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REACTIONS OF SILYL AND GERMYL KETONES WITH ALKYLIDENEPHOSPHORANES

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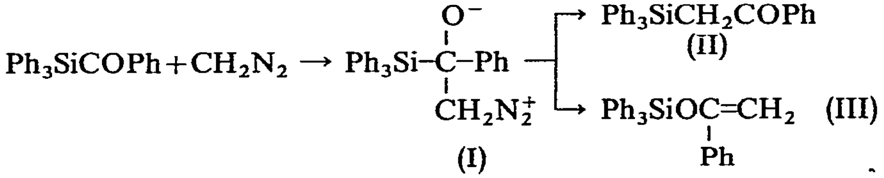
Previous studies have shown that silyl ketones undergo unusual reactions with alkoxides[1,2] and with diazomethane[3]. Among the products found in each case were silyl ethers, arising from attack of the oxygen of the carbonyl group on the adjacent silicon atom, leading to cleavage of a silicon–carbon bond. Thus the reaction of benzoyltriphenylsilane with diazomethane which gave a mixture of phenacyltriphenylsilane (II) and triphenylsiloxystyrene (III) could be satisfactorily explained as the decomposition by alternate pathways of the 1 : 1 adduct (I). Thus reformation of



$$\mathrm{Ph_3SiCOPh + CH_2N_2 \rightarrow Ph_3Si{-}\overset{O^-}{\underset{\underset{(I)}{CH_2N_2^+}}{C}}{-}Ph} \begin{cases} \rightarrow \mathrm{Ph_3SiCH_2COPh}\ \ \mathrm{(II)} \\ \rightarrow \mathrm{Ph_3SiO\underset{Ph}{C}{=}CH_2}\ \ \mathrm{(III)} \end{cases}$$

the carbonyl group accompanied by the migration of the triphenylsilyl group to the methylene carbon with loss of nitrogen, would result in the formation of the homologous β-ketosilane, a normal product from the reaction of a ketone with diazomethane[4]. On the other hand, attack of the anionic oxygen on silicon would lead, through breaking of the silicon–carbon bond, formation of the carbon–carbon double bond, and loss of nitrogen, to the siloxystyrene, a hitherto unknown type of product from this reagent. This latter reaction appears to be closely related to the rearrangement of silylcarbinols to the isomeric silyl ethers[5,6].

Seyferth and Grim[7] have commented on the similarities of diazomethane and methylenetriphenylphosphorane, each species having an important contributing structure in which the methylene group bears negative charge. Thus the investigation of the reactions of alkylidenephosphoranes with silyl and germyl ketones was a logical extension of our investigations of the chemical behaviour of these compounds.

In the light of the preceding knowledge several modes of decomposition of the silicon-containing betaine (IV), the expected initial adduct of a benzoylsilane with methylenetriphenylphosphorane, might be expected. Intramolecular anionic attack on silicon would result in silicon–carbon bond cleavage, and carbon–carbon double bond formation, leading to siloxystyrene and triphenylphosphine. Alternatively, attack by oxygen on phosphorus would lead in the usual way to the normal Wittig

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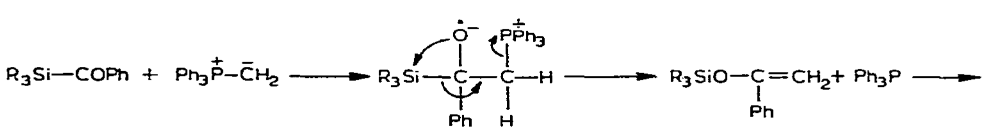
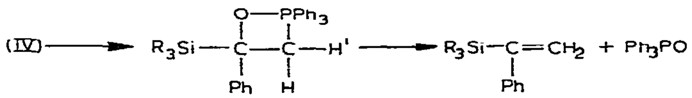
* Dow-Corning Silicones of Canada Fellow, 1965–66.



