

the sample of di-*tert*-butyldiazomethane used to initiate these studies.

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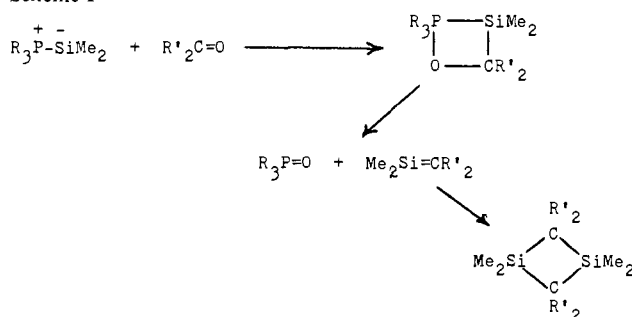
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Reactions of Hexamethylsilacyclopropane with Carbonyl Compounds in the Presence of Tertiary Phosphines. The Possible Intermediacy of a Dimethylsilylenephosphane

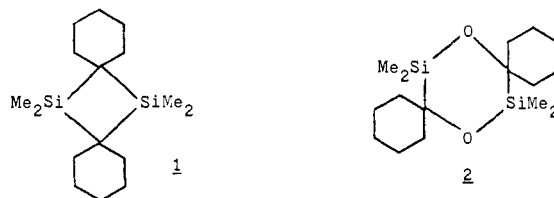
Sir:

The SiC₂ ring of hexamethylsilacyclopropane (hexamethylsilirane) is highly reactive as a result of its high ring strain.^{1,2} At 70-80 °C hexamethylsilirane undergoes dimethylsilylene transfer reactions to suitable substrates such as organosilicon hydrides,^{1b} dimethyldimethoxysilane,^{1b} internal olefins,^{1c} and internal acetylenes.^{1e,3} We became interested in the possible preparation and synthetic utilization of a silylenephosphane, R₃P⁺-Si⁻Me₂, an interesting and potentially reactive organosilicon/phosphorus intermediate which had not been reported previously. In particular, we were interested in the reactions of such an intermediate with aldehydes and ketones. A possible reaction course which is a simple analog of the well-known Wittig reaction of alkylidenephosphoranes is shown in Scheme I.

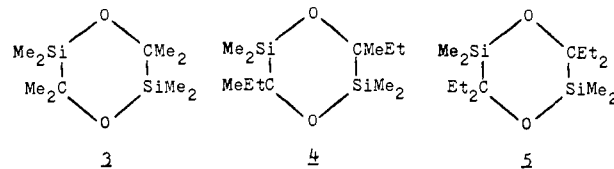
Scheme I



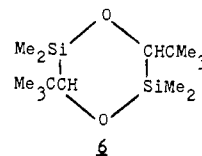
To examine this possibility, a solution containing 3.60 mmol of triphenylphosphine, 3.99 mmol of cyclohexanone, and 3.64 mmol of hexamethylsilirane^{1a} in 1 mL of benzene was stirred and heated at 75 °C under argon for 14 h. Removal of benzene at reduced pressure, followed by addition of hexane and cooling to -60°C gave white crystals of triphenylphosphine (87% recovery). GLC examination of the filtrate showed the presence of a single product, mp 100-102 °C, 26% yield, which was identified not as **1**, but rather as the 1,4-dioxo-2,5-disilacy-



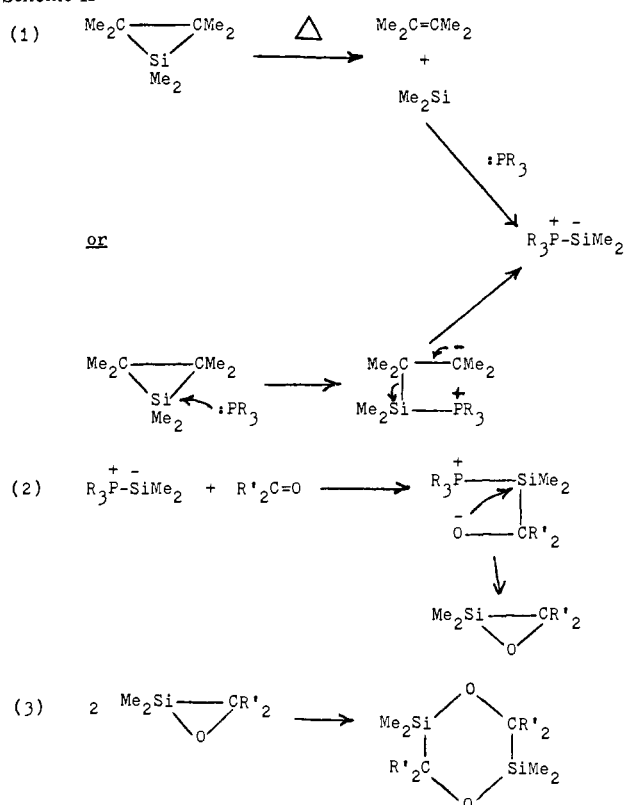
clohexane derivative **2**. Its C, H analysis was in agreement with this formulation; its mass spectrum showed the expected molecular ion at m/e 312; its ¹H NMR spectrum showed signals due to methyl substituents on silicon and to cyclohexylidene groups in the correct integrated ratio. Similar reactions using acetone, methyl ethyl ketone, and diethyl ketone were carried out and gave **3** (53%), **4** (13%, mixture of isomers) and **5** (3%), respectively. The product yield of the hexamethylsilirane-



