Preparation and Spectral Properties of β -Silyl-Substituted α , β -Unsaturated Ketones

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The preparation of 4,4-dimethyl-4-silacyclohexadien-1-one, 4,4-diphenyl-4-silacyclohexadien-1-one, 4,4-dimethyl-4-silacyclohex-2-enone, and 4-trimethylsilyl-3-buten-2-one is reported. The effect of the silyl center on the $n \rightarrow \pi^*$ transition in their uv spectra is discussed.

Brook's discovery of the unusual spectral properties of α -silvl ketones stimulated research to determine the mechanism of silicon's effect.^{2,3} A shift to lower energy in an $n \rightarrow \pi^*$ transition can be produced either by lowering the energy of the excited π^* state or by raising the energy of the ground state. Theoretical molecular orbital models indicate that the π^* state could be stabilized by interaction with the empty d orbitals on silicon.^{4,5} The energy level of the ground state n electrons has been probed by basicity⁶ and appearance potential measurements.^{7,8} The energy of the π^* state has been determined from the polarographic half-wave potential for adding an electron to the system.^{7,8}

A related effort has been the preparation of new systems in which different types of interaction of the silvl center with unsaturated chromophores may be discovered.9-12

Numerous α,β -unsaturated carbonyl systems have been prepared and their uv spectra reported. However, no system containing a silvl center interacting with a carbonyl functionality through a conjugating carbon-carbon double bond has been reported.18

We felt that such a system would be of interest for the following reasons. Stabilization of the $n \rightarrow \pi^*$ transition in a α -silvl ketones is mainly produced by destabilization of the ground state by inductive electron release from the silvl center.^{3,14} Stabilization of the excited π^* state by overlap with the empty d orbitals on silicon also occurs but is much less important. In a β -silyl-substituted α,β -unsaturated ketone, inductive effects by silicon on the n electrons of oxygen will be much less important, since inductive effects are known to diminish rapidly with distance. Zimmerman has also calculated that in the n $\rightarrow \pi^*$ state of an α,β -unsaturated ketone a charge separation develops in which the β carbon becomes partially negatively charged, while the carbonyl oxygen becomes

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partially positively charged.¹⁵ Silicon is well known to stabilize a negative charge adjacent to it, possibly by

$$C = C - C = O \xrightarrow{n\nu} {}^{-\delta}C - C = C - O^{+\delta}$$

 $d_{\pi} - p_{\pi}$ overlap.¹⁶⁻¹⁸ Hence, we expected a β -silyl center to have a pronounced effect on the $n \rightarrow \pi^*$ transition in an α,β -unsaturated ketone, owing to its ability to stabilize the polar excited π^* state. To test these ideas, we have prepared 4.4-dimethyl-4-silacyclohexadien-1-one, 4,4-diphenyl-4-silacyclohexadien-1-one, 4,4dimethyl-4-silacyclohex-2-enone, and 4-trimethylsilyl-3buten-2-one.

We have previously reported the preparation of 4,4dimethyl-4-silacyclohexadien-1-one¹³ by the selenium dioxide oxidation of 4,4-dimethyl-4-silacyclohexanone.19 While this method works, problems with removal of traces of foul-smelling organo selenium by-products caused us to seek a cleaner reaction. 4.4-Dimethyl-4-silacvclohexadien-1-one has also been prepared by oxidation of 4,4-dimethyl-4-silacyclohexanone using 2,3dichloro-5,6-dicyanoquinone (DDQ) in refluxing benzene.^{20,21}

4.4-Diphenyl-4-silacyclohexadien-1-one was prepared by oxidation of 4,4-diphenyl-4-silacyclohexanone, a previously unknown compound. Our sequence began with the preparation of diphenyldiallylsilane^{22,23} by the in situ trapping of allyl Grignard by diphenyldichlorosilane. Diphenyldiallylsilane was converted to 4,4diphenyl-4-sila-1,7-heptanediol by Brown's hydroboration-oxidation sequence^{24,25} in high yield owing to the directive effect of the γ -silyl center.²⁶ The diol was oxidized using Jones reagent.^{27,28} However, the yield was not good owing to competitive cleavage of the phenyl-silicon bonds by acid.^{29, 30} The diacid was