(IV)

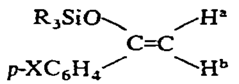


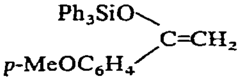
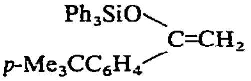
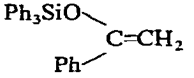
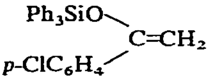
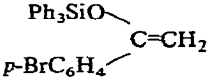
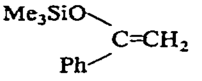
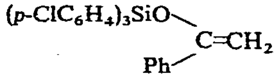
products, in this case a silylstyrene, together with triphenylphosphine oxide[8]. A route to a β-ketosilane can also be written, but seems improbable.

When the reactions between a variety of benzoylsilanes and methylenetriphenylphosphorane were investigated, it was found that regardless of the nature of the groups attached to silicon or of the p-substituents on the benzoyl group, the only product detected was the siloxystyrene. The results are summarized in Table 1, along with the NMR data for the new compounds.

TABLE 1

SILOXYSTYRENES[a] FROM SILYL KETONES WITH METHYLENETRIPHENYLPHOSPHORANE



Ketone	*Siloxystyrene*	*% Yield*	H^a	H^b	$J_{ab}(Hz)$
$Ph_3SiCOC_6H_4OMe$-*p*		[b]	4.22	4.65	2.0
$Ph_3SiCOC_6H_4CMe_3$-*p*		39	4.28	4.73[e]	2.0
$Ph_3SiCOPh$		48	4.34	4.77	2.0
$Ph_3SiCOC_6H_4Cl$-*p*		[b]	4.33	4.76	3.0
$Ph_3SiCOC_6H_4Br$-*p*		82	4.42	4.78	2.2
$Me_3SiCOPh$		79[b,c]	4.32[d]	4.81	1.3
$(p\text{-}ClC_6H_4)_3SiCOPh$		47	4.35[d]	4.88	2.0

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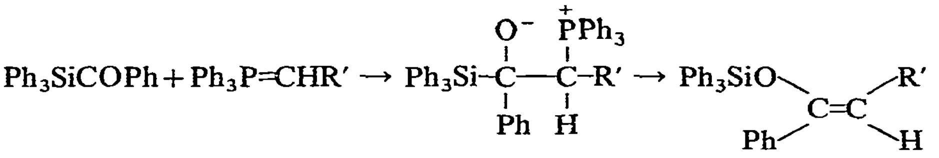
[a] NMR spectra, determined in CCl_4 except as noted, are given in ppm downfield from TMS, used as internal standard. [b] Siloxystyrene prepared from reaction of ketone with diazomethane, see ref. 3. [c] Siloxystyrene decomposed during isolation. Yield based on acetophenone isolated. [d] NMR spectrum run in $CDCl_3$. [e] tert-Butyl signal observed at 1.32 ppm.

α-(Triphenylsiloxy)styrene, from benzoyltriphenylsilane and methylenetriphenylphosphorane, was identified by mixed melting point with an authentic sample[3] and by its characteristic spectra. While this siloxystyrene was relatively stable and could be purified by chromatography on silica gel, and by recrystallization, several of the siloxystyrenes were very unstable, readily hydrolyzing to silanol and acetophenone on attempted isolation and purification. In these cases they were observed in the crude reaction mixture by their characteristic spectra. All siloxystyrenes show medium to strong absorption in the 6.15–6.20 μ region attributed to C=C stretch of the vinyl ether linkage, and strong broad bands in the 9.3–9.5 μ region, associated with Si–O–C stretching. In addition, all siloxystyrenes had three very characteristic strong bands at approximately 7.6, 7.7 and 7.8 μ, except for α-(triphenylsiloxy)-*p*-bromostyrene which lacked the band at 7.8 μ. The NMR spectra show the expected two doublets at about 4.3 and 4.7 ppm, for the two different vinyl protons, with spin–spin coupling constants of 1.3–3 Hz, as shown in Table 1. This data was interpreted as follows.

