Silyl-substituted α,β -Unsaturated Ketones from the Reaction of Silvlvinvlmetallic Reagents with Acid Anhydrides

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The reactions of a series of silyl-substituted vinylmetallic reagents with acetic and benzoic anhydride have been investigated as a general route to α,β -unsaturated ketones having a silvl group attached to the carbon-carbon double bond. The reaction has been found to be generally applicable for acetyl derivatives provided low temperatures are used but the reaction with benzoic anhydride gives poorer results. The i.r. and u.v. spectra of the ketones are discussed. The characterization of novel 1,4-dienes obtained as byproducts in the syntheses is also described.

Les réactions d'une série de réactifs vinylmétalliques substitués par le silyle sur l'anhydride acétique et benzoique ont été étudiées comme voie générale d'accès aux cétones α,β insaturées avec un groupe silvle attaché à la double liaison carbone-carbone. La réaction est d'application générale pour les dérivés acétyles pourvu qu'on se place aux basses températures mais avec l'anhydride benzoique, cette réaction conduit à des résultats plus pauvres. Les spectres i.r. et u.v. des cétones ont été discutés. La caractérisation des diènes-1,4 nouveaux produits secondaires des synthèses, a été également donnée.

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Some years ago several α,β -unsaturated ketones having a silvl group directly attached to the carbon-carbon double bond were synthesized by the hydrosilylation of an acetylenic ketone (1, 2). However, the reaction led to a mixture of α - and β -silvlvinyl ketones which proved to be difficult to separate (eq. 1).

[1] $R_3SiH + HC \equiv CCOMe \longrightarrow$

F

$$R_3S_i$$
 $C = C$ H R_3S_i $C = CH_3$ CH_3CO

More recently Felix and Weber (3) described a different synthetic approach to β -silylvinyl ketones involving dehydrogenation of the saturated γ -ketosilanes (eq. 2). Another route recently

[2] $R_3SiCH_2CH_2COCH_3 \rightarrow R_3SiCH=CHCOCH_3$

used to prepare β -silylvinyl ketones and aldehydes involved the hydrolysis of silylallyl ethers (4) (eq. 3). It appeared to us that a more gen-

[3]
$$R \rightarrow O \rightarrow CR' = C = CR''(SiMe_3) \xrightarrow{H^+}_{H_2O}$$

 $R' \rightarrow C \rightarrow CH = CR''(SiMe_3)$

erally applicable route to both α - and β -silvl

would be through the coupling of silvlvinylmetallic reagents with anhydrides, and the following deals with such couplings using acetic and benzoic anhydride.

Four previously described organometallic reagents were utilized: α -lithiovinyltriphenylsilane (1), (5), 1-lithio-1-triphenylsilyl-2-phenylethylene-E (2) (5), α -trimethylsilylvinylmagnesium bromide (3) (6), and β -trimethylsilylvinylmagnesium bromide (4) (6). All four reagents coupled with acetic anhydride to give the acetyl derivatives 1a, 2a, 3a, and 4a and the triphenylsilyl reagents, 1 and 2, coupled with benzoic anhydride to give the benzoyl derivatives 1b and 2b. Using the optimum conditions for these preparations as described in Table 1, the yields varied from 30-80%. In general the couplings with acetic anhydride afforded reasonable yields, but the trimethylsilyl Grignard reagents, 3 and 4, gave none of the expected benzoyl derivatives under any conditions attempted. All the α,β -unsaturated ketones obtained were stable to mild acidic or basic conditions and the volatile ketones 3a and 4a could be converted into 2,4-dinitrophenylhydrazones in good yield.

The reactions and the products formed are shown in Scheme 1.

The ketones were found to be very sensitive towards 1,4-addition reactions and in order to minimize further reactions during their preparaisomers of this interesting class of compound tion it was necessary to use low temperatures. BROOK AND DUFF: α,β-UNSATURATED KETONES



SCHEME 1. Reactions of silvlvinylmetallic reagents with acid anhydrides.