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esterified with methanol and cyclized by a modified Dieckmann reaction to close the six-membered ring.³¹ The enolate anion formed in the cyclization was trapped by addition of trimethylchlorosilane to yield the corresponding silyl enol ether. This prevents the reverse reaction which occurs if quenching of the anion is slow as it is by addition of water.³² This silyl enol ether was refluxed overnight in aqueous methanolic HCl. Hydrolysis of the trimethylsilyl group, decarboxylation of the β -keto acid, and a significant amount of undesired cleavage of phenyl-silicon bonds occurred in this step.^{29,30} 4,4-Diphenyl-4-silacyclohexanone thus prepared was oxidized to the corresponding dienone by DDQ.^{20,21}

4,4-Dimethyl-4-silacyclohex-2-enone could not be prepared by treatment of 4,4-dimethyl-4-silacyclohexanone¹⁹ with either a limited amount of selenium dioxide or DDQ. When less than 1 equiv of oxidizing reagent was used, the only products obtained were the dienone and starting ketone. Apparently, the desired enone is more easily oxidized than the starting ketone.

This problem was overcome as follows. 4,4-Dimethyl-4-silacyclohexanone was converted to the corresponding enol acetate by House's procedure.³³ The enol acetate was brominated with N-bromosuccinimide,³⁴ to form two allylic bromides in comparable yield. Apparently, the silyl center did not significantly stabilize a radical center either on a carbon α or on one β to it. The allylic bromide with the bromine β to silicon undergoes fragmentation during the subsequent solvolysis.^{35,36} The allylic bromide with bromine α to silicon undergoes elimination to yield the desired enone (eq 1). Unfortunately, any intermediate enol acetate which was not brominated hydrolyzes to the starting ketone. Separation of the starting ketone from the product enone was accomplished by preparative gas chromatography.

4-Trimethylsilyl-3-buten-2-one was prepared from 4-trimethylsilylbutan-2-one³⁷ by the same reaction sequence used to prepare 4,4-dimethyl-4-silacyclohex-2enone. Reaction with acetic anhydride leads to three isomeric enol acetates: 2-acetoxy-4-trimethylsilyltrans-2-butene (I), 2-acetoxy-4-trimethylsilyl-cis-2-butene (II), and 2-acetoxy-4-trimethylsilyl-1-butene (III).³³ Only I and II react with N-bromosuccinimide to yield bromides capable of undergoing elimination to the desired product.³⁴

The ir of these silyl-substituted α,β -unsaturated ketones is of some interest. The C–O double-bond stretch in the silyl compounds is only slightly different from that observed in the analogous all-carbon compounds (see Table I). The only case where a significant difference is observed is 4,4-dimethyl-4-silacyclohexadien-1-one, which comes at 1648 cm⁻¹ compared to 1664 cm⁻¹ for 4,4-dimethylcyclohexadien-1-one.¹⁵ By comparison, the C–O stretch of trimethylsilyl methyl

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| INFRARED SPECTI | RAL COMPARISONS | ja . |
|------------------------------------|----------------------------------|--|
| Compd Trimethylvinylsilane | C=O stretch, cm ⁻¹ | $\begin{array}{c} C = C \text{ stretch}, \\ em^{-1} \\ 1597^b \end{array}$ |
| (CH ₄) ₃ Si | 1683 (s) 1701 (w) | 1586 (w) |
| | 1685 (s) 1706 (w) | 1620 |
| | 1678 (s) | 1573 (w) |
| | 1684 (s) | 1626 (w) |
|)sio | 1648 (s) | 1584 (s) |
| ×>-o | 1664 (s) | 1630 (s) |
| Ph Si O | 1653 (s) | 1586 |
| Ph Ph | 1652 (s) | 1626° |
| | | |

^a All spectra were determined on a Beckman IR-7 instrument in cyclohexane solution. ^b Reference 39. ^c Reference 46.

ketone comes at 1645 cm⁻¹,³⁸ while that of *tert*-butyl methyl ketone, the carbon analog, comes at 1718 cm⁻¹,³⁹ Another example is trimethylsilyl phenyl ketone, whose C–O double-bond stretch comes at 1618 cm⁻¹,⁴⁰ compared with 1680 cm⁻¹ for *tert*-butyl phenyl ketone.⁴¹ Clearly, the ground-state C–O double bond is much more perturbed in α -silyl ketones than in our silyl-substituted α,β -unsaturated ketones.