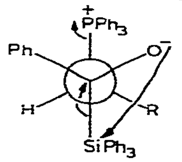
The signal at about 4.7 ppm below TMS is assigned to the proton *cis* to the phenyl or *p*-substituted phenyl group by analogy with similar assignments in styrene and some of its derivatives[9], and by consideration of the changes in resonance position produced as the *p*-substituents vary. Electronic effects of the *p*-substituents on the styrene-phenyl group would be expected to influence the proton *trans* to it (H^a) much more than the *cis* proton (H^b), since the C–H^a bond lies essentially parallel to the polarization axis through the benzene ring and its *p*-substituent, whereas the C–H^b bond is roughly perpendicular to the axis. Since electron-withdrawing groups on the benzene ring should deshield the *trans* proton, the *trans*-H signal would be expected to shift downfield as the *p*-substituent successively changed in the order MeO, tert-Bu, H, Cl, Br. An examination of Table 1 shows in fact that this is the order observed for the high field proton, H^a. The position of the signal for the low field proton remains essentially constant as the substituents change, except for the *p*-MeO compound where the proton has shifted to higher field: the low field proton H^b is, then, the proton *cis* to the phenyl group.

Benzoyltriphenylsilane also reacted with alkyl-substituted methylenephosphoranes such as ethylidene- and propylidenetriphenylphosphorane. Again only rearrangement products, assigned the structures α-(triphenylsiloxy)-*trans*-β-methylstyrene (Va) and α-(triphenylsiloxy)-*trans*-β-ethylstyrene (Vb), were isolated from the reactions, and the reaction was highly stereoselective since of the two possible geometric isomers of the siloxyalkene, only one was detected.

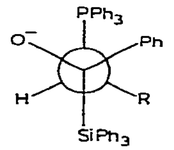


(Va)R' = Me
(Vb)R' = Et

The structures of the compounds were assigned on the basis of the NMR spectra which showed the vinyl proton signal as a 1-proton quartet at 5.19 ppm and a 1-proton triplet at 5.10 ppm for the methyl- and ethylstyrenes respectively. This position is at slightly lower field than that observed for the proton *cis* to the phenyl group, H^b, in the siloxystyrenes, the lower position being in accord with the effect of alkyl groups on vinyl protons in simple alkenes: *e.g.* 2-methyl-2-butene (5.21 ppm) and 2-methyl-1-propene (4.66 ppm)[10]. Hence the alkenes are logically assigned the *trans* configuration in which the vinyl proton is *cis* to the phenyl group. Stereochemical arguments also can be advanced supporting this assignment. The Newman projection of what would appear to be the required conformation of the intermediate betaine is shown in (A). By analogy with normal elimination reactions in which the leaving groups are *trans* and coplanar with one another, as the anionic oxygen atom attacks silicon leading to cleavage of the Si–C and C–P bonds, collapse of the sp^3 geometry to sp^2 will yield the alkene in which hydrogen and the phenyl group are *cis* to one another. The other possible diastereomeric betaine in which the Ph_3Si and Ph_3P groups are *trans* and coplanar (B) would be expected to be less stable than (A) because in (B) the relatively large Ph group is gauche to both the large (PPh_3) and medium sized (CH_3 or Et) groups, whereas in (A), Ph is gauche to large (PPh_3) and small (H) groups[11]. These two conformations presumably can be in equilibrium with one another through reversible equilibria between the betaines and the starting materials[8], but the stereoselectivity of the reaction is remarkable.



(A)

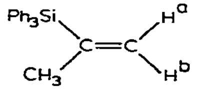
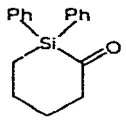
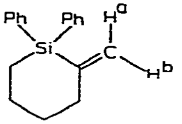
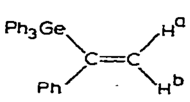
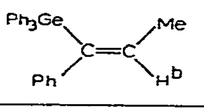


(B)

