing 0.012 mol of the above material was added, all at once, 3.02 g (0.010 mol) of acetyltriphenylsilane. After stirring for 10 min at room temperature solid triphenylchlorosilane (3.25 g, 0.011 mol) was added to the deep yellow solution. The yellow color disappeared, some warming was noticed, and on stirring for 1 h at room temperature a thick white suspension was obtained. Work-up with dilute hydrochloric acid and ether gave 5.6 g of yellow oil which was dissolved

in 25 ml of benzene. Addition of 200 ml of methanol and cooling the solution to -20° gave 3.82 g (68%) of 1-triphenylsiloxy-1-triphenylsilylethylene, m.p. 110–113°. Recrystallization from hexane and other hydrocarbon solvents gave very unsharp melting material containing a considerable amount of trapped solvent. The analytical sample, m.p. 120–121°, was obtained by several recrystallizations from benzene-methanol: m/e 560 (1, M), 546 (1, M – CH₂), 482 (5, M – PhH), 457 (23, Ph₃SiOSiPh₂), 379 (36, 457 – PhH), 259 (100, Ph₃Si); i.r. (CCl₄) 6.05 (weak, C=C), 7.0, 9.0 (SiPh), 8.3 (s), 9.9 μ (s); n.m.r. (CDCl₃); 4.67 (1H, d, J = 1.8 Hz) and 5.13 (1H, d, J = 1.8 Hz, =CH₂), 7.1–7.7 p.p.m. (30H, m, aryl).

Anal. Calcd for C₃₈H₃₂OSi₂: C, 81.38; H, 5.75. Found: C, 80.92; H, 5.73.

Isolation of 1-Triphenylsiloxy-1-triphenylsilylethane (3) from the Photolysate

Following the photolysis of 4.00 g of acetyltriphenylsilane in cyclohexane the product was worked-up by chromatography to give an oil upon elution with benzene – carbon tetrachloride. Crystallization of this oil from pentane gave largely 1 in the first two crops. (This was further recrystallized to give 0.30 g of pure 1.)

Removal of solvent from the mother liquor gave 1.08 g of thin oil which on crystallization from pentane gave 0.48 g of a solid, m.p. 135–144°, judged from its n.m.r. spectrum to consist of a mixture of **2**, 5.20 and 4.72 p.p.m. (doublets, J = 1.8 Hz), and a second compound, 1-triphenylsiloxy-1-triphenylsilylethane (3), δ 4.56 (1H, quartet, J = 7.5 Hz) and 1.48 p.p.m. (3H, doublet, J = 7.5 Hz).

The presence of **2** was confirmed by the i.r. spectrum in which all of the bands present in the spectrum of pure **2** were seen. One-half of this solid mixture (0.24 g) after seven recrystallizations from heptane gave 0.05 g of white solid, m.p. $156-159^{\circ}$, which consisted of **3**, contaminated with a trace of **2**. The mixed m.p. of this solid with pure **3**, (m.p. $163-164^{\circ}$, prepared as described below) was $159-163^{\circ}$.

The second half of the solid mixture of 2 and 3 (0.26 g) was treated with 10 ml of dioxane and 3 ml of 3 M aqueous sodium hydroxide over 40 min at room temperature. Work-up with dilute hydrochloric acid and ether gave a solid mixture of triphenylsilanol (identified by i.r.) and 3.

Chromatography on silica gel gave upon elution with 1:1 benzene – carbon tetrachloride a thick oily fraction which was crystallized, then recrystallized from heptane to give 0.087 g of pure 3, m.p. $163-164^{\circ}$, mixed m.p. with authentic material, $163-164^{\circ}$.