On the other hand, the C–C double-bond stretch in our silyl compounds all comes at considerably longer wavelength than in the analogous all-carbon compounds. However, the C–C double bond of trimethylvinylsilane is also shifted⁴² to 1597 cm⁻¹, whereas the



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TABLE I

C-C double bond of normal 1-alkenes comes at ~ 1650 cm^{-1.43} Hence, we believe the ir spectra indicate little perturbation of the ground state of the α,β -unsaturated carbonyl chromophore in our compounds.

In the uv spectra of these β -silyl-substituted α,β unsaturated ketones, the $n \rightarrow \pi^*$ transitions were identified by their characteristic vibrational fine structure as well as by the fact that the band shifted to shorter wavelengths in ethanol than in cyclohexane⁴⁴ (see Experimental Section for details). Authentic samples of 4,4-dimethylcyclohex-2-enone,⁴⁵ 4,4-dimethylcyclohexadien-1-one,¹⁵ 4,4-diphenylcyclohexadien-1-one,⁴⁶ 2-cyclohexenone, and methyl vinyl ketone were prepared and their spectral properties compared under identical conditions.

The λ_{\max} of the $n \rightarrow \pi^*$ transition in all of the silvl compounds is shifted to longer wavelength than their carbon analogs. The transition for 4,4-dimethyl-4-silacyclohexadien-1-one is stabilized by 5.6 kcal/mol compared with that of 4,4-dimethylcyclohexadien-1-one (see Table II). This transition is stabilized by 5.2

TABLE II ULTRAVIOLET SPECTRAL DATA $n \rightarrow \pi^*$

| Compd | Registry no. | λ _{max} in Å (band) (ε) | 0-0 band in Å |
|------------------------------------|-----------------|-------------------------------------|------------------|
| | 30518-19-5 | 3725 (0-3) (16) | 4180 |
| ~ -0 | 1073-14-9 | 3470 (0-3) (15) | 3885ª |
| Ph Si O | 34564-64-2 | 3740 (0-3) (19) | 4205 |
| Ph ph | 13304-12-6 | 3500 (0-3) (25) | 3920b |
| | 34564-66-4 | 3500 (0-2) (35) | 3865 |
| (CH ₃) ₃ Si | 34564-67-5 | 3380 (0-3) (49) | 3860 |
| | 1073-13-8 | 3400 (0-2) (26) | |
| ~ _0 | 930-68-7 | 3430 (0-2) (28) | |
| \sim | 78-94-4 | 3300 (0-3) (22) | |

^a The 0–0 band for 4,4-dimethylcyclohexadien-1-one has been reported at 3770 Å (see ref 15). We have prepared this conpound from 4,4-dimethylcyclohex-2-enone⁴⁶ by oxidation with either selenium dioxide or DDQ. In both cases we find the 0–0 band at 3885 Å. However, this may not be an experimental discrepancy but a difference in interpretation. The experimental section of ref 15 reports a band at 3883 Å in cyclohexane. ^b Reference 15.

kcal/mol in 4,4-diphenyl-4-silacyclohexadien-1-one compared with 4,4-diphenylcyclohexadien-1-one.⁴⁶ Comparison of energies of the 0-0 bands¹⁵ of the $n \rightarrow \pi^*$ transitions for these compounds yields similar values for the stabilization by the silyl center. This observation that a diphenylsilyl group has approximately the same effect as a dimethylsilyl group supports our view that the effect of the silyl center on the $n \rightarrow \pi^*$ transition is mainly due to stabilization of the polar π^* excited state. This is true, since a diphenylsilyl group is expected to have a smaller inductive electron-releasing effect than a dimethylsilyl group. Phenyl groups are well known to be inductively electron withdrawing.⁴⁷