The net result of these side reactions was the formation of 1,4-dienes. For example, treatment of α -lithiovinyltriphenylsilane with an excess of acetic anhydride at room temperature afforded a crystalline product (59% yield) along with a small amount of the α,β -unsaturated ketone. This product was assigned the structure 5. The i.r. spectrum showed strong bands at 5.70 and 6.12μ which are generally diagnostic of a vinyl acetate. The n.m.r. spectrum showed an aromatic multiplet (30H), two multiplets (each 1H) at δ 6.26 and 5.50 (vinyl protons), a similar multiplet (2H) at 2.95 attributable to the methylene group between two double bonds, and two singlets (each 3H) at 1.88 and 1.83 p.p.m. attributed to the two different methyl groups. The mass spectrum showed the expected parent ion at m/e 656. The geometry shown for the vinyl acetate double bond of 5 is assumed. Based on similar evidence, products from the reaction of 3 with acetic anhydride and 1 and 4 with benzoic anhydride were assigned structures 6, 7, and 8, respectively (geometries assumed). The reaction thus appears to be general. As additional structural evidence 6 was subjected to the reactions shown in eq. 4.

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Lithium aluminum hydride reduction followed by acid hydrolysis afforded the β -ketosilane 9 in high yield. This base-sensitive compound in aqueous alkaline dioxane gave the ketone 10 in 72% yield.

An obvious mechanism for the formation of these dienes is the 1,4-addition of the vinyl-

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			_		M.p. or	Calcd.		Found			
F	M	Anhydride (mol)	(°C) Prod	Product(s)	roduct(s) (%)	B.p./mm Hg (°C)	C	н	C	Н	
Ph₃Si	Н		- 78	1 <i>a</i>	82	115-116	80.44	6.14	80.69	6.25	
Li	H	Acetic (2.5)	25	5	59	189–190	80.44	6.14	80.11	6.12	
Ph₃Si	H -C	$\mathbf{Banzois}\left(1,2\right)$	- 78	1 b	42	120–121	83.03	5.68	82.75	5.61	
Li	Н		- 78	7	38	175–177	83.03	5.68	83.06	5.75	CA
Ph₃Si C=	H =C Ph	Acetic (2.0)	- 78	2a	67	127–128	83.12	5.98	82.89	5.83	N. J. CHEM
Ph ₃ Si C=	H =C Ph	Benzoic (1.1)	- 78	2b	29	120-121	84.94	5.62	84.88	5.48	. VOL. 51, 1973
Me ₃ Si	H H	Acetic (3.0)	-120	3 <i>a</i> ª	29 ^b	140/760	59.09	9.92	_	_	
BrMg	H			6	_	120/0.3	59.09	9.92	58.82	9.94	
Me ₃ Si		Acetic (3.0)	- 120	4a ^c	66 ^{<i>b</i>}	_	59.09	9.92	58.72	9.89	
H Me ₃ Si C H	MgBr H =-C MgBr	Benzoic (1.0)	- 78	8	59	190/0.2					

TABLE 1. Preparation of α,β -unsaturated ketones

^eCharacterized as the 2,4-dinitrophenylhydrazone, m.p. 163-164°. Anal. Calcd. for $C_{13}H_{18}N_4O_4Si$: C, 48.43; H, 5.63; N, 17.38. Found: C, 48.41; H, 5.61; N, 17.31. ^eYield determined by g.l.p.c. analysis of crude product. ^cAlso characterized as the 2,4-DNPH, m.p. 171-172°. Anal. Calcd. for $C_{13}H_{18}N_4O_4Si$: C, 48.43; H, 5.63; N, 17.38. Found: C, 48.20; H, 5.99; N, 17.13.

metallic reagent to the α , β -unsaturated ketone, in the normal manner, to give an enolate ion which is then acetylated or benzoylated by the remaining anhydride. To confirm this pathway 3-triphenylsilylbut-3-en-2-one (1*a*) was treated with an equimolar amount of α -lithiovinyltriphenylsilane (1) at -78° . Hydrolysis gave the expected β -ketosilane 11 in high yield (see eq. 5).



The important features of the i.r. and u.v. spectra of the α , β -unsaturated ketones are given in Tables 2 and 3. The carbonyl stretching wavelengths (5.93–6.05 μ) are normal for α , β -unsaturated ketones (typically 5.94–6.02 μ (7)), as previously noted by Felix and Weber (3) for a series of β -silylvinyl ketones. The shift to longer wavelength in the more polar solvent, acetonitrile, is also as expected (8).