Synthesis of 1-Triphenylsiloxy-1-triphenylsilylethane (3)

A solution of 0.70 g (0.0023 mol) of 1-triphenylsilylethanol in 40 ml of dry toluene containing 0.4 ml (0.005 mol) of pyridine and 0.0023 mol of triphenylbromosilane (prepared by the treatment of 0.60 g of triphenylsilane with bromine in carbon tetrachloride) was heated at reflux for 17 h, and then was cooled and worked-up by adding two volumes of ether and washing the solution twice with water to remove pyridinium hydrobromide. Removal of the solvent with the rotary evaporator gave an oil which, upon crystallization from petroleum ether $(60-70^{\circ})$ gave 0.73 g (56%) of 1-triphenylsiloxy-1-triphenylsilylethane (3), m.p. 159–164°. Recrystallization from heptane gave m.p. 163–164°. The mixed m.p. of this with a sample of the same compound obtained from the rearrangement of the isomeric bis(triphenylsilyl)ethanol (9) was not depressed.

Determination of the Relative Yields of 1, 2, and 3

Photolysis of 1.00 g of acetyltriphenylsilane in 60 ml of cyclohexane (over $2\frac{1}{4}$ h) and chromatography on silica gel using elution with 10% benzene in carbon tetrachloride gave 0.48 g of thick oil, whose 100 MHz expanded scale n.m.r. spectrum was utilized in the regions of (a) 6.0, (b) 5.1, and (c) the multiplet 4.7–4.2 p.p.m., to establish the relative yields of compounds 1, 2, and 3 as 28:44:28. Knowing that the mixture of the three accounts for at most 50% of the photolysate, upper limits of 14, 22, and 14%, respectively, may be assigned to the yields of 1, 2, and 3.

Isolation of 3 from the Photolysis of Acetyltriphenylsilane in Methanol Containing Pyridine

A suspension of 0.15 g of acetyltriphenylsilane in 10 ml of methanol containing 50 μ l of pyridine was irradiated for 35 min when an i.r. spectrum showed that no starting acylsilane remained. A fine precipitate was present in the solution. Cooling to -20° and filtration then gave 0.005 g of white solid, m.p. 149–155°, the n.m.r. and i.r. spectra of which indicated it to be 3. Two recrystallizations from carbon tetrachloride – methanol gave about 2 mg of 3, m.p. 163–165°, mixed m.p. 163–164°.

The Photolysis of Phenylacetyltriphenylsilane in Cvclohexane

A solution of 9.80 g of phenylacetyltriphenylsilane in 300 ml of dry cyclohexane was irradiated for 6 h until no starting acylsilane remained. Removal of the solvent gave a thick oil which was dissolved in 350 ml of hexane. On standing at -20° overnight 0.93 g (12%) of crude solid β -triphenylsiloxy- β -triphenylsilylstyrene (5) was obtained. Recrystallization from carbon tetrachloride gave 0.60 g (7.7%) of pure material, m.p. 233–235°. (In other runs, using a similar procedure pure 5 was obtained in yields of 6.6, 7.3, and 9.0%.)

The mother liquor was then evaporated to dryness and the resulting oil was dissolved in 50 ml of methylene chloride. Addition of 200 ml of methanol gave, on standing, 3.69 g of solid which was recrystallized from methylene chloride – methanol to give 3.51 g (41%) of a second product, 2-triphenylsiloxy-2-triphenylsilyl-1,3-diphenylpropane (6), m.p. 195–199°. (Yields of 39, 37, and 41% of this product were obtained in other runs.)

The solvent was evaporated from the mother liquor (which originally gave the 3.69 g of crude 6) until less than 100 ml remained and on standing 3.13 g (34%) of benzyltriphenylsilane was obtained as large crystals, m.p. $97-99^\circ$. This was identified by mixed m.p. with the authentic material, (In other runs, yields of 29, 33, and 34% were obtained.)