This difference in inductive effects has been observed in the spectra of α -silvl ketones. The λ_{\max} of the $n \rightarrow$ π^* transition in *tert*-butyl methyl ketone comes at $34,800 \text{ cm}^{-1}$, whereas in trimethylsilyl methyl ketone it comes at 26,900 $cm^{-1.14}$ Thus, the stabilization of the n $\rightarrow \pi^*$ transition by a trimethylsilyl group amounts to 22.6 kcal/mol. On the other hand, the λ_{\max} of the $n \rightarrow \pi^*$ transition in triphenylmethyl methyl ketone comes at 33,100 cm⁻¹, whereas in triphenylsilyl methyl ketone it comes at 26,600 cm^{-1.14} Thus, the stabilization of the $n \rightarrow \pi^*$ transition by a triphenylsilyl group amounts to 18.5 kcal/mol. In the corresponding phenyl ketones, a trimethylsilyl group is found to stabilize the $n \rightarrow \pi^*$ transition by ~4 kcal/ mol more than a triphenylsilyl group when both are compared with those of the corresponding carbon compounds. This difference in stabilization probably occurs because the trimethylsilyl group has a larger inductive electron-releasing effect, causing a greater destabilization of the ground state.

Further, stabilization by the silvl center in α,β -unsaturated ketones appears to be additive. Comparison of the λ_{\max} for the n $\rightarrow \pi^*$ transition in 4,4-dimethyl-4-silacyclohex-2-enone with that observed for 4,4-dimethylcyclohex-2-enone and 2-cyclohexenone indicates a stabilization by the silvl center of ~ 2.4 kcal/ mol. Comparison of the λ_{max} for the $n \rightarrow \pi^*$ transition in 4-trimethylsilyl-3-buten-2-one with that observed in methyl vinyl ketone indicates a stabilization by the silyl center of ~ 2.1 kcal/mol. Thus, the stabilization by a β -silvl center of the $n \rightarrow \pi^*$ transition in an enone system is approximately half that observed in the β silyl dienone systems. Apparently, the geometry about the carbon-carbon double bond is not important, since the open-chain silvl enone in which the carboncarbon double bond is trans shows almost the same stabilization.

In conclusion, the effect of a β -silyl center on the n $\rightarrow \pi^*$ transition in α,β -unsaturated ketones is much smaller than the stabilization by silicon in α -silyl ketones. The mechanism of this stabilization may be primarily the interaction of the silyl center with the polar excited π^* state.

Experimental Section

All reactions were carried out under an atmosphere of nitrogen. Melting points are uncorrected. Ir spectra were determined in CCl₄ solution on a Perkin-Elmer 337, unless otherwise noted. Nmr spectra were run on a Varian HA-100 using 10% solutions in CCl₄. Benzene, methylene chloride, 1,2-dichloroethane, or tetramethylsilane was used as an internal standard. Microanalysis was performed by Elek Microanalytical Laboratory or by Schwarzkopf Microanalytical Laboratory. All uv spectra were run on a Cary 14 in either spectro-quality cyclohexane or in ethanol. High resolution mass spectra were run on an AEI MS-902 instrument. Exact mass determination of the composi-

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tion of important ions were carried out at a resolution of at least 10,000 by peak matching with peaks of known mass of perfluorokerosene: ionizing voltage 70 eV; filament emission 480 μ A; source temperature 150°.

4,4-Dimethyl-4-silacyclohexadien-1-one.—In a dry 50-ml round-bottom flask equipped with a reflux condenser and a magnetic stirring bar 1 g (7 mM) of 4,4-dimethyl-4-silacyclohexanone, ¹⁹ 5.0 g (22 mM) of DDQ, and 30 ml of dry benzene were refluxed for $24 \text{ hr.}^{20,21}$ It was then chromatographed through a short alumina column with ether. The solvent was removed by evaporation under reduced pressure at 25° . The residue was then bulb to bulb distilled at 0.1 mm. Essentially pure 4,4-dimethyl-4-silacyclohexadien-1-one (600 mg) was thus obtained. Analytical samples were purified by preparative gas chromatography on a 0.25 in. \times 5 m 20% DC QF-1 column at 130°. (For ir data, see Table I). The uv spectrum showed peaks at 4180 Å (ϵ 4), 3985 (9), 3885 (13), 3725 (16), 3570 (14), 3440 (10), 3220 (6), and 2275 (1.8 \times 10⁴) in cyclohexane. In 95% ethanol one observes peaks at 3540 Å (ϵ 30) and 2330 (1.2 \times 10⁴). The nmr spectrum contained the following: s (6 H) at δ 0.22, d (2 H) at 6.71 (J = 15 Hz), d (2 H) at 6.98 ppm (J = 15 Hz) in CH₂Cl₂; (J = 15 Hz) in CL₂; (2 H) at 6.70, d (2 H) at 6.93 ppm (J = 15 Hz) in CL₂O₁₂, in CCL₄; s (6 H) at δ 0.22, d (2 H) at 6.71, d (2 H) at 7.12 ppm (J = 15 Hz) in acetone. This type of shift of the β proton in α,β -unsaturated ketones has been observed previously. The β proton shifts downfield in solvents of higher dielectric constant. Anal. Caled for C7H10OSi: C, 60.82; H, 7.29. Found: C, 60.55; H, 7.24