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The i.r. carbonyl band of β -ketosilanes is generally shifted to about 0.1 μ longer wavelength than that of their carbon analogs (9) (e.g. Me₃SiCH₂COMe, 5.89; Me₃CCH₂COMe, 5.82 μ). This effect, probably attributable to inductive release from silicon toward the carbonyl group, may not be as strongly pronounced in the α -silylvinyl ketones since the acetyl derivatives 1*a*-4*a* absorb at very similar wavelengths.

Unfortunately only one of the six compounds prepared, 4a, showed a band (*ca.* 6.29 μ) which could be clearly assigned to a carbon-carbon double bond stretch. No similar band was observed in the α -isomer, 3a. Triphenylsilyl compounds in general have i.r. absorption at 6.28 μ and above, associated with the phenyl groups, which probably obscure the carbon-carbon double bond stretch in the four triphenylsilyl ketones.

Five of the six ketones prepared show a u.v. $n \rightarrow \pi^*$ absorption band which shifts to shorter wavelength with increasing solvent polarity (Table 3). The two trimethylsilyl ketones 3a and 4a also show a $\pi - \pi^*$ band which shifts to longer wavelength with increasing solvent polarity. This shift, about 10 nm on changing from cyclohexane to water, is similar to that found in analogous carbon compounds (8).

Although the silyl-substituted α , β -unsaturated ketones undergo $n-\pi^*$ transitions at slightly lower energy than analogous carbon or unsubstituted compounds (typically 305–340 nm, ϵ 25–100) (7) the small effect is in marked contrast to the effect of direct silicon substitution at the carbonyl chromophore. For example, replacement of a methyl group of acetone by a triphenyl-silyl group results in a lowering of the $n \rightarrow \pi^*$ transition energy by about 26 kcal/mol. Effects of this magnitude (which would have resulted in a shift in λ_{max} from 320 to about 450 nm with silyl substitution) can definitely be ruled out for both α - and β -silylvinyl ketones.

It has been suggested (3) that the main effect of the β -silyl substituent on the $n \rightarrow \pi^*$ transition of α,β -unsaturated ketones is in stabilizing the π^* excited state. The similarity in the $n \rightarrow \pi^*$ absorption of the α - and β -silyl isomers 3a and 4a tends to support this and confirms that direct conjugative interaction between the β -silicon atom and the carbonyl group is unimportant (eq. 6).

[6]
$$Si - C = C - C = 0 \iff \overline{S}i = C - C = C - \overline{O}$$

However, if lowering the π^* level is the only significant effect of silyl substitution then one would predict similar π - π^* absorption bands for 3a and 4a. This is clearly not the case. The $\pi \to \pi^*$ band of the β -silylvinyl isomer, 4a, occurs at 13 nm longer wavelength (*ca.* 8 kcal/ mol lower energy) and with a somewhat higher extinction coefficient, a result which is not inconsistent with conjugative interaction. It is also of interest to compare the $\pi \to \pi^*$ bands of 3aand 4a in methanol (Table 3) with those of methyl vinyl ketone (λ_{max} (ethanol) 210), 3-methylbut-3-en-2-one (218), and pent-3-en-

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		U.v. $\lambda_{\max}(\varepsilon)^b$			
Compound	I.r. C=O stretch ^a	$n \rightarrow \pi^*$	Other bands		
Ph ₃ Si					
C=CH ₂	5.98 µ	<u>329</u> nm (76) ^c	_		
MeCO					
Ph ₃ Si					
C=CH ₂	6.03s, 6.09w	322(77), $333(99)$, 344(110), $357(89)$,	248 nm (12 300) ⁴		
PhCO		370(48)			
Ph ₃ Si					
C=CHPh	5.93	e	257 (15 700) ^s		
MeCO					
Ph ₃ Si					
C=CHPh	6.05	330(344), <u>345(</u> 348) ^g , 359(273), 377(112)	267 (16 200) ^s 248 (24 200) ^d		
PhCO		557(275), 577(112)	2.0 (2. 200)		
Me ₃ Si					
C=CH ₂	5.98	332(48), 341(45), 355(29), 374(9)	207.5 (7630) ^h		
MeCO		555(27); 57 ((7)			
Me₃Si H					
C==C	5.88w, 5.95s	327(52), <u>337(</u> 54), 351(49), 365(30), <u>382(10)</u>	219.5 (10 900) ^h		
Н СОМе		505(50), 502(10)			