Unlike the above situation where aryl silyl ketones were found to yield only

TABLE 2

SILYL AND GERMYL ALKENES FROM THE WITTIG REACTION

Ketone	*Product*	*Yield*	H^a	H^b	H^{other}	$J_{ab}(Hz)$
$Ph_3SiCOCH_3$		75	5.41^a	5.91^a	1.97^a	
		75	5.12^a	5.70^a		3
$Ph_3GeCOPh$		72	5.55	6.19		2
$Ph_3GeCOPh$		81		6.53	1.65	7

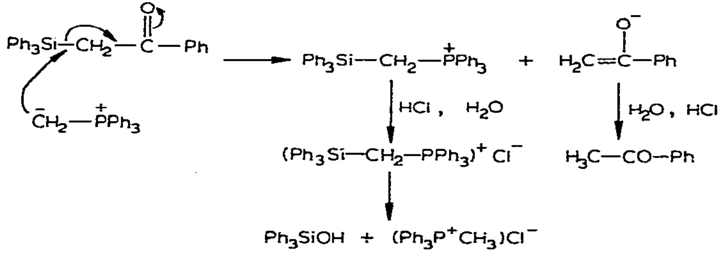
[a] Multiplets, due to further splitting.

siloxyalkenes, the reactions of methylenetriphenylphosphorane with alkyl silyl ketones such as acetyltriphenylsilane or 1,1-diphenylsilacyclohexan-2-one were found to yield only the normal Wittig products isopropenyltriphenylsilane and 1,1-diphenyl-2-methylene-silacyclohexane. Isopropenyltriphenylsilane was identified by comparison of its properties with those of an authentic sample[12] while the 1,1-diphenyl-2-methylenesilacyclohexane was identified from its analysis and spectra.

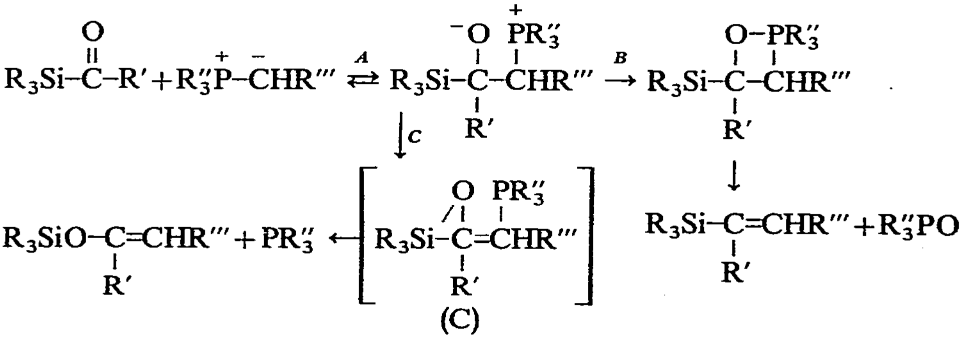
Similarly, when benzoyltriphenylgermane was treated with methylene- or ethylidenetriphenylphosphorane, the only products isolated were those of the normal Wittig reaction, α-(triphenylgermyl)styrene, independently synthesized, and α-(triphenylgermyl)-*trans*-β-methylstyrene. The data for the compounds is given in Table 2.

Comparable arguments to those advanced for the siloxystyrenes lead to the assignment of the high field vinyl proton (H^a) as that *trans* to the phenyl group and the lower field proton (H^b) as that *cis* to phenyl. The fact that in the α-(triphenylgermyl)-β-methylstyrene the vinyl proton comes at even lower field leads to the assignment of the stereochemistry of this compound as *trans*.

Finally, when phenacyltriphenylsilane was treated with methylenetriphenylphosphorane the major products were acetophenone and triphenylsilanol. This result may be explained as a β-elimination reaction of the silyl ketone. Nucleophilic β-eliminations are highly characteristic of silyl compounds having electronegative groups in the β-position[13]. The resulting silylphosphonium salt would be expected to hydrolyze to give the observed triphenylsilanol[7]. Phenacyltriphenylgermane appeared to react in the same way, acetophenone being found in moderate yield.