Diphenyldiallylsilane prepared from allylmagnesium bromide and diphenyldichlorosilane in THF had physical properties in agreement with literature values.^{22,23} Their spectrum had a C-C double-bond stretch at 1630 cm⁻¹; nmr d (4 H) at δ 2.05 (J = 9.5 Hz), m (4 H) at 4.85, m (2 H) at 5.75, m (10 H) at 7.32 ppm.

4,4-Diphenyl-4-sila-1,7-heptanediol was prepared by hydroboration and oxidation of diphenyldiallylsilane.^{24,25} The crude product (87% yield) was purified by recrystallization from ethern-hexane, mp 83-85°. Its ir spectrum had a broad O-H band centered at 3330 cm⁻¹; nmr (in acetone- d_{δ}) m (4 H) at δ 1.14, m (4 H) at 1.58, m (4 H) at 3.52, s (2 H) at 3.77, m (10 H) at 7.35 ppm. Anal. Calcd for C₁₈H₂₄O₂Si: C, 71.95; H, 8.05. Found: C, 71.80; H, 7.94.

4,4-Diphenyl-4-sila-1,7-heptanedioic Acid.—In a 5-l. flask equipped with a mechanical stirrer, a thermometer, and an addition funnel 170 g (0.57 mol) of 4,4-diphenyl-4-sila-1,7-heptanediol was dissolved in 700 ml of reagent acetone in an ice-salt bath; 1.14 l. of Jones reagent was added at a rate such that the temperature remained below 20°.25,26 The mixture was stirred for an additional 15 min. The organic layer was separated, and the aqueous layer was extracted with three 500-ml portions of ether. The combined organic layers were extracted with 20% sodium hydroxide solution until the extract was basic. This basic aqueous solution was then acidified with concentrated HCl and extracted with three 500-ml portions of ether. The ether extracts were dried over anhydrous MgSO4 and filtered, and the solvent was removed by evaporation under reduced pressure. A 50% yield of crude diacid was obtained. The diacid was purified by recrystallization from acetone-n-hexane, mp 143-144°. Its ir spectrum in CH₃CN solvent had a C-O double-bond stretch at 1740 cm⁻¹; nmr (acetone- d_6) m (4 H) at δ 1.47, m (4 H) at 2.33, m (10 H) at 7.47, s (2 H) at 10.40 ppm. Anal. Calcd for $C_{18}H_{20}O_4Si:$ C, 65.82; H, 6.14%. Found: C, 65.98; H, 6.13.

Dimethyl-4,4-diphenyl-4-sila-1,7-heptanedioate.—Crude diacid (90 g) dissolved in 600 ml of methanol containing 5 ml of concentrated H_2SO_4 in a 1-liter flask was refluxed overnight. The volume of the solution was reduced to one-third by evaporation under reduced pressure. Ether (500 ml) was added and the solution was extracted twice with 100-ml portions of water followed by 100-ml portions of 10% NaOH until the extracts were basic. The organic layer was dried over anhydrous MgSO₄ and filtered, and the solvent was removed by evaporation under reduced pressure. The residue was distilled through a short-path distillation column, bp 150° (0.001 mm).

