

# ESR Investigation of the Photochemical Reaction of Aroysilanes with Phosphorous Compounds

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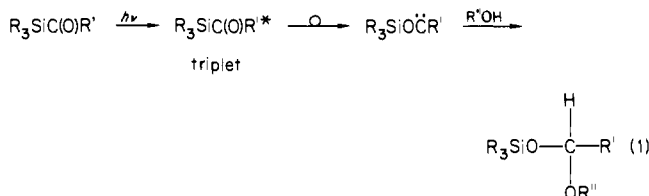
Contribution from the Istituto dei Composti del Carbonio Contenenti Eteroatomi e loro Applicazioni del C.N.R., I-40064 Ozzano Emilia, Italy, the Centro C.N.R. sulla Chimica e la Struttura dei Composti Eterociclici e loro Applicazioni, c/o Istituto di Chimica Organica dell'Università, I-50121 Firenze, Italy, and the Istituto di Chimica Organica dell'Università, I-09100 Cagliari, Italy. Received July 2, 1984

**Abstract:** Radicals of general structure  $\text{Ar}(\text{R}_3\text{Si})\dot{\text{C}}-\text{OP}(\text{O})\text{Ph}_2$  have been observed by ESR upon reaction of aroysilanes,  $\text{Ar}(\text{R}_3\text{Si})\text{CO}$ , with tetraphenylbiphosphine under UV irradiation. The same radicals could in fact be obtained in the reaction of aroysilanes with diphenylphosphine oxide and di-*tert*-butyl peroxide (DBP). Addition of  $\text{OP}(\text{OEt})_2$  to the carbonyl oxygen was also observed when photolyzing mixtures of aroysilanes, diethyl phosphite, and DBP. In contrast, the photochemical reaction of the same silanes with tetraethyl pyrophosphite led to the detection of radicals,  $\text{Ar}[(\text{EtO})_2\text{O}]\dot{\text{P}}\text{C}-\text{OSiR}_3$ , having the phosphonyl substituent  $\alpha$  to the carbon radical center and the silyl group linked to the oxygen atom. Two possible mechanisms which may account for the formation of the observed species, one involving fragmentation of the aroyl-silicon bond and the other the intermediation of a siloxy carbene, are discussed, and experimental evidence is reported in favor of the former one.

Acylsilanes are known to be more reactive species than the corresponding aryl alkyl ketones. In particular the photochemical behavior of these compounds is very peculiar as they have been suggested to react through two different mechanisms. Thus photolysis of acylsilanes in carbon tetrachloride has been proposed to involve Norrish type I cleavage of the silicon-acyl bond to give  $\text{R}_3\text{Si}\cdot$  and  $\text{RCO}\cdot$  radicals which then react with solvent.<sup>2</sup> Although from a CIDNP study of the same system it has been inferred that the formation of the observed products in  $\text{CCl}_4$  is more likely to take place via an acylsilane- $\text{CCl}_4$  exciplex, in other halogenated solvents the experimental observations are consistent with a mechanism involving an authentic silyl-acyl triplet pair.<sup>3</sup> The same fragmentation seems also to occur in hydrocarbons, although in this case the silyl radicals prefer to add to the carbonyl oxygen of the acylsilane itself. The resulting spin adducts then evolve via disproportionation and recombination reactions to a number of products.<sup>4</sup> Evidence for the intermediacy of the self-adducts  $\text{R}_3\text{Si}(\text{R}')\dot{\text{C}}\text{OSiR}_3$  has been provided by ESR spectroscopy in a number of cases.<sup>5,6</sup> The homolytic cleavage of the silicon-acyl bond has been shown to take place also thermally.<sup>6,7</sup>

In contrast, photolysis of acylsilanes in alcoholic solutions containing trace amounts of pyridine gives rise to insertion products whose formation has been explained through the intermediacy of a siloxycarbene (eq 1).<sup>8,9</sup>

Because of our current interest in the reactivity of phosphorous compounds with both photoexcited carbonyl derivatives and carbenes, we have undertaken an ESR study of the photochemical



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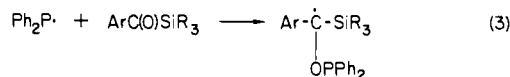
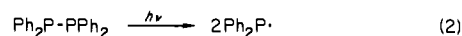
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reaction of a number of aroysilanes with tetraphenylbiphosphine, diphenylphosphine oxide, diethyl phosphite, and tetraethyl pyrophosphite.