Some comment as to the different courses of reaction that α-ketosilanes take with methylenephosphoranes seems pertinent. The general mechanism of the Wittig reaction involves, as discrete steps, *A*, the formation of the betaine, generally a reversible reaction, and *B*, reaction of the betaine to give the cyclic oxyphosphorane leading to the normal Wittig product. Either of steps *A* or *B* may be rate-determining, depending primarily on the type of methylenephosphorane, *i.e.* on the nature of



R″ and R‴. When the phosphorane is resonance-stabilized, for example when R‴ = aryl, *A* is the slow rate-controlling step. However, when the phosphorane is a reactive species, with charge localized on carbon, addition step *A* is fast and step *B* is slow and rate-controlling, especially when electron-releasing groups on phosphorus make it a poor site for nucleophilic attack by the oxygen anion. Superimposed on this reaction sequence when silyl ketones are involved, there appears to be an alternative pathway *C*, proceeding via the transition state (C), which must compete with step *B* of the normal Wittig reaction. In cases when *B* is slow and rate-determining as in reactions involving the alkylidenetriphenylphosphoranes, *C* would be more likely to compete favourably*. However, the finding that benzoylsilanes give only siloxyalkenes, but alkyl silyl ketones such as acetyltriphenylsilane give exclusively the normal silylalkene indicates that the nature of R′, the group attached to the carbonyl carbon atom, plays a dominant role in establishing which of steps *B* or *C* is the lower energy pathway. When charge released from silicon toward the carbon of the carbonyl group in the process leading to double bond formation can be delocalized by R′ (as when R′ = aryl) then attack by oxygen on silicon completely dominates attack by oxygen on phosphorus. Otherwise, (as when R′ = alkyl) attack by oxygen on phosphorus occurs exclusively.

Finally, it remains to emphasize again the similarity of the reaction described here with other reactions of benzoylsilanes. In virtually all cases where the carbonyl group undergoes nucleophilic attack, leading to creation of anionic oxygen on the carbon adjacent to silicon, be it by alkylidenephosphorane, as observed here, by diazomethane[3], by certain organometallic reagents**, or indirectly by alkoxide ion[1,2], or where the hydroxyl group of an α-hydroxysilane is converted to an alkoxide ion, attack on silicon with silicon–oxygen bond formation and silicon–carbon bond cleavage is observed. These rearrangements are less prevalent, and much slower when the R group attached to the carbinol or carbonyl centre is alkyl, rather than aryl. In addition these rearrangements appear to be characteristic of carbon-functional silicon compounds since in no case has rearrangement been observed where germanium is adjacent to the carbonyl or carbinol group.

EXPERIMENTAL

All reactions involving the use of organometallic reagents and alkylidenephosphoranes were carried out in dry apparatus under an atmosphere of dry nitrogen. Ether was distilled from sodium immediately prior to use. The preparations of the ketones used have been described elsewhere[14].

The reaction of benzoyltriphenylsilane with methylenetriphenylphosphorane

To a suspension of 3.64 g (0.01 mole) of anhydrous methyltriphenylphosphonium bromide in 50 ml of anhydrous ether, was added dropwise 10 ml (0.01 mole)

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* Kinetic investigations of the silylcarbinol rearrangement, which proceeds from an intermediate similar to that shown here for step *C*, have shown that the isomerization process, *i.e.* Si–O bond formation and Si–C bond cleavage, is rapid, involving a relatively small energy of activation, E_a 8–11 kcal/mole[6].

** Unreported studies by J. M. Duff of these laboratories have shown that addition of phenyllithium to benzoyltriphenylsilane yields a complex mixture of products, one which is the silyl ether resulting from rearrangement of the expected silylcarbinol.

of phenyllithium. The phosphonium salt dissolved and an intense yellow colour (due to the methylenephosphorane) appeared. After stirring for 60 minutes a solution of 3.65 g (0.01 mole) of benzoyltriphenylsilane in 75 ml of anhydrous ether was added dropwise to the methylenephosphorane over a period of 2 h. The yellow colour of both reagents faded gradually during the addition and a white precipitate was observed to form. The reaction mixture was stirred for a further 24 h and then poured into 100 ml of dry hexane. The sticky white solid, A, was filtered off and the solvents were removed under reduced pressure to yield a pale yellow oil B.