An 80% yield of a light yellow oil was obtained. Its ir spectrum in CCl₄ solution had a strong C-O double-bond stretch at 1745 cm⁻¹; nmr m (4 H) at δ 1.39, m (4 H) at 2.25, s (6 H) at 3.47, m (10 H) at 7.36 ppm. Its mass spectrum (Table III) was characterized by an acylium ion and by two siliconium ions

TABLE III

| | | Rel intensity, |
|--|------------------|-------------------|
| | Mass | % |
| Ph Ph Si $C^+=0$ CO_2CH_3 | 325 | 11 |
| $PhSi^+ \longrightarrow CO_2CH_3 CO_2CH_3$ | 279ª | 100 |
| Ph_Si ⁺ CO ₂ CH ₃ | 269 ^b | 93 |
| Caled for CHOSi | 270 1052 Found | 270 1040 |

^a Calcd for $C_{14}H_{19}O_4Si$: 279.1052. Found: 279.1040. ^b Calcd for $C_{16}H_{17}O_2Si$: 269.0997. Found: 269.0954.

formed by fragmentation at the quaternary silyl center. The exact masses of the two intense siliconium ions were determined.

4,4-Diphenyl-4-silacyclohexanone.-In a dry 2-l. three-necked round-bottom flask equipped with a mechanical stirrer, a pressure equalizing addition funnel, and a reflux condenser was placed 1 mol of sodium hydride and 11. of dry toluene. The mixture was stirred at reflux, while 70 g (0.22 mol) of dimethyl 4,4-diphenyl-4-sila-1,7-heptanedioate was added during 4 hr, followed by 66 g (0.6 mol) of trimethylchlorosilane.³¹ The mixture was filtered and stripped of solvents at atmospheric pressure. was refluxed overnight with 300 ml of methanol, 100 ml of H_2O , and 25 ml of concentrated HCl. The solution was extracted with three 100 ml portions of ether. The combined organic layer was dried over anhydrous MgSO4 and filtered, and the solvent was removed by evaporation under reduced pressure. The residue was distilled through a 10-cm Vigreux column. A central fraction, bp 190° (0.5 mm), 10 g (12% yield), solidified on standing and was further purified by recrystallization from ether-n-hexane, mp 93-94°. Its ir spectrum was characterized by a C-O double-bond stretch at 1720 cm⁻¹ in CCl₄ solution; nmr (1,2-dichloroethane) m (4 H) at δ 1.46, m (4 H) at 2.54, m (10 H) at 7.43 ppm. Anal. Calcd for C₁₇H₁₈OSi: C, 76.64; H, 6.81. C, 76.58, 76.82; H, 6.82, 6.77. Found:

4,4-Diphenyl-4-silacyclohexadien-1-one.—In a dry 100-ml round-bottom flask equipped with a reflux condenser and a magnetic stirring bar was placed 2 g (7.5 mM) of 4,4-diphenyl-4-silacyclohexanone, 5.1 g (22.6 mM) of 2,3-dichloro-5,6-dicyano-quinone (DDQ) and 50 ml of benzene. The mixture was refluxed for 24 hr with stirring.^{20,21} It was then chromatographed through a short alumina column with ether. Solvent was removed by evaporation under reduced pressure; 800 mg of a thick yellow oil was obtained (40% yield). The oil solidified on standing at 0°. It was purified by recrystallization from methanol at 0°, to yield a slightly yellow solid: mp 67.3-67.9°; for ir spectrum, see Table I; nmr (CCl₄) d (2 H) at 7.40 ppm; nmr (acetone) δ d (2 H) at 6.96 (J = 14.8 Hz), m (12 H) at 7.50 ppm;⁴⁸ uv (cyclohexane) peaks at 4205 Å (ϵ 3), 4010 (9), 3900 (15), 3740 (19), 3590 (15), 3460 (9), and 3320 (3) in cyclohexane; uv (95% EtOH) λ_{max} 3540 Å (ϵ 28). Anal. Calcd for C₁₇H₄OSi: C, 77.82; H, 5.38. Found: C, 77.78; H, 5.62.