Characterization of β-Triphenylsiloxy-β-Triphenylsilylstyrene (5)

Compound 5 on recrystallization from methylene chloride – methanol had m.p. $234-235^{\circ}$. The solid was heated to 234° for a few minutes to remove trapped

solvent (decrepitation was observed during heating): m/e636 (13, M), 559 (0.5, M – Ph), 457 (25, Ph₃SiOSiPh₂), 379 (23, 457 – PhH), 259 (100, Ph₃Si); n.m.r. (C₆D₆) δ 6.32 (1H, s), 6.8–7.8 p.p.m. (39H (35 required), m, aryl). Anal. Calcd. for C₄₄H₃₆OSi₂: C, 82.97; H, 5.70. Found: C, 82.96; H, 5.76.

Degradation of 5

(a) Aqueous Alkaline Dioxane

A few milligrams of 5 in dioxane was treated with 1 ml of 10% sodium hydroxide. The solution was heated for 5 min, and then was cooled and worked-up with dilute acid and ether to give a white solid. The i.r. spectrum of this material showed it to consist of triphenylsilanol (2.70 μ) and a small amount of phenylacetic acid (3-4, (broad), 5.85 μ) which was also notable by its odor. No other products were detected.

(b) Lithium Aluminum Hydride

To a suspension of 0.33 g (0.00052 mol) of 5 in 20 ml of dry di-*n*-butyl ether was added 0.08 g (0.002 mol) of lithium aluminum hydride. The suspension was heated for 2 h. Work-up with dilute HCl gave an oil which was chromatographed on silica gel. Elution with carbon tetrachloride gave 0.11 g (83%) of triphenylsilane as an oil in the first three fractions. This was crystallized from pentane to give 0.06 g of the pure solid, m.p. $41-44^\circ$, identified by mixed m.p. with authentic material.

Further elution with carbon tetrachloride gave 0.06 g ($\sim 18\%$) of unidentified material.

Elution with benzene gave, in the first two fractions, 0.12 g (61%) of crude phenylacetyltriphenylsilane as an oil. Crystallization from ethanol at -20° gave 0.06 g (30%) of pure acylsilane, m.p. 93–95°, mixed m.p. 93–95°.

Further elution of the column with benzene gave 0.06 g (27%) of crude triphenylsilanol.

Characterization of 2-Triphenylsiloxy-2-triphenylsilyl-1,3-diphenylpropane (6)

Several recrystallizations from methylene chloride – methanol gave the pure material, m.p. 199–200°, which was finely ground up and was pumped on at 115°/0.1 mm prior to analysis: m/e 637 (3, M – PhCH₂), 636 (4, M – PhCH₃), 468 (34, M – Ph₃Si), 457 (14, Ph₃SiOSi-Ph₂), 259 (100, Ph₃Si); i.r. (CCl₄) 6.88 (C—Ph) 7.0, 9.0 μ (Si—Ph); n.m.r. (CCl₄) 6.358 (4H, broadened AB system, J = 14 Hz, CH₂Ph), 6.5–7.7 p.p.m. (41H, m, aryl).

Anal. Calcd. for $C_{51}H_{44}OSi_2$: C, 84.02; H, 6.08. Found: C, 84.03; H, 5.97.

Degradation of 6 in Aqueous Alkaline Diglyme

To a solution of 0.80 g of 6 in 50 ml of diglyme was added 5 ml of water and 1.20 g of potassium hydroxide. The solution was heated to reflux for $4\frac{1}{2}$ h, and then was acidified and extracted thrice with ether. Drying and removal of solid gave an oil which showed almost no silicon-phenyl absorption at 7 and 9 μ in the i.r. Chromatography on silica gel eluting first with benzene and then with methylene chloride gave 0.18 g (77%) of 1,3-diphenylpropan-2-ol, 7, $n_{\rm D}^{23}$ 1.5699 (lit. $n_{\rm D}^{20}$ 1.5723 (10)).