TABLE 2. Spectral data for α , β -unsaturated ketones

*Carbon tetrachloride solution, s = strong, w = weak. *Cyclohexane solvent. Maxima underlined for $n \to \pi^*$ bands. *Fine structure not resolved. 4Expected $\pi \to \pi^*$ transition of benzoyl group. *The $n \to \pi^*$ band is buried. 'Band associated with the triphenylsilylstyryl system (e.g. trans-Ph₃SiCH=CHPh 261 nm (ϵ 15 000)). *The $n \to \pi^*$ band is a shoulder of the more intense bands. *Measured in 1 mm silica cells with nitrogen purging.

TABLE 3.	Effect of solvent polarity on spectra
	U.v. (A

	1.r.(μ)		U.v. $(\lambda_{\max} nm)$					
Compound	CCl ₄	MeCN	Band	C ₆ H ₁₂	MeCN	МеОН	H₂O	
1 <i>a</i>	5.98	5.99	$n ightarrow \pi^*$	329	322	317	_	
1 b	6.03, 6.05	6.05 (broad)	$n \rightarrow \pi^*$	344	338	330	_	
3 <i>a</i>	5.98	6.01	$n ightarrow \pi^*$	332	323	319		
			$\pi ightarrow \pi^*$	207.5	208	210	216	
4a	5.88, 5.95	5.90, 5.97	$n \rightarrow \pi^*$	338	331	325	_	
	·		$\pi \rightarrow \pi^*$	219.5	221.5	223	229	

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2-one $(220 \text{ nm})^1$ (10). Whereas methyl substitution at the double bond causes moderate shifts to longer wavelength (8 nm for α and 10 nm for β) silyl substitution either causes a slightly greater increase (13 nm for β), or no increase at all in the transition wavelength.

To gain some insight into possible causes of these unexpected shifts we have carried out preliminary molecular orbital calculations of the CNDO/2 type (11) on the five model compounds, methyl vinyl ketone, 3-methylbut-3-en-2-one, *trans*-pent-3-en-2-one, and the silyl (*i.e.* SiH₃) analogs of the latter two compounds. Bond lengths were obtained from standard tables (12) and *S*-trans geometries were used. The important results are summarized, in a qualitative manner, in Fig. 1. As expected, each



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Fig. 1. Qualitative illustration of the results of CNDO calculations for silyl- and methyl-substituted α , β -unsaturated ketones.

compound showed an n-type orbital as the highest filled molecular orbital and a π -type orbital at somewhat lower energy. The lowest energy unfilled molecular orbital was also of the π -type and is designated as π^* . The calculations showed a slight raising of the n level on substitution at the double bond with the effect being greatest, though still small, for the α -silyl compound. The π^* level remained relatively unchanged with either α - or β -methyl substituents but with silyl substituents the π^* energy was substantially lowered. These results are in accord with the observed longer $n \rightarrow \pi^*$ transi-

¹There is no significant difference between methanol and ethanol solvent as regards the $\pi \to \pi^*$ transitions in α,β -unsaturated ketones (8). tion wavelength in the silvl isomers. The effect of substitution on the π molecular orbital was somewhat unexpected. While methyl substitution caused a raising of the level silvl substitution resulted in an equally pronounced lowering of the energy. The predicted result on the $\pi \to \pi^*$ transition are thus a bathochromic shift for the carbon-substituted ketones, as observed, while with the silvl ketones the net effect on the transition energy would depend on the relative amounts by which the π and π^* levels were affected. Our calculations predicted a net bathochromic shift on silvl substitution (i.e. π^* lowered more than π). However, it is reasonable to expect that these effects would depend to some extent on the position of the silvl substituent and the anomalous $\pi \to \pi^*$ spectra of the silyl ketones could thus be explained by different degrees of interaction of an α - or β -silyl group with the π and π^* orbitals.