acetic anhydride was slowly distilled through a 30-cm spiral wire distillation column from a stirred solution of 19.9 g (0.14 mol) of 4,4-dimethyl-4-silacyclohexanone¹⁹ in 40 ml of acetic anhydride containing 300 mg of p-toluenesulfonic acid.38 The amount of acetic acid in the distillate was determined by pmr After 5 hr the theoretical amount of acetic acid integration. had been collected. One gram of sodium acetate was then added to neutralize the p-toluenesulfonic acid. The solution was cooled, diluted with 150 ml of ether, and extracted with two 50-ml portions of sodium bicarbonate solution. It was dried over anhydrous MgSO4 and filtered, and the solvent was removed by evaporation under reduced pressure at room temperature. The residue was distilled through a 10-cm Vigreux column. A central fraction, 15.5 g (60% yield), bp 116-117° (30 mm), was collected. Its ir spectrum was characterized by a C-O double-bond stretch at 1750 and a C-C double-bond stretch at 1680 cm⁻¹ (weak) (this is typical for C-C double bonds in enol acetates³³); nmr s (6 H) at δ 0.03, t (2 H) at 0.69 (J = 7 Hz), d of t (2 H) at 1.11 $(J_{\rm d} = 5.5 \,{\rm Hz}, J_{\rm t} = 2 \,{\rm Hz})$, s (3 H) at 1.92, t (2 H) at 2.19 (J = 7 Hz), t of t (1 H) at 5.24 ppm $(J_t = 5.5 \text{ Hz}, J_t = 1 \text{ Hz})$. Anal.

⁽⁴⁸⁾ F. H. Cottee and C. J. Timmons, J. Chem. Soc. B, 326 (1968).

Calcd for $C_9H_{16}O_2Si$: C, 58.65; H, 8.75. Found: C, 58.48; H, 8.80.

4,4-Dimethyl-4-silacyclohex-2-enone.—In a dry 500-ml flask equipped with a reflux condenser and a magnetic stirring bar was placed 15.5 g (84.4 mM) of 1-acetoxy-4,4-dimethyl-4-sila-1-cyclohexene, 16.5 g (92.6 mM) of N-bromosuccinimide, 100 ml of reagent carbon tetrachloride, and a catalytic amount of benzoyl peroxide. The mixture was heated to reflux.³⁴ Reaction was complete within 3 min. Succinimide was removed by filtration. CCl₄ was removed by evaporation under reduced pressure. To the residue was added 150 ml of THF and 25 g of Na₂CO₃ dissolved in 150 ml of water.³⁴ This solution was heated at reflux for 1 hr. The solution was cooled and the layers were separated. The aqueous layer was extracted with two 50-ml portions of ether. The combined organic layers were dried over anhydrous MgSO₄ and filtered, and the solvent was removed by evaporation under reduced presure at 25°. The residue was chromatographed on an alumina column. A mixture of the desired enone and the starting ketone was eluted with 1:1 ether*n*-hexane. The ketone and enone were separated by preparative gas chromatography on a 0.25 in. \times 5 m 20% DC QF-1 column at 120°. For its ir spectrum, see Table 1. Its nmr spectrum (CCl₄) contained the following: s (6 H) at δ 0.19, m (2 H) at 1.03, m (2 H) at 2.56, d (1 H) at 6.47 (J = 1445 Hz), d (1 H) at 6.82 ppm (J = 14.5 Hz). The chemical shifts of the downfield doublets showed a solvent dependence with the $cis-\beta$ proton shifting downfield in solvents of higher dielectric constant.⁴⁸ In cyclohexane the doublets were found at 6.45 and 6.72 ppm; in dioxane at 6.50 and 6.88 ppm; in acetone at 6.48 and 6.97 ppm; and finally in acetonitrile at 6.51 and 7.01 ppm. The uv spectrum in cyclohexane showed peaks at 3865 Å (ϵ 7), 3675 (23), 3500 (35), 3390 (35), 3260 (26), 3120 (15) and 2155 (1.0×10^4). In 95% EtOH one observes peaks at 3295 Å (ϵ 30) and 2220 (3.7×10^3) . Anal. Calcd for C₇H₁₂OSi: C, 59.94; H, 8.62%. Found: C, 59.79; H, 8.85.