The carbinol was treated with 0.20 g of *p*-nitrobenzoyl chloride in 1 ml of pyridine for 30 min at room temperature. Work-up with ether and saturated aqueous sodium bicarbonate gave an oil which was crystallized from hexane to give 0.25 g (63%, based on 6) of 1,3-diphenyl-2-

propyl *p*-nitrobenzoate, m.p. $72-78^{\circ}$. Recrystallization from hexane gave 0.18 g of pure material, m.p. $78-79^{\circ}$ (lit. m.p. $80-81^{\circ}$ (11)).

Thermal Rearrangement of 6 to Pentaphenyl-2-(1,2,3triphenylpropyl)-disiloxane (8)

A sample of 1.60 g of 6 was heated at 210° for 90 min. An n.m.r. spectrum of the resulting glass indicated that a quantitative isomerization to a disiloxane, **8**, had occurred. Crystallization from methylene chloride – methanol gave 1.57 g of solid which was recrystallized to give 1.36 g (85%) of pure **8**, m.p. 150–151.5°. The sample was finely ground up and was pumped on at 80°/0.1 mm prior to analysis: m/e 728 (0.4, M), 726 (0.2, M – H₂), 636 (0.4, M – PhCH₃), 457 (100, Ph₃SiOSiPh₂), 379 (58, 457 – PhH); i.r. (CCl₄), 6.88 (C—Ph), 7.0, 9.0 (Si—Ph), 9.3 μ (broad, SiOSi); n.m.r. δ 3.52 (4H, AB system, J = 16 Hz, CH₂Ph), 6.5–7.7 p.p.m. (40H, m, aryl).

Anal. Calcd. for $C_{51}H_{44}OSi_2$: C, 84.02; H, 6.08. Found: C, 83.99; H, 5.87.

Degradation of 8 in Aqueous Alkaline Diglyme

To a solution of 0.37 g (0.0005 mol) of 8 in diglyme was added 1 ml of 50% potassium hydroxide. Heating for 3 h followed by work-up with water gave a thin oil which showed no silicon-phenyl absorption at 7 and 9 μ in the i.r. spectrum.

Chromatography on silica gel gave, on elution with carbon tetrachloride, 0.11 g (80%) of 1,2,3-triphenylpropane, n_D^{23} 1.5858, the i.r. and n.m.r. spectra of which were identical to those of the authentic material, prepared as follows:

To a solution of 3.0 g of 1,2,3-triphenylpropan-2-ol (prepared by the addition of 2 equiv of benzylmagnesium chloride to methyl benzoate) in 95% ethanol was added 15 g of freshly prepared Raney Nickel (activity grade W1). The suspension was refluxed for 16 h. Filtration and removal of solvent gave an oil which was chromatographed on silica gel. Elution with carbon tetrachloride gave 1.30 g (46%) of 1,2,3-triphenylpropane which after distillation had $n_{\rm D}^{24}$ 1.5883 (lit. $n_{\rm D}^{30}$ 1.5864 (12)).

The Photolysis of Phenylacetyltriphenylsilane in Methanol

A suspension of 0.20 g of phenylacetyltriphenylsilane in 10 ml of methanol was irradiated for 90 min. Removal of the solvent gave a yellowish oil whose n.m.r. spectrum was almost identical to that of the crude photolysate from cyclohexane, and had the following bands: δ 2.81 (s, benzyltriphenylsilane), 3.55 (m, 2-triphenylsiloxy-2-triphenylsilyl-1,3-diphenylpropane (6) and superimposed singlet due to triphenylmethoxysilane), and 6.3 p.p.m. (s, β -triphenylsiloxy- β -triphenylsilylstyrene (5)).

The photolysis of phenylacetyltriphenylsilane in methanol containing pyridine gave virtually identical results.