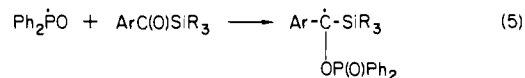
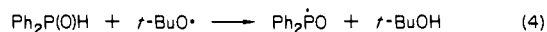
## Results and Discussion

Photolysis in the ESR cavity of deoxygenated toluene solutions of tetraphenylbiphosphine and aroysilanes below room temperature leads to the detection of ketyl radicals (**1**) containing an aryl ring and a phosphorus nucleus coupled with the unpaired electron. The formation of **1** might be accounted for by reactions 2 and 3, involving photolytic cleavage of the P-P bond<sup>10</sup> followed by addition of diphenylphosphinyl to the oxygen of the aroysilane.

Although examples of spin adducts of  $\text{Ph}_2\text{P}\cdot$  radicals with ketones<sup>11</sup> and quinones<sup>12</sup> have been reported, the identification of the observed radical is not obvious since in recent studies<sup>13</sup> we



have found that the photochemical reaction of quinones with  $\text{Ph}_4\text{P}_2$  leads to the formation of both diphenylphosphinyl ( $\text{Ph}_2\text{P}\cdot$ ) and diphenylphosphonyl ( $\text{OPPh}_2$ ) radical adducts. To ascertain the actual nature of radicals **1**, the same silanes were let to react with diphenylphosphine oxide and di-*tert*-butyl peroxide under UV irradiation. In these conditions the spectra of the diphenylphosphonyl adducts formed through reactions 4 and 5 were identical with those obtained when using  $\text{Ph}_4\text{P}_2$ , thus indicating that the same radical species are formed in the two cases. This



implies that the biphosphine undergoes inadvertent oxidation, possibly during the preparation of the sample, and that  $\text{OPPh}_2$  is more reactive than  $\text{Ph}_2\text{P}\cdot$  toward aroysilanes. On the basis of these results, we assign the structure  $\text{Ar}(\text{R}_3\text{Si})\dot{\text{C}}-\text{OP}(\text{O})\text{Ph}_2$  to radicals **1**.

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**Table I.** ESR Parameters for Radicals  $\text{Ar}(\text{R}_3\text{Si})\dot{\text{C}}\text{-OP}(\text{O})\text{Ph}_2$  (**1**) and for  $\text{Ar}(\text{R}_3\text{Si})\dot{\text{C}}\text{-OP}(\text{O})(\text{OEt})_2$  (**2**) in *tert*-Butylbenzene

radical	Ar	R	$a(^{31}\text{P})$	$a(^{29}\text{Si})$	other splittings	$g$	$T, \text{K}$
<b>1a</b>	Ph	Me	32.26 <sup>a</sup>		4.47 ( $\text{H}_o$ ), 1.52 ( $\text{H}_m$ ), 5.10 ( $\text{H}_p$ )	2.0029	243
<b>1b</b>	Ph	Ph	32.13 <sup>b</sup>	10.15	4.35 ( $\text{H}_o$ ), 1.49 ( $\text{H}_m$ ), 5.04 ( $\text{H}_p$ )	2.0030	273
<b>1c</b>	4-ClC <sub>6</sub> H <sub>4</sub>	Ph	32.42		4.46 ( $\text{H}_o$ ), 1.48 ( $\text{H}_m$ ), 0.50 ( $^{35}\text{Cl}$ )	2.0034	273
<b>1d</b>	4-MeOC <sub>6</sub> H <sub>4</sub>	Ph	30.27		4.42 ( $\text{H}_o$ ), 1.43 ( $\text{H}_m$ ), 0.66 (OMe)	2.0030	243
<b>1e</b>	2-thienyl	Me	23.15		7.29 ( $\text{H}_3$ ), 1.50 ( $\text{H}_4$ ), 6.89 ( $\text{H}_5$ )	2.0034	273
<b>2a</b>	Ph	Me	34.66		4.54 ( $\text{H}_o$ ), 1.56 ( $\text{H}_m$ ), 5.23 ( $\text{H}_p$ )	2.0029	393
<b>2b</b>	Ph	Ph	35.01		4.49 ( $\text{H}_o$ ), 1.58 ( $\text{H}_m$ ), 5.22 ( $\text{H}_p$ )	2.0029	373
<b>2c</b>	4-ClC <sub>6</sub> H <sub>4</sub>	Ph	34.27		4.55 ( $\text{H}_o$ ), 1.65 ( $\text{H}_m$ ), 0.48 ( $^{35}\text{Cl}$ )	2.0034	393
<b>2d</b>	4-MeOC <sub>6</sub> H <sub>4</sub>	Ph	34.84		4.43 ( $\text{H}_o$ ), 1.34 ( $\text{H}_m$ ), 0.62 (OMe)	2.0030	373