The infrared spectrum of the oil (thin film) had three characteristic strong peaks at 7.60, 7.70 and 7.80 μ, a peak at 6.18 μ (C=C–O) and bands at 7 (Si–Ph and P–Ph) and 9 μ(Si–Ph). The oil was dissolved in a minimum of cold dry hexane and was added to a 1 × 6″ silica gel column. The column was eluted with 200 ml of 95:5 cyclohexane/benzene to yield 1.87 g of crude α-(triphenylsiloxy)styrene, m.p. 65–72°. This material was recrystallized from dry pentane to yield 1.76 g (48 %) of α-(triphenylsiloxy)styrene, m.p. 77–79°, mixed melting point with an authentic sample[4] 78–80°.

The solid A was extracted with benzene and the insoluble material filtered off. The solvent was removed under reduced pressure to yield 0.47 g of triphenylphosphine. A further 1.31 g of triphenylphosphine was recovered by eluting the column with 100 ml of chloroform. Thus the total yield of triphenylphosphine, m.p. 78–79°, was 1.78 g (68 %). The benzene-insoluble material was soluble in water and methanol, gave a red flame test and gave a pale yellow precipitate with silver nitrate indicating it to be lithium bromide.

α-(Triphenylsiloxy)-p-bromostyrene

Following the above procedures 2.26 g (0.005 mole) of (*p*-bromobenzoyl)triphenylsilane treated with 0.005 mole of methylenetriphenylphosphorane over 24 h yielded 2.13 g of crude α-(triphenylsiloxy)-*p*-bromostyrene, m.p. 71–75°. The infrared spectrum showed bands at 6.18 μ due to the vinyl ether, 7 and 9 μ due to Si–Ph, and two peaks at 7.61 and 7.70 μ in the region where other siloxystyrenes show three strong bands. Several recrystallizations from dry n-pentane yielded 1.93 g (82 %) of product, m.p. 83–85°; ultraviolet spectrum: λ_{max} (cyclohexane), 217 (20,400) 262 (9,300) mμ. (Found: C, 68.57; H, 4.67. $C_{26}H_{21}BrOSi$ calcd.: C, 68.28; H, 4.60 %.)

α-(Triphenylsiloxy)-p-tert-butylstyrene

Following the general procedures described above 2.11 g (0.005 mole) of (*p*-tert-butylbenzoyl)triphenylsilane on treatment with 0.005 mole of methylenetriphenylphosphorane gave 1.43 g of crude orange oil after chromatography on silica gel. The oil crystallized on scratching and was recrystallized from pentane to yield 1.09 g (49 %) of pure α-(triphenylsiloxy)-*p*-tert-butylstyrene, m.p. 101–102°; ultraviolet spectrum, λ_{max} (cyclohexane); 249 (2,750), 262 (s) (2,200) mμ. (Found: C, 83.22; H, 6.99. $C_{30}H_{30}OSi$ calcd.: C, 83.61; H, 6.97 %.)

α-[Tris(p-chlorophenyl)siloxy]styrene

Following the above procedures 0.005 mole of methylenetriphenylphosphorane treated with 2.34 g (0.005 mole) benzoyltris(*p*-chlorophenyl)silane gave on workup and chromatography, 1.13 g of colourless oil. The oil resisted all attempts to induce it to crystallize for several weeks. When finally the oil did crystallize it was found to be no longer the original siloxystyrene. The compound was recrystallized from a 1:1 ether/hexane mixture to yield 0.91 g of a crystalline solid, m.p. 163–165°, believed to be phenacyl tris(*p*-chlorophenyl)silyl ether, presumably formed by an oxidation of the siloxystyrene: ultraviolet spectrum; λ^{max} (cyclohexane); 267 (28,000), 274 (20,000), 290 (s) (450), 320 (s) (91) mμ. (Found: C: 63.28; H, 4.17; mol. wt. osmometer, 490. $C_{26}H_{19}Cl_3O_2Si$ calcd.: C, 62.85; H, 3.95%; mol. wt., 481.)