2-Acetoxy-4-trimethylsilyl-2-butene.-In a dry 100-ml flask equipped with a reflux condenser and a magnetic stirring bar was placed 5.5 g (38.2 mM) of 4-trimethylsilyl-2-butanone,³⁷ 50 ml of acetic anhydride, and 300 mg of p-toluenesulfonic acid.³³ The mixture was stirred at reflux overnight. The reflux condenser was then replaced with a 10-cm Vigreux column, 40 ml of solvent was removed by distillation over 1 hr, and 1 g of sodium acetate was then added to neutralize the acid. After cooling, the mixture was placed in a separatory funnel with 150 ml of ether. The organic laver was washed with three 20-ml portions of sodium bicarbonate solution. It was dried over anhydrous MgSO4 and filtered, and the solvent was removed by evaporation under reduced pressure. The residue was distilled through a 10-cm Vigreux column. A fraction, 2 g (30% yield), bp 100- $120^{\circ}/(30 \text{ mm})$, was collected. The three possible enol acetates were separated by preparative gas chromatography on a 0.25 in. \times 5 m 20% FFAP column at 120°. The relative ratios of 2-acetoxy-4-trimethylsilyl-trans-2-butene (I), 2-acetoxy-4-trimethylsilyl-*cis*-2-butene (II), and 2-acetoxy-4-trimethylsilyl-1-butene (III) were found to be I:II:III 5:3:1. The ir spectrum of (III) showed a C-O double-bond at 1740 cm⁻¹. The ir spectra of pure I and II were characterized by a C–O double-bond stretch at 1755 cm⁻¹. The nmr spectrum of I showed s (9 H) at δ 0.0, d of quartets (2 H) at 1.30 ($J_d = 8.2 \text{ Hz}$, $J_q = 1.2 \text{ Hz}$), d of t (3 H) at 1.85 ($J_d = 1.2 \text{ Hz}$, $J_t = 1.2 \text{ Hz}$), s (3 H) at 1.98, and t of quartets (1 H) at 4.83 ppm ($J_t = 8.2 \text{ Hz}$, $J_q = 1.2 \text{ Hz}$). The nmr spectrum of II was nearly identical. The mass spectrum of I was determined. Major ions at P - 42 and P - 43 were observed. Loss of ketene (P - 42) to form the parent ketone is a known process in the mass spectra of enol acetates.^{49,50} Loss of CH₃C=O by α cleavage is often observed in the mass spectra of acetates. The exact mass of the parent ion and the P - 42 ion were determined. Parent ion + calcd for C₉H₁₈O₂Si: 186.1075. Found: 186.1076. P - 42 calcd for C₉H₁₈O₂Si: C, 58.01; H, 9.74. Found: C, 57.74; H, 9.71. **4-Trimethylsilyl-3-buten-2-one.**—In a dry 100-ml flask

equipped with a reflux condenser and a magnetic stirring bar 2.0 g (10.8 mM) of 2-acetoxy-4-trimethylsilyl-2-butene was refluxed with 1.8 g (10.1 mM) of N-bromosuccinimide in 25 ml of CCl₄ and a catalytic amount of benzoyl peroxide.³¹ The reaction was complete within 3 min. Succinimide was removed by filtration. CCl, was removed under reduced pressure at 25°. The residue in 20 ml of THF was stirred overnight at 25° with 5 g of Na₂CO₃ in 20 ml of water. The aqueous layer was separated and extracted twice with two 20-ml portions of ether. The combined organic layers were washed with a saturated NaCl solution, dried over anhydrous MgSO4, filtered, and evaporated under reduced pressure at room temperature. The residue was bulb to bulb distilled at 0.15 mm; 1.01 g of volatile material was obtained. The desired enone was separated from the starting ketone by preparative gas chromatography on a 0.25 in. \times 5 m Recover by preparative gas enformatography of a 0.25 nr. \times 5 nr. \times 5 nr. \oplus 5 nr (1.1 \times 10⁴); uv (95% EtOH) peaks at 3260 Å (ϵ 60.5), 2230 (1.3×10^4) . The base peak in the mass spectrum of 4-trimethylsilylbut-3-en-2-one was a siliconium ion formed by loss of a methyl radical from the parent ion. The exact mass of the parent ion and the P - 15 were determined. Parent ion + calcd for C₇H₁₁OSi: 142.0813. Found: 142.0784. P - 15 calcd for C₆H₁₁OSi: 127.0578. Found: 127.0550.

Registry No.—I, 34564-95-9; II, 34564-96-0; III, 34564-70-0; diphenyldiallylsilane, 10519-88-7; 4,4-diphenyl-4-sila-1,7-heptanediol, 34564-72-2; 4,4-diphenyl-4-sila-1,7-heptanedioic acid, 34564-73-3; dimethyl 4,4-diphenyl-4-sila-1,7-heptanedioate, 34564-74-4; 4,4-diphenyl-4-silacyclohexanone, 34564-75-5; 1-acetoxy-4,4-dimethyl-4-sila-1-cyclohexene, 34599-24-1.

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