<sup>a</sup> $da(^{31}\text{P})/dT = -66 \text{ mG/K}$ . <sup>b</sup> $da(^{31}\text{P})/dT = -60 \text{ mG/K}$ .

**Table II.** ESR Parameters for Radicals  $\text{Ar}[(\text{EtO})_2(\text{O})\text{P}]\dot{\text{C}}\text{-OSiR}_3$  (**3**) in *tert*-Butylbenzene

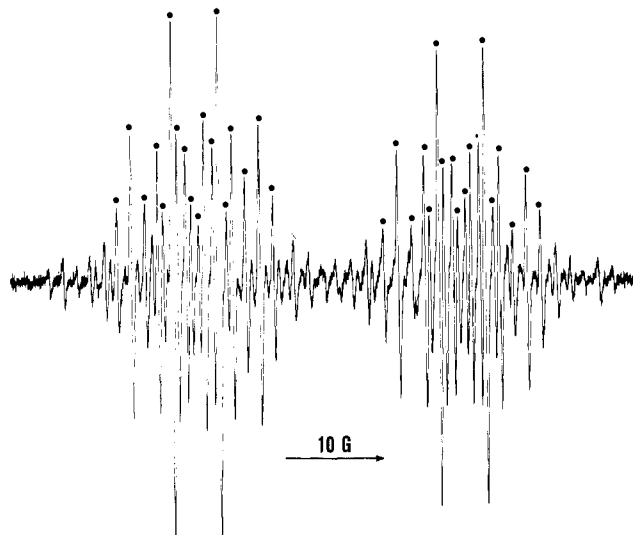
radical	Ar	R	$a(^{31}\text{P})$	$a(^{29}\text{Si})$	other splittings	$g$	$T, \text{K}$
<b>3a</b>	Ph	Me <sub>3</sub> Si	27.62	7.14	4.26 ( $\text{H}_o$ ), 1.44 ( $\text{H}_m$ ), 4.82 ( $\text{H}_p$ )	2.0029	358
<b>3b</b>	Ph	Ph <sub>3</sub> Si	27.53 <sup>a</sup>		4.16 ( $\text{H}_o$ ), 1.47 ( $\text{H}_m$ ), 4.83 ( $\text{H}_p$ )	2.0029	403
<b>3c</b>	4-ClC <sub>6</sub> H <sub>4</sub>	Ph <sub>3</sub> Si	26.96		4.32 ( $\text{H}_o$ ), 1.51 ( $\text{H}_m$ ), 0.40 ( $^{35}\text{Cl}$ )	2.0035	383
<b>3d</b>	4-MeOC <sub>6</sub> H <sub>4</sub>	Ph <sub>3</sub> Si	26.56		4.17 ( $\text{H}_o$ ), 1.30 ( $\text{H}_m$ ), 0.51 (OMe)	2.0030	413
<b>3e</b>	2-thienyl	Me <sub>3</sub> Si	23.12		7.19 ( $\text{H}_3$ ), 1.47 ( $\text{H}_4$ ), 6.64 ( $\text{H}_5$ )	2.0034	392

<sup>a</sup> $da(^{31}\text{P})/dT < 1 \text{ mG/K}$ .