The study of silyl-substituted α , β -unsaturated ketones is in an early stage at present and, in our opinion, more compounds, particularly suitable carbon and other Group IV analogs will be required before final conclusions may be drawn regarding their spectral properties. The present work has introduced a synthetic method which should serve to remedy the deficiency of compounds. Additionally, the demonstrated ease with which these compounds undergo 1,4-addition reactions has shown that they will be versatile intermediates in synthetic organosilicon chemistry.

Experimental

Experiments involving reactive organometallic reagents were carried out under nitrogen using dried, purified solvents. I.r. spectra were recorded on a Perkin-Elmer 237B instrument using 0.1 mm sodium chloride cavity cells. U.v. spectra were determined on Bausch and Lomb or Perkin-Elmer instruments in 10 mm silica cells for $n \rightarrow \pi^*$ bands and 1 mm cells in the short wavelength region. N.m.r. spectra were determined on Varian A-60 or HR 100 instruments. Melting points were determined on a Fisher-Johns apparatus and are uncorrected.

Conditions of most runs, together with details of yields and analyses are summarized in Table 1.

3-Triphenylsilylbut-3-en-2-one (1a)

A solution of α -bromovinyltriphenylsilane (1.83 g, 5.0 mmol) in dry diethyl ether (75 ml) at room temperature was treated with 3.75 ml (6 mmol) of *n*-butyllithium in hexane (1.6 M). The resulting light yellow solution was stirred for 5 min then was cooled to ca. -78° using a Dry-Ice – acetone bath. Addition of acetic anhydride (0.944 ml, 10 mmol) to the resultant light-yellow suspension gave a fine white suspension. After 30 min at

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- 78° work-up with saturated aqueous ammonium chloride gave a thick oil which crystallized from 30 ml of pentane to give the desired product (1.35 g, 82%) as white solid, m.p. 112-115°. Recrystallization from hexane gave the analytical sample, m.p. 115-116°; n.m.r. (CCl₄) δ 6.27, 6.10 (2d, each 1H, J = 2 Hz) and 2.05 p.p.m. (s, 3H).

2-Acetoxy-3,5-bis(triphenylsilyl)hexa-2,5-diene (5)

When the above preparation was carried out at -20° a mixture (*ca.* 3:2, respectively) of the ketone 1*a* and compound 5 was obtained.

Addition of acetic anhydride to a solution of α -lithiovinyltriphenylsilane at room temperature gave a 59% yield of **5** on crystallization of the crude reaction product from pentane. Recrystallization from methylene chloride – methanol gave analytically pure material, m.p. 189–190°.

a-Triphenylsilylvinyl Phenyl Ketone (1b)

To a solution of the organolithium reagent, prepared as above, from 0.92 g (2.5 mmol) of α -bromovinyltriphenylsilane in ether at -78° was added 0.68 g (3.0 mmol) of benzoic anhydride. After 30 min the resultant suspension was worked-up with saturated aqueous ammonium chloride solution to give an oil. The spectra of this oil indicated that a mixture of products was present. Chromatography on silica gel gave vinyltriphenylsilane (0.26 g, 36%) on elution with carbon tetrachloride. Elution with 1:1 benzene – carbon tetrachloride gave an oil (0.63 g) which was crystallized from hexane to give 0.41 g (42%) of the desired ketone, m.p. 116–120°. Recrystallization from hexane gave pure material, m.p. 120–121°; n.m.r. (CCl₄) δ 6.35, 6.21 p.p.m. (2d, J = 2 Hz).

1-Benzoyloxy-1-phenyl-2,4-bis(triphenylsilyl)penta-1,4-diene (7)

In a similar experiment to the above, the organolithium reagent from 0.45 g (1.23 mmol) of α -bromovinyltriphenylsilane was treated at -78° with benzoic anhydride (0.31 g, 1.35 mmol). The crude product obtained after work-up was crystallized from methylene chloride – methanol to give 0.18 g (38%) of compound 7, m.p. 175–180°. Recrystallization from hexane gave the analytical sample, m.p. 175–177°; i.r. (CCl₄) 5.77, 6.26 μ (vinyl benzoate); n.m.r. (CCl₄) 8 6.33, 5.50 (2m, each 1H, C=CH₂), 3.25 p.p.m. (m, 2H, C=C-CH₂-C=C); mass spectrum 780 (2%, M), 303 (70%, Ph₂SiOCOPh), 259 (100%, Ph₃Si).