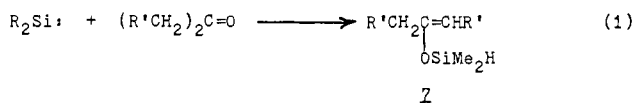
triphenylphosphine-cyclohexanone reaction could be improved by using an excess of the phosphine and of the ketone. A still better yield of **2** was obtained (48%) in a reaction carried out at 110 °C in which the silirane was added slowly to the phosphine-ketone mixture during the course of 2 h. Even more substantial yield improvement was achieved when the latter procedure was used in a reaction in which triphenylphosphine was replaced by dimethylphenylphosphine. Thus a reaction of 5.26 mmol of Me₂PhP, 1.5 mmol of cyclohexanone, and 0.83 mmol of hexamethylsilirane was carried out by adding the silirane to the hot (120 °C) phosphine-ketone solution (under argon) over a 2-h period and heating the resulting mixture for another 2 h at 120 °C. Product **2** was obtained in 92% yield (GLC). A similar reaction carried out at 98 °C with diethyl ketone gave **5** in 72% yield. Pivaldehyde also was found to react with the hexamethylsilirane-dimethylphenylphosphine system at 75 °C (18.5 h) to give **6** in 97% yield.



Scheme II



A likely mechanism by which these 1,4-dioxo-2,5-disilacyclohexanes are formed is shown in Scheme II. The phosphine is essentially a catalyst in this process since it is recovered unchanged at the end of the reaction. However, it does appear to be intimately involved in this reaction. No 1,4-dioxo-2,5-disilacyclohexane products were obtained when hexamethylsilirane and aliphatic ketones were heated together in the absence of a tertiary phosphine. The fact that the more nucleophilic dimethylphenylphosphine is much more effective in giving good product yields than is triphenylphosphine also speaks strongly for phosphine participation in this reaction. Moreover, Japanese workers have reported that reactions of silylenes ($\text{Me}_2\text{Si}^{4,5}$ and $\text{Me}_3\text{SiSiPh}^6$) with the ketones used in this study in the absence of a tertiary phosphine give silyl enol ethers as products (eq 1), rather than 1,4-dioxo-2,5-disilacyclohexanes. Products of type 7 were obtained regardless of the



method of generation of the silylene: thermally, at 500 °C in the gas phase,⁴ or photochemically in solution.^{5,6} Only in the case of nonenolizable ketones such as 2-adamantanone and norbornone were 1,4-dioxo-2,5-disilacyclohexane-type products obtained when dimethylsilylene was generated by photolysis.⁵

It would seem then that the betaine formed by reaction of the dimethylsilylenephosphorane with the ketone (Scheme II) decomposes in a manner analogous to the decomposition of the betaine derived from reaction of a sulfur ylide with a carbonyl compound, a process which gives an oxirane and a sulfide.⁷ The strong Si-O covalent bond energy and the reluctance of a silicon-carbon double bond to form very likely serve to steer the decomposition in the direction of oxasilirane formation so that a Wittig-type process does not occur.

Reduction of such 1,4-dioxo-2,5-disilacyclohexanes with lithium aluminum hydride results in formation of dimeth-

ylsilyl-substituted carbinols, $\text{Me}_2\text{HSiC}(\text{OH})\text{R}_2$, so that the hexamethylsilirane-dimethylphenylphosphine-ketone reaction also is of preparative interest. More detailed studies of this new reaction are in progress and will be reported at a later date.

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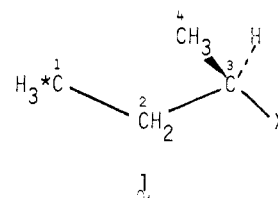
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γ -Methyl Substituent Effect on Vicinal Coupling Constants Involving Carbon-13

Sir:

The γ effect on ^{13}C chemical shielding, which arises from gauche 1,4 carbon atoms,¹ has been used widely in ^{13}C chemical shift assignments. This effect has been interpreted² in terms of a model which emphasizes the steric interactions between the hydrogens on the C-1 and C-4 atoms in the arrangement **1**. In the present study, it is shown from both ex-



perimental and theoretical results that the γ -methyl or -methylene substituents on C-3 decrease the magnitude of the vicinal ^{13}C coupling constants ($^3J_{\text{CX}}(180^\circ)$) between the C-1 atom and the trans oriented nuclear spin X in **1**. Moreover, it is essential to be aware of the γ -methyl effect in using vicinal coupling constants in molecular conformational studies as the effects are shown to be substantial and lead to results which would appear to be anomalous.

In a previous study³ it was found that vicinal ^{13}C - ^{13}C coupling constants in a series of 1-substituted butyl compounds (for which conformational averaging is expected) were uniformly greater in magnitude than the $^3J_{\text{CC}}(180^\circ)$ for a series of 11-substituted 1-methyladamantanes (one might expect these to conform to the largest values entering the averaged coupling constants in the butyl series). In the same study³ it was shown that the Fermi-contact contributions (INDO-FPT^{4,5}) to $^3J_{\text{CC}}(180^\circ)$ in the series *trans*-butane, equatorial