Since, however, aroylsilanes, owing to their photolability, may undergo fragmentation of the aroyl-silicon bond with formation of secondary radicals, the above assignment must be substantiated by additional experimental evidence. The following findings indicate that the starting organometallic ketone is indeed attacked by the diphenylphosphonyl radical. In the case of the adduct from benzoyltriphenylsilane (**1b**), the satellite lines due to  $^{29}\text{Si}$  ( $I = 1/2$ ,  $n.a. \approx 4\%$ ) could be observed and the corresponding hyperfine splitting measured as 10.15 G. Since  $\text{Ph}(\text{Ph}_3\text{Si})\dot{\text{C}}\text{OMR}_n$  radicals are characterized by silicon coupling of ca. 10–11 G,<sup>6,14</sup> we may be reasonably confident that also in radical **1b**, the  $\text{Ph}_3\text{Si}$  group is still linked to the aroyl carbon atom. Further, the unusually large line width observed in the adducts from benzoyltrimethylsilane (**1a**) and 2-thienyltrimethylsilane (**1e**) ( $\Delta H_{pp} = 0.55 \text{ G}$ ) is conceivably due to unresolved coupling with the protons of the methyl groups, this again suggesting that the  $\text{Me}_3\text{Si}$  substituent is directly bonded to the radical carbon center. A further noticeable feature is the marked temperature dependence of the  $^{31}\text{P}$  splitting exhibited by adducts **1a** and **1b**, which is characteristic of a phosphorus nucleus  $\beta$  to a radical center and eclipsing, in the lower energy conformation, the  $2p_z$  orbital on the  $\alpha$  carbon.

Radical adducts with the similar structure  $\text{Ar}(\text{R}_3\text{Si})\dot{\text{C}}\text{-OP}(\text{O})(\text{OEt})_2$  (**2**) could be obtained by photolyzing mixtures of aroylsilanes, diethyl phosphite and di-*tert*-butyl peroxide in toluene or *tert*-butylbenzene (see Table I). These species are thought to be formed through a mechanism analogous to that outlined in reactions 4 and 5; their identification relies on the consistency of the spectral parameters with the proposed structure and again on the large line width ( $\Delta H_{pp} = 0.56 \text{ G}$ ) observed in the trimethylsilyl derivative **2a** which is attributed to unresolved splitting from the methyl protons of the  $\alpha$  silyl group.

The photoreaction of aroylsilanes with tetraethyl pyrophosphate is a more intriguing process. As soon as the irradiation is started, ESR signals from two different radicals become detectable, their intensity increasing with time. One of these is unambiguously identified as the self-adduct  $\text{Ar}(\text{R}_3\text{Si})\dot{\text{C}}\text{-OSiR}_3$  on the basis of the spectral parameters previously reported.<sup>6</sup> The second radical (**3**) exhibits coupling of the unpaired electron with the aryl ring of the starting ketone and with a  $^{31}\text{P}$  nucleus (see Table II). Radical **3** shows a remarkable thermal stability as its spectrum can be detected between 173 and 420 K, although stronger signals are generally obtained at higher temperatures. Prolonged irradiation gradually leads to the disappearance of the self-adduct while a third radical (**4**) containing two different phosphorus nuclei is formed (see Figure 1). Due to superposition of the lines, the spectrum of the latter species has been fully interpreted only in



**Figure 1.** ESR spectrum obtained after prolonged irradiation at 393 K of a *tert*-butylbenzene solution of  $\text{Ph}(\text{Me}_3\text{Si})\text{CO}$  and  $[(\text{EtO})_2\text{P}]\text{O}$  and showing signals from  $\text{Ph}[(\text{EtO})_2(\text{O})\text{P}]\dot{\text{C}}\text{-OSiMe}_3$  (marked lines) and from  $\text{Ph}[(\text{EtO})_2(\text{O})\text{P}]\dot{\text{C}}\text{-OP}(\text{OEt})_2$ .

the case of  $\text{Ph}(\text{Me}_3\text{Si})\text{C}=\text{O}$ , and the measured parameters at 393 K are  $a_o$  4.31,  $a_m$  1.42,  $a_p$  4.91,  $a(^{31}\text{P})$  26.90,  $a(^{31}\text{P})$  14.54 G,  $g$  2.0029. A spectrum identical with that of **3** is obtainable when using triethyl phosphite,  $\text{P}(\text{OEt})_3$ , instead of the pyrophosphate.