Hydrolysis of 350 mg (0.007 mole) of this compound, dissolved in acetone with 5 ml of 10% hydrochloric acid over 2 h gave an oil on removal of the solvents, which was taken up in ether and dried. The yellow oil resulting on removal of the ether yielded, on elution from a silica gel column with benzene 316 mg (83%) of hexakis(*p*-chlorophenyl)disiloxane, m.p. 209–210°, (lit.[15] 210°) after recrystallization from pentane/CCl_4, and then, on elution with acetone, 79 mg of crude phenacyl alcohol, recrystallized from benzene to give 41 mg (51%) of phenacyl alcohol, m.p. 89–92°, identified by mixed melting point and comparison of its infrared spectrum with that of an authentic sample.

α-(*Trimethylsiloxy*)*styrene*

A mixture of 0.01 mole of methylenetriphenylphosphorane and 1.78 g (0.01 mole) of benzoyltrimethylsilane in 75 ml of ether was stirred for 6 h and then poured into 100 ml of dry hexane and the precipitate of lithium bromide filtered off. The hexane solution concentrated to approximately 10 ml was added to a 1 × 4″ silica gel column which was eluted with 400 ml of 90:10 cyclohexane/benzene. No product was obtained from this solvent. The column was then further eluted with 75 ml of 50:50 benzene/chloroform to yield 0.95 g (79%) of acetophenone, whose infrared spectrum was identical with that of an authentic sample, $n_D^{19°}$ 1.5346 (lit[19] 1.5342), 2,4-dinitrophenylhydrazone, m.p. 249–250°; the mixed m.p. with an authentic sample was not depressed.

α-(*Triphenylsiloxy*)-*trans*-β-*methylstyrene*

To a rapidly stirred suspension of 3.78 g (0.01 mole) of ethyltriphenylphosphonium bromide in 50 ml of anhydrous ether was added dropwise 0.01 mole of phenyllithium over a period of 30 minutes. An intense yellow colour developed during the addition. After stirring an additional hour a solution of 3.65 g (0.01 mole) of benzoyltriphenylsilane in 75 ml of anhydrous ether was added dropwise over 30 min. After 48 h stirring workup with hexane as above gave a pale yellow oil. The NMR spectrum showed a one-proton quartet at 5.19 ppm and a three-proton doublet at 1.55 ppm, *J* 7 Hz. This showed clearly that one of the two possible isomers of the olefin greatly predominated. The crude product was then chromatographed on silica gel to yield 1.90 g of a colourless oil with spectra almost identical to those of the original oil. The product could not be induced to crystallize by scratching or cooling and was finally purified by vacuum sublimation at 80° and 3.2 mm pressure to give a white solid which was recrystallized from dry pentane to yield 100 mg (2.7%) of pure α-(triphenylsiloxy)-*trans*-β-methylstyrene, m.p. 80–82°. A further 1.7 g of oil remained which on seeding slowly crystallized yielding 1.6 g of α-(triphenylsiloxy)-*trans*-β-methylstyrene, m.p. 78–82°. Decomposition occurred readily and several recrystallizations were required before a sharp melting point was obtained. The total yield of pure product, m.p. 80–82°, was 0.90 g (22%). The NMR spectrum of the pure material showed the same peaks as the crude material and there were no significant differences between the infrared spectra of the crude and the pure product: ultraviolet spectrum; λ_{max} (cyclohexane); 217 (28,300), 262 (12,700) mμ. (Found: C, 82.42; H, 5.80. $C_{27}H_{24}OSi$ calcd.: C, 82.64; H, 6.12%.)