Photolysis of Phenylacetyltriphenylsilane in Carbon Tetrachloride

The photolysis of 0.50 g (0.0013 mol) of phenylacetyltriphenylsilane in 15 ml of carbon tetrachloride was complete in 2 h. Removal of the solvent gave a yellow oil, whose i.r. spectrum showed only negligibly weak carbonyl absorptions. The n.m.r. spectrum of the crude product showed peaks attributable to three identifiable products: bibenzyl (2.81 p.p.m.), benzyltriphenylsilane (2.85 p.p.m.), and 1,1,1-trichloro-2-phenylethane (3.75 p.p.m.). An array of minor peaks indicated that an appreciable number of minor products were also formed.

The entire product was briefly treated with dilute potassium hydroxide in aqueous tetrahydrofuran to convert triphenylchlorosilane to triphenylsilanol. Chromatography on silica gel, eluting with carbon tetrachloride, and then with 1:1 carbon tetrachloride – benzene, gave 0.18 g of non-polar oil which was crystallized from methanol to give 0.12 g (26%) of benzyltriphenylsilane as large clear crystals, m.p. 96–97°, mixed m.p. 96–97°.

Elution of the column with ether gave a white solid which was recrystallized from heptane to give 0.19 g (52%) of triphenylsilanol, m.p. $153-154^{\circ}$, identified by mixed m.p.

The presence of bibenzyl and 1,1,1-trichloro-2-phenylethane, identified in the n.m.r., and of hexachloroethane, were confirmed by g.l.p.c. analysis using the following conditions: column, 20 ft \times 1/4 in. 20% Carbowax 20M on Chromosorb G; column temperature, 240°; detector, 300°; injector port, 285°; flow rate 90 ml/min. Following a small scale photolysis (0.20 g of phenylacetyltriphenylsilane in 5 ml of carbon tetrachloride) the photosolution was concentrated. The g.l.p.c. trace showed peaks with retention times of 1.1, 2.1, 3.3, and 5.4 min which were identified, by injection of the authentic material, as being due to carbon tetrachloride, hexachloroethane, 1,1,1-trichloro-2-phenylethane, and bibenzyl, respectively. The origin of a fifth minor peak, at 2.7 min, is unknown.

Preparative g.l.p.c. gave a small amount of pure 1,1,1trichloro-2-phenylethane, the n.m.r. and i.r. spectra of which were identical to those of the authentic material prepared by the coupling of trichloromethylmagnesium chloride with benzyl chloride (13).

No attempt was made to measure the yields of the latter three products but it was apparent both from the n.m.r. spectrum of the crude photolysate and from g.l.p.c. analysis that 1,1,1-trichloro-2-phenylethane was a major product, being present in greater yield than the benzyltriphenylsilane (26%). The hexachloroethane and bibenzyl are formed in somewhat lower yields.

The Photolysis of Acetyltriphenylsilane in cis-1,2-Dichloroethylene

A solution of 0.50 g (0.0017 mol) of acetyltriphenylsilane in 10 ml of freshly distilled cis-1,2-dichloroethylene was irradiated for 6 h. The solvent was removed to give about 2 ml of liquid. Chromatography on a $1\frac{1}{2}$ in. \times 3 in. silica gel column, eluting with carbon tetrachloride, gave about $1\frac{1}{2}$ ml of sweet-smelling liquid (oligomerized solvent). Elution with 1:3 benzene - carbon tetrachloride gave 0.31 g of solid material which was recrystallized from methylene chloride – methanol to give 0.18 g (34%)of trans-1-chloro-2-triphenylsilylethylene, m.p. 127-129°. Two more recrystallizations from hexane and a final one from methylene chloride - methanol gave the analysis sample, m.p. 131–132°: m/e 320 (4, M), 284 (7, M – HCl), 259 (12, Ph₃Si), 242 (23, M - 78), 218 (18, Ph₂SiCl), 180 (100, unknown); i.r. (CCl₄) 7.0, 9.0 (Si-Ph), 10.52 μ (trans-CH=CH-); n.m.r. (CCl₄), δ 6.30, 6.63 (2H, AB system with $J_{AB} = 15$ Hz, trans-CH=CH---), 7.2-7.6 p.p.m. (15H, m, aryl).