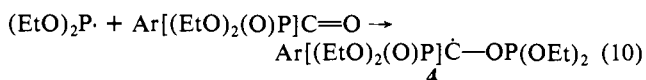
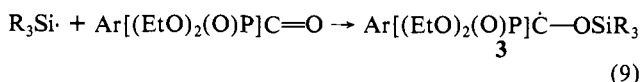
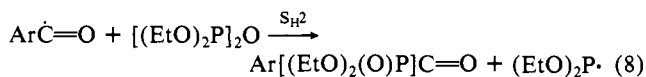
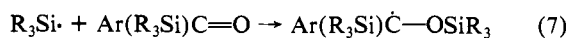
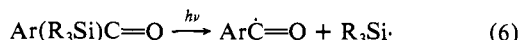
Radicals **3** have been assigned the structure  $\text{Ar}[(\text{EtO})_2(\text{O})\text{P}]\dot{\text{C}}\text{-OSiR}_3$  on the basis of the following considerations: (i) The ESR parameters for the species obtained from  $\text{Ph}(\text{Me}_3\text{Si})\text{C}=\text{O}$  are practically identical, if allowing for the different experimental conditions, with those reported for the radical  $\text{Ph}[(\text{EtO})_2(\text{O})\text{P}]\dot{\text{C}}\text{-OSiMe}_3$  generated by addition of  $\text{Me}_3\text{Si}\cdot$  to  $\text{Ph}[(\text{EtO})_2(\text{O})\text{P}]\dot{\text{C}}\text{-O}$ .<sup>13</sup> (ii) The relatively small line width ( $\Delta H_{pp} = 0.23 \text{ G}$ ) characterizing the spectra of radicals **3a** and **3e** is in contrast with the presence of a  $\text{Me}_3\text{Si}$  group directly bound to the radical carbonyl carbon. (iii) The  $^{29}\text{Si}$  splitting (7.14 G) determined in the species obtained from benzoyltrimethylsilane is typical of siloxymethyl radicals  $\text{Ph}(\text{R})\dot{\text{C}}\text{-OSiR}_3$  (ca. 7–8 G).<sup>6–14</sup> (iv) The  $^{31}\text{P}$  splitting is practically temperature independent as expected for a phosphorus nucleus  $\alpha$  to the radical center. Similarly we believe that radical **4**, detected upon prolonged photolysis, has the structure  $\text{Ph}[(\text{EtO})_2(\text{O})\text{P}]\dot{\text{C}}\text{-OP}(\text{OEt})_2$ , differing from that of **3** only in the group linked to the carbonyl oxygen, because of the similarity of the aryl protons and the ca. 27-G  $^{31}\text{P}$  splittings in the two radicals. The smaller  $^{31}\text{P}$  coupling (14.54 G) is very close to the phosphorus splitting measured in  $\text{Ph}_2\dot{\text{C}}\text{-OP}(\text{OEt})_2$  (14.97

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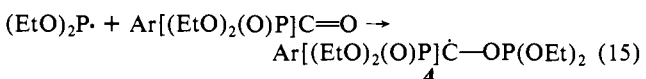
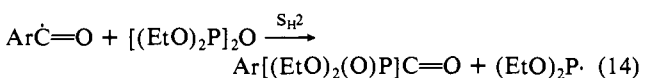
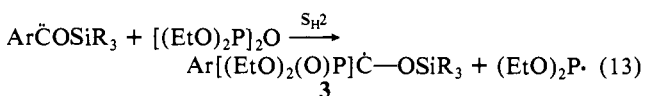
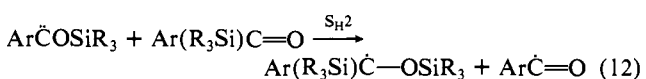
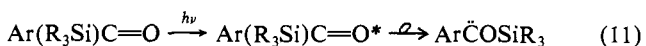
G)<sup>15</sup> and therefore is assigned to a P(OEt)<sub>2</sub> group.

The formation of radicals **3** and **4** is unexpected, and its rationalization poses more than one problem. Actually, if aroylsilanes behaved similarly to benzophenone,<sup>15</sup> one would anticipate reaction of their photoexcited triplet state with pyrophosphite to give the diethoxyphosphinyl and diethoxyphosphonyl (**2**) adducts. Since neither of these radical species has been detected nor plausible rearrangement can be envisaged for their conversion into radical **3**, a different reaction pattern must be conceived.

In view of the photochemical lability of aroylsilanes referred to in the introduction, the radicals observed in their photoreaction with pyrophosphite might be formed via one of the two mechanisms shown below and involving, respectively, homolysis of the aroyl-silicon bond (eq 6-10)



or photorearrangement of the aroylsilane to siloxycarbene (eq 11-15).