3-Triphenylsilyl-4-phenylbut-3-en-2-one (2a)

1-Bromo-1-triphenylsilyl-2-phenylethylene-Z (13) (1.50 g, 3.4 mmol; prepared by dehydrobromination of 1,2dibromo-1-triphenylsilyl-2-phenylethane with pyridine) in 50 ml of dry ether at room temperature was treated with *n*-butyllithium (4 mmol). The resultant deep yellow solution was cooled to -78° and then was treated with acetic anhydride (0.82 ml, 8.0 mmol) to give a fine gelatinous suspension. Work-up after 30 min with ammonium chloride solution gave a thick clear oil which was crystallized from hexane to give 0.91 g (67%) of the desired ketone, m.p. 127–128°; n.m.r. (CCl₄) δ 6.90 (s, 1H, C=CH—) and 1.80 p.p.m. (s, 3H, CH₃CO—).

α -Triphenylsilylbenzalacetophenone (2b)

Using the same molar quantities as above, and identical conditions, treatment of the organolithium reagent from 2 with benzoic anhydride gave a complex mixture of products. Crystallization of the crude product from ethanol gave 0.71 g (58%) of *trans*- β -triphenylsilylstyrene. The residual product was chromatographed on silica gel. Elution with 1:1 benzene – carbon tetrachloride gave an oil (0.61 g) which was crystallized from hexane to give 0.46 g (29%) of the required ketone, m.p. 117–119°. Recrystallization from hexane gave m.p. 120–121°, n.m.r. δ 7.0–7.9 p.p.m. (aromatic multiplet).

4-Trimethylsilylbut-3-en-2-one (4a)

The Grignard reagent prepared from 16.1 g (0.09 mol) of B-bromovinyltrimethylsilane and magnesium (2.43 g. 0.1 g atom) in 300 ml of tetrahydrofuran was cooled to $ca. -120^{\circ}$ in a liquid nitrogen – methylcyclohexane slush bath. The solution was treated (all at once) with 30.6 g (28.4 ml; 0.3 mol) of acetic anhydride. After 5 min the resultant suspension was allowed to warm up, and then was diluted with ether and worked-up. The organic layer was thoroughly washed with sodium bicarbonate solution to remove acetic acid and excess anhydride, was dried $(MgSO_4)$ and then was distilled to a head temperature of 105°. The residue, 10.55 g of light yellow liquid, contained some THF and unidentified material along with the desired α , β -unsaturated ketone. G.l.p.c. analysis of the solution indicated a yield of ca. 66%. Pure samples of the ketone were obtained by preparative g.l.p.c. using a 5 ft. $\times \frac{1}{2}$ in. column of 20% SE 30 on Chromosorb W (oven temperature 95°). The pure ketone was a colorless mobile liquid with a pleasant camphoraceous odor, n_{p}^{21} 1.4480; i.r. (CCl₄) 10.08 µ; n.m.r. (CCl₄) δ 6.89 and 6.40 (J = 19.5 Hz, CH=CH, AB pattern), 2.20 (s, 3H, CH₃CO---), 0.14 p.p.m. (s, 9H, Me₃Si). The large coupling constant between the vinylic protons and the presence of a band at 10.08 µ in the i.r. spectrum indicate that the ketone has trans-stereochemistry.

A sample of the purified ketone (0.10 g) was dissolved in dimethyl sulfoxide (10 ml) containing 0.16 g of 2,4dinitrophenylhydrazine and one drop of concentrated hydrochloric acid. A precipitate formed, and after 5 min methanol was added to give 0.16 g of an orange solid. Recrystallization from methylene chloride – methanol gave the pure dinitrophenylhydrazone (0.14 g, 66%), m.p. 171–172°; n.m.r. (CDCl₃) δ 6.81, 6.51 (AB, J =19.5 Hz, 2H) 2.18 (s, 3H, CH₃C=N—), and 0.22 p.p.m. (s, 9H, Me₃Si).