Anal. Calcd. for $C_{20}H_{17}ClSi$: C, 74.86; H, 5.43. Found: C, 75.00; H, 5.21.

A similar procedure was used in working-up the

photolysis of acetyltriphenylsilane in *trans*-1,2-dichloroethylene. In this case, the yield of pure isolated 1-chloro-2triphenylsilylethylene was 45%.

The Photolysis of Acetyltriphenylsilane in Trichloroethylene

A solution of 1.00 g of acetyltriphenylsilane in 100 ml of trichloroethylene was irradiated for 5 h. The solvent was distilled until only 30 ml remained. An i.r. spectrum of the distillate showed that acetyl chloride was present. Treatment of the distillate with excess aniline afforded, after work-up and recrystallization 0.08 g (18%) of acetanilide, m.p. 112–114°, identified by mixed m.p.

The solvent was removed from the residual photosolution at the rotary evaporator to give 3.85 g of sweetsmelling oil. Distillation in the Kugelrohr (110° , 0.7 mm) gave 1.55 g of volatile liquid which appeared to be largely oligomerized solvent. The nonvolatile residue, 2.13 g of brown oil, was dissolved in ether and the solution was stirred with water to convert any chlorosilane to triphenylsilanol. Work-up gave a brown oil which showed a strong silanol peak at 2.70 μ in the i.r.

Chromatography on silica gel gave, on elution with carbon tetrachloride, a small amount of oil in the first few fractions and then small amounts of white solid over many fractions. The combined solid (0.42 g) was recrystallized from methylene chloride – methanol to give 0.33 g (28%) of dichlorovinyltriphenylsilane, m.p. 125–132°. Three further recrystallizations from methylene chloride – pentane raised the m.p. to 132–133°; *in/e* 356, 354 (2, M), 319 (3, M – Cl), 318 (3, M – HCl), 278, 276 (4, 5, M – 78), 218 (100, Ph₂SiCl); n.m.r. (CCl₄), δ 6.50 (1H, S, C=CH), 7.2–7.7 p.m. (15H, m, aryl).

Anal. Calcd. for $C_{20}H_{16}Cl_2Si$: C, 67.70; H, 4.54. Found: C, 67.67; H, 4.56.

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- 1. A. G. BROOK, P. J. DILLON, and R. PEARCE. Can. J. Chem. 49, 133 (1971).
- A. G. BROOK and J. M. DUFF. J. Am. Chem. Soc. 89, 454 (1967).
- 3. J. M. DUFF. Ph.D. Thesis. University of Toronto, Toronto, Ontario. 1970.
- 4. A. G. BROOK, D. M. MACRAE, and W. W. LIMBURG. J. Am. Chem. Soc. **89**, 5493 (1967).
- 5. A. G. BROOK, G. E. LEGROW, and D. M. MACRAE. Can. J. Chem. 45, 239 (1967).
- A. G. BROOK and N. V. SCHWARTZ. J. Org. Chem. 27, 2311 (1962).
- H. MERTEN and H. GILMAN. J. Am. Chem. Soc. 76, 5798 (1954).
- 8. C. EABORN and H. NIEDERPRÜM. J. Chem. Soc. **1963**, 797.
- 9. A. G. BROOK, C. M. WARNER, and M. E. MCGRISKIN. J. Am. Chem. Soc. 81, 981 (1959).
- K. IVANOV and G. VASILEV. C.R. acad. bulgare sci. 9, 61 (1956). Chem. Abstr. 52, 2817 (1958).
- 11. D. PAPA, E. SCHWENK, and B. WHITMAN. J. Org. Chem. 7, 587 (1942).
- 12. K. ISHIMURA. Bull. Chem. Soc. Jap. 16, 397 (1941).
- 13. J. VILLIÉRAS. Bull. Soc. Chim. Fr. 1520 (1967).