As far as the siloxycarbene mechanism is concerned, reaction 12 seems most unlikely since silicon-carbon bonds are known to be generally inert toward divalent carbon intermediates.<sup>16</sup> Moreover, in the photolytic reaction of diphenyldiazomethane with trialkyl- or triarylsilanes, the Ph<sub>2</sub>C: carbene was found to preferentially abstract hydrogen from the H-Si bond rather than attack silicon.<sup>17</sup>

Reaction 13 is instead consistent with our previous observation that the analogues of radical **3**, i.e., Ar<sub>2</sub>C-P(O)(OEt)<sub>2</sub>, are formed when reacting triplet diphenylcarbene with tetraethyl pyrophosphite, although no radicals were detected in the similar reaction with triethyl phosphite.<sup>15</sup> However reaction 13 requires the intermediacy of a siloxycarbene triplet, since the corresponding singlet is expected to give a phosphorus ylide.<sup>16</sup> A further limiting condition is that β scission of the oxygen-phosphorus bond in the biradical adduct between carbene and pyrophosphite must take place faster than triplet-singlet conversion to avoid formation of the ylide.

The following experiments were carried out with the aim to establish the possible intervention of the siloxycarbene triplet but

proved unsuccessful. Thus, no triplet ESR signals were observed upon irradiation of PhC(O)SiMe<sub>3</sub> or *p*-ClC<sub>6</sub>H<sub>4</sub>C(O)SiPh<sub>3</sub> in an ethanol matrix at 77 K either in the absence or in the presence of the benzophenone sensitizer, whereas under similar conditions irradiation of Ph<sub>2</sub>CN<sub>2</sub> gave a strong spectrum of the Ph<sub>2</sub>C: triplet.

Further, mass spectral analysis of the products of the photoreaction of Ph<sub>2</sub>CN<sub>2</sub> and PhC(O)SiMe<sub>3</sub> (1:2 m/m) in degassed benzene did not reveal any Ph<sub>2</sub>CN<sub>2</sub>C(Ph)OSiMe<sub>3</sub> or Ph<sub>2</sub>C=C(Ph)OSiMe<sub>3</sub> expected from the coupling of the siloxycarbene with either Ph<sub>2</sub>CN<sub>2</sub> or Ph<sub>2</sub>C:, thus indicating that these compounds, even if formed, represent less than 3% of the total reaction products arising from Ph<sub>2</sub>CN<sub>2</sub>. The major products were Ph<sub>2</sub>CN<sub>2</sub>CPh<sub>2</sub>, Ph<sub>2</sub>CO, Ph<sub>2</sub>CN<sub>2</sub>C(Ph)SiMe<sub>3</sub>, and Ph<sub>2</sub>C=CPh<sub>2</sub>. Minor quantities of other unidentified products were also formed, none of which contained the SiMe<sub>3</sub> moiety.

If the reaction proceeds via the cleavage of the aroyl-silicon bond, both R<sub>3</sub>Si· and ArC·O radicals should be present in solution. In particular the detection of silyl radicals should provide convincing evidence for this route, since they are not expected to be formed by eq 11-13. Spin-trapping experiments using the radical scavengers 2-methyl-2-nitrosopropane and 1,3,5-trinitrobenzene were therefore attempted.

When a benzene solution of Ph(Me<sub>3</sub>Si)C=O was photolyzed in the presence of *t*-BuN=O, the benzoyl radical PhC·O could be actually trapped as PhC(O)N(O)-*t*-Bu (*a*<sub>N</sub> 7.96 G, *g* 2.0068). A second spectrum due to *t*-Bu<sub>2</sub>NO· was also detectable, while no signals due to the silyl adduct were observed.