1-Benzoyloxy-1-phenyl-3,5-bis(trimethylsilyl)penta-1,4-diene (8)

A solution of the Grignard reagent, prepared from 5.37 g (0.03 mol) of β -bromovinyltrimethylsilane and 0.80 g (0.033 g atom) of magnesium in THF (100 ml), at $ca. -78^{\circ}$, was treated with benzoic anhydride (6.80 g, 0.03 mol). After 30 min the resultant white suspension was warmed to room temperature and was worked-up as above by adding ether, and then washing in succession with ammonium chloride and sodium bicarbonate solutions. Removal of solvent at reduced pressure gave an oil which was chromatographed on silica gel, eluting with 1:1 benzene – carbon tetrachloride, to give the compound **8**, as a clear thick oil (2.51 g, 59%). This product

was air sensitive, turning yellow on standing. A sample was distilled (190°/0.2 mm Hg, Kugelrohr); mass spectrum 408 (1%, M), 303 (6.5%, M - PhCO), 105 (70%, PhCO), 73 (100%, Me₃Si); i.r. (CCl₄) 5.75, 6.25 µ (C=0 and C=C of a vinyl benzoate); n.m.r. (CCl₄, 100 MHz, see structure below) δ 6.06 (H_A), 5.93 (H_B), 5.54 (H_c),



2.92 (H_X) ($J_{AX} = 7.4$, $J_{BX} = 11.4$, $J_{CX} = 1.2$, $J_{AC} = 19.6$, $J_{AB} = J_{BC} = 0$ Hz), 0.06 p.p.m. (s, 18H, 2Me₃Si).

3-Trimethylsilylbut-3-en-2-one (3a)

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The Grignard reagent prepared from α -bromovinyltrimethylsilane (27.9 g, 0.15 mol) and magnesium (4.03 g, 0.16 g atom) in THF (275 ml) was diluted with ether (175 ml) and the solution was cooled to $ca. -120^{\circ}$ in a liquid nitrogen - methylcyclohexane slush bath. To the rapidly stirred suspension was added 71.2 g (67 ml; 0.60 mol) of acetic anhydride. After 5 min the mixture was warmed to room temperature and was worked-up as above using ammoniun chloride and sodium bicarbonate solutions. Distillation of the organic layer to a head temperature of 100° gave 33.6 g of light yellow residue. An n.m.r. spectrum indicated that this liquid contained a 1:1 mixture of the desired ketone and the diene, 6. A similar experiment carried out at -78° gave a 1:4 mixture of ketone and diene respectively.

The volatile product was pumped (25°/0.1 mm) into a Dry-Ice - acetone trap to give 7.7 g of light yellow liquid. This liquid was estimated (by g.l.p.c.) to contain 82% of the desired ketone along with three minor unidentified contaminants. The approximate yield of ketone is thus 29%

The ketone was purified by preparative g.l.p.c. using the conditions described above for its isomer. The pure compound, a faintly yellow, pleasant-smelling liquid, n_{D}^{21} 1.4396, boiled at 140° (760 mm) with decomposition. It also decomposed slowly at room temperature but was stable at -20° in the dark. N.m.r. (CCl₄) δ 6.54 and 6.22 $(2d, each 1H, J = 2 Hz, C=CH_2), 2.31 (s, 3H, CH_3CO),$ 0.19 p.p.m. (s, 9H, Me₃Si).

A sample of the impure ketone (0.71 g; 82%) was dissolved in DMSO (10 ml) containing 2,4-dinitrophenylhydrazine (1.0 g) and one drop of concentrated hydrochloric acid. The 0.68 g of product was purified by chromatography on silica gel, m.p. 163-164°; n.m.r. (CCl_4) δ 6.24, 5.95 (2d, each 1H, J = 1.5 Hz), 2.20 (s, 3H, CH₃CO), 0.26 p.p.m. (s, 9H, Me₃Si).