*t*-BuN=O is known to be an unsuitable scavenger for silyl radicals,<sup>18</sup> while nitro derivatives readily undergo addition to give persistent arylsilyloxy nitroxides.<sup>19</sup> Photolysis of benzene solutions of Ph(Me<sub>3</sub>Si)C=O or *p*-ClC<sub>6</sub>H<sub>4</sub>(Ph<sub>3</sub>Si)C=O in the presence of 1,3,5-trinitrobenzene gave actually rise to strong ESR spectra of 3,5-dinitrophenyl trimethylsilyloxy nitroxide (*a*<sub>N</sub> 12.96 G, *a*<sub>o</sub> ≈ *a*<sub>p</sub> 3.27 G, *g* 2.0046) or 3,5-dinitrophenyl triphenylsilyloxy nitroxide (*a*<sub>N</sub> 13.16, *a*<sub>o</sub> 3.14, *a*<sub>p</sub> 3.39, *a*<sub>2N</sub> 0.23 G, *g* 2.0047). The spectral parameters were checked with those of the authentic nitroxides prepared by addition to the nitro compound of the appropriate silyl radicals generated by hydrogen abstraction from Me<sub>3</sub>SiH and Ph<sub>3</sub>SiH.

In conclusion, the above results strongly disfavor the siloxycarbene mechanism and indicate that the photochemical reaction of aroylsilanes with tetraethyl pyrophosphite or triethyl phosphite can be satisfactorily described by the reaction sequence 6-10, where the key step is the homolytic cleavage of the aroyl carbon-silicon bond.

## Experimental Section

Benzoyltrimethylsilane,<sup>20</sup> benzoyltriphenylsilane,<sup>6</sup> (4-chlorobenzoyl)-triphenylsilane,<sup>21</sup> (4-methoxybenzoyl)triphenylsilane,<sup>21</sup> and 2-thenoyltrimethylsilane<sup>22</sup> were prepared according to described procedures, whereas tetraphenylbiphosphine, diphenylphosphine oxide, diethyl phosphite, triethyl phosphite, and tetraethyl pyrophosphite were commercially available as was di-*tert*-butyl peroxide.

All samples for the ESR measurements were thoroughly deoxygenated by bubbling dry nitrogen through the solution and irradiated within the spectrometer cavity with UV light from a 1-kW high-pressure mercury lamp, which was filtered through a water solution of NiSO<sub>4</sub> and CoSO<sub>4</sub>. The ESR spectra were recorded on a Bruker ER 200 spectrometer equipped with an NMR gaussmeter, frequency counter, and the standard variable temperature device.

**Photoreaction of Diphenyldiazomethane with Benzoyltrimethylsilane.** To 3 mL of a *tert*-butylbenzene solution of 0.516 mmol of Ph<sub>2</sub>CN<sub>2</sub> previously degassed with the freeze-thaw technique was added 1.032 mmol of Ph(Me<sub>3</sub>Si)C=O, and the mixture was irradiated (G.E.C.

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250-W high-pressure lamp) for 6 h (disappearance of the red color) under nitrogen. Analytical GLC analysis were performed on a HP 5790 A chromatograph with a 25 m OV101 cross-linked fused capillary column (internal diameter 0.2 mm) equipped with a HP 5970 mass selective detector: Ph<sub>2</sub>CN<sub>2</sub>CPh<sub>2</sub> mass spectrum (relative intensity), *m/e* 360 (26.7), 283 (100), 180 (68.5), 166 (21.4), 165 (97.5), 77 (75.1); Ph<sub>2</sub>CN<sub>2</sub>C(P h)SiMe<sub>3</sub> mass spectrum, *m/e* 356 (1), 180 (16.8), 176 (51.6), 77 (30.5), 73 (100).

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**Registry No.** 1a, 94930-06-0; 1b, 94930-07-1; 1c, 94930-08-2; 1d, 94930-09-3; 1e, 94930-10-6; 2a, 94930-11-7; 2b, 94930-12-8; 2c, 94930-13-9; 2d, 94930-14-0; 3a, 94943-96-1; 3b, 94930-15-1; 3c, 94930-16-2; 3d, 94930-17-3; 3e, 94930-18-4; Ph<sub>2</sub>CN<sub>2</sub>Ph<sub>2</sub>, 3746-21-2; Ph<sub>2</sub>CN<sub>2</sub>C(Ph)SiMe<sub>3</sub>, 94930-05-9; Ph(Me<sub>3</sub>Si)C=O, 5908-41-8; Ph<sub>2</sub>CN<sub>2</sub>, 883-40-9; benzoyltriphenylsilane, 1171-49-9; (4-chlorobenzoyl)triphenylsilane, 1172-90-3; (4-methoxybenzoyl)triphenylsilane, 1174-56-7; 2-thenoxytrimethylsilane, 88372-95-6; tetraphenylbiphosphine, 1101-41-3; diphenylphosphine oxide, 4559-70-0; diethyl phosphite, 762-04-9; triethyl phosphite, 122-52-1; tetraethyl pyrophosphite, 21646-99-1; di-*tert*-butyl peroxide, 110-05-4.

## Geometry of Cyclohexaamylose Inclusion Complexes with Some Substituted Benzenes in Aqueous Solution Based on Carbon-13 NMR Chemical Shifts

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**Abstract:** The orientation and position of the guest molecules, benzoic acid, *p*-hydroxybenzoic acid, and *p*-nitrophenol in the cyclohexaamylose ( $\alpha$ -CD) inclusion complex have been determined by comparing the  $\alpha$ -CD complexation-induced <sup>13</sup>C shifts of guests with quantum chemical predictions. The nonpolar environmental effects produced by the  $\alpha$ -CD cavity on the <sup>13</sup>C shifts of included guest molecules have been formulated by the so-called solvent effect theory. The geometries of the complexes predicted theoretically were consistent with those in aqueous solution determined by <sup>1</sup>H NMR and those in the solid by the X-ray method.

Cycloamyloses, also well-known as cyclodextrins (which will be denoted by CD, hereafter), are cyclic oligosaccharides composed of at least six (1 → 4)-linked  $\alpha$ -D-glucosyl residues.<sup>1</sup> Each CD molecule has a toroidal, hollow, truncated cone with primary and secondary hydroxyl groups crowning the narrower and wider rims, respectively. The interior of each CD cavity contains two rings of C-H groups and a ring of glucose oxygen atoms. Hence, the interior is relatively hydrophobic, whereas the exterior is relatively hydrophilic. The most important property of CD is its ability to admit a variety of guest molecules into its hydrophobic cavity, without any covalent bonds being formed. Consequently, CDs have interested many investigators of diverse fields in both science and industry.<sup>1</sup>

High-resolution NMR spectroscopy is one of the most useful methods in the analysis of the structure and molecular dynamics of CD inclusion complexes both in aqueous solution<sup>2</sup> and in the solid state.<sup>3</sup> Earlier <sup>13</sup>C NMR studies of  $\alpha$ -CD (CD with six glucosyl residues) inclusion complexes with benzoic acid (BA),

*p*-nitrophenol (PNP), and *p*-nitrophenolate in aqueous solution have shown that the included head (head: Figure 1A) carbons are largely shielded (high-field shift) compared to the deshielding (low-field shift) of corresponding para (tail: Figure 1A) carbons.<sup>2c,d</sup> The directions of the carboxyl group of BA and the nitro group of PNP into the  $\alpha$ -CD cavity have been clearly demonstrated by <sup>1</sup>H nuclear Overhauser enhancement experiments.<sup>2c,d</sup> Similar distinctive patterns of <sup>13</sup>C displacements have been also observed for *p*-hydroxybenzoic acid (PHBA), and it has been concluded that the carboxyl group of PHBA is directed into the  $\alpha$ -CD cavity.<sup>2h</sup> A variety of substituted benzenes are known to show quite similar <sup>13</sup>C high-field (head) and low-field shifts (tail), irrespective of the kinds of substituents if their sizes are matched.<sup>2h,4</sup> If the origin of these <sup>13</sup>C displacements is accounted for, these characteristic <sup>13</sup>C displacements induced by complexation with  $\alpha$ -CD may be useful in inferring the extent of the host-guest complexation and the orientation of the guest in the  $\alpha$ -CD cavity.

In general, there are several kinds of nonbonded interactions, which may influence the <sup>13</sup>C chemical shifts of a given carbon.<sup>5,6</sup> Among them, the electrical environmental effects are expected to be the major contributor to the  $\alpha$ -CD complexation-induced <sup>13</sup>C displacements of head and tail carbons of the guest molecules, as these shifts are induced by transference of the guest molecule from the free state, surrounded by polar water molecules, to the relatively nonpolar  $\alpha$ -CD cavity. This expectation is supported by the observations of the different trends of <sup>13</sup>C displacements in the high-resolution solid-state <sup>13</sup>C NMR spectra of corresponding  $\alpha$ -CD inclusion complexes.<sup>3e</sup> In the solid state, the  $\alpha$ -CD complexation-induced shifts are caused by transference of the guest molecule from the free state, surrounded by the same molecules, to the CD cavity.

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