2-Acetoxy-3,5-bis(trimethylsilyl)hexa-2,5-diene (6)

The less volatile product in the above preparation was distilled (120°/0.3 mm; Kugelrohr) to give the pure diene as an oil, n_D^{22} 1.4616; i.r. (liquid film) 5.70, 6.09 μ (C=C-O-COCH₃); n.m.r. (CCl₄) δ 5.42, 5.25 (2m, each 1H, C=CH₂), 2.75 (m, 2H, C=C-CH₂-C=C), 2.01 and 1.95 (2s, each 3H, MeC-C and MeC-O), 0.11 and 0.06 p.p.m. (2 s, each 9H, 2 Me₃Si); mass spectrum

284 (1%, M), 169 (13%, M - Me₃Si), 73 (100%, Me₃Si), 43 (19%, MeCO).

Degradation of 2-Acetoxy-3,5-bis(trimethylsilyl)hexa-2,5-diene (6)

(A) To 3,5-Bis(trimethylsilyl)hex-5-en-2-one (9)

A solution of 6 (14.2 g, 0.05 mol) in diethyl ether (100 ml) containing lithium aluminum hydride (1.14 g, 0.03 mol) was heated to reflux for 30 min. The resultant suspension was cautiously worked-up with a slurry of ice and ammonium chloride. Hydrochloric acid (10%) was added to dissolve the aluminum salt and the organic layer was separated, dried, and distilled to give 11.1 g (92%) of pure β -ketosilane 9, n_D^{22} 1.4600; i.r. (film) 5.89 μ (C=O, β to Si); u.v. (cyclohexane) λ_{max} 285 nm (ϵ 92); n.m.r. (CCl₄) δ 5.42 and 5.23 (2m, each 1H, C==CH₂), 1.9 (s, 3H, CH₃CO), 0.04 (s, 18H, 2 Me₃Si), 2-3 p.p.m. (complex, 3H, CH2-CH); mass spectrum 242 (12%, M), 73 (100%, Me₃Si) 43 (10%, CH₃CO).

Anal. Calcd. for C₁₂H₂₆OSi₂: C, 59.43; H, 10.81. Found: C, 59.64; H, 10.91.

(B) 5-Trimethylsilylhex-5-en-2-one (10)

A solution of 9.2 g of 3,5-bis(trimethylsilyl)hex-5-en-2-one (9, above) in dioxane (50 ml) - water (10 ml) was treated with 0.5 g of potassium hydroxide. The resultant solution was stirred at room temperature for 20 min and then was diluted with ether (3 vol) and was worked-up with dilute hydrochloric acid. The organic layer was dried and distilled to give pure 5-trimethylsilylhex-5-en-2-one (10), (5.02 g, 78%), b.p. 80.5°/10 mm; n_D²⁰ 1.4460; i.r. (CCl₄) 5.81 μ (C=O); u.v. (cyclohexane) λ_{max} 281 nm (ϵ 27); n.m.r. (CCl₄) δ 5.53 and 5.34 (2m, each 1H, C=CH₂), 2.45 (m, 4H,-CH₂-CH₂-), 2.10 (s, 3H, CH₃CO), 0.10 p.p.m. (s, 9H, Me₃Si).

Anal. Calcd. for C₉H₁₈OSi: C, 63.47; H, 10.65. Found: C, 63.30; H, 10.68.

3,5-Bis(triphenylsilyl)hex-5-en-2-one (11)

A solution of α -bromovinyltriphenylsilane (1.83 g, 5 mmol) in diethyl ether (50 ml) at room temperature was treated with 3.44 ml (5.5 mmol; 1.6 M) of n-butyllithium. After 20 min the solution was cooled to ca. -78° and 1.64 g (5 mmol) of 3-triphenylsilylbut-3-en-2-one (1a) was added. The resultant suspension was worked-up with saturated ammonium chloride solution after 5 min to give a glass. Crystallization from hexane gave the required product as white needles, m.p. 131-133° (2.06 g, 67%). Several recrystallizations from hexane and methylene chloride - methanol raised the m.p. to 138–140°; i.r. (CCl₄) 5.90 μ (C=O β to Si); n.m.r. (CCl₄); 100 MHz) δ 5.97 and 5.60 (2m, each 1H, C=CH₂), 3.6-2.5 (m, 3H, CH₂--CH), 1.60 p.p.m. (s, 3H, CH₃CO).

Anal. Calcd. for C42H38OSi2: C, 82.03; H, 6.23. Found: C, 81.92; H, 6.15.

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