α-Triphenylsiloxy-trans-β-ethylstyrene

Following the above procedure 3.92 g (0.01 mole) of n-propyltriphenylphosphonium bromide was treated with 0.01 mole of phenyllithium. The solution was then stirred for a further 60 min and then 3.64 g (0.01 mole) of benzoyltriphenylsilane in ether was added dropwise over a period of 2 h. Workup after 16 h, followed by chromatography, gave 2.91 g of a colourless oil which failed to crystallize. The substance decomposed rapidly to triphenylsilanol and phenyl propyl ketone despite all precautions. The same result was obtained in several duplicate experiments. The phenyl propyl ketone was identified as its 2,4-dinitrophenylhydrazone derivative m.p. 188–189° (lit.[16] 190°), yield 2.03 g (73%).

1,1-Diphenyl-2-methylenesilacyclohexane

A solution of 207.3 mg (0.788 mmole) of 1,1-diphenylsilacyclohexan-2-one in 15 ml of anhydrous ether was added dropwise to a stirred solution containing 0.788 mmole of methylenetriphenylphosphorane. The yellow colour of the Wittig reagent was discharged and a white precipitate formed. The suspension was stirred for 4 h and then was drowned in 10% hydrochloric acid. Workup gave a colourless oil which was chromatographed on silica gel using 50 ml of carbon tetrachloride to yield 159.2 mg (75%) of 1,1-diphenyl-2-methylenesilacyclohexane, $n_D^{19^\circ}$ 1.5912. The infrared spectrum showed Si–Ph bands at 7 and 9 μ and three bands at 10.72, 11.21 and 11.60 μ respectively. The first of these appears to be a general feature of the 1,1-diphenylsilacyclohexane derivatives[17]. (Found: C, 80.13; H, 7.54. $C_{18}H_{20}Si$ calcd.: C, 79.97; H, 7.59%.)

Reaction of triphenylacetylsilane with methylenetriphenylphosphorane

To 0.0025 moles of methylenetriphenylphosphorane in 10 ml of ether was added 760 mg (0.0025 mole) of acetyltriphenylsilane dissolved in 20 ml of anhydrous ether. The reaction mixture was stirred for 12 h and then was hydrolyzed with 25 ml of 10% hydrochloric acid. The ether layer was separated and dried over anhydrous magnesium sulphate. The solution was evaporated under reduced pressure and the resulting white solid was recrystallized from ethyl alcohol to yield 581 mg (75%) of 2-(triphenylsilyl)propene, m.p. 93–94°. The mixed melting point with an authentic sample[12] was not depressed and the spectra were identical to those of the authentic material.

Reaction of benzoyltriphenylsilane with benzylidenetriphenylphosphorane

To a suspension of 3.89 g (0.01 mole) of benzyltriphenylphosphonium chloride in 100 ml of ether was added dropwise 0.01 mole of phenyllithium. The phosphonium salt dissolved and an intense red colour was observed. A solution of 3.64 g (0.01 mole) of benzoyltriphenylsilane in 100 ml of dry toluene was then added. The solution was heated during the addition and for a further ten days. The intense red colour of the phosphorane was slowly discharged during this period and a yellow precipitate was observed to form. Workup, using 10% hydrochloric acid, gave an oil which was dissolved in boiling ether: upon cooling in ice, 0.37 g of triphenylphosphine oxide, m.p. 158° after recrystallization from ether, separated. Pentane was then added to the ethereal solution and 0.29 g of hexaphenyldisiloxane m.p. 220–224° was obtained. The remaining crude product was chromatographed on silica gel. The column was eluted with 200 ml of cyclohexane to yield 1.1 g of hexaphenyldisiloxane. Hence, the total yield of hexaphenyldisiloxane after recrystallization from carbon tetrachloride/hexane, was 1.31 g (51 %), m.p. 221–224°, identified by mixed melting point.

The column was eluted with 150 ml of benzene/cyclohexane to yield 97 mg (34 %) of triphenylphosphine, m.p. 78–79°, identified by a mixed melting point determination.

The column was then eluted with 100 ml of benzene to yield 0.51 g (24 %) of triphenylsilanol, m.p. 150–152° after recrystallization from carbon tetrachloride. The sample was identified by a mixed melting point determination and by comparison of its infrared spectrum with that of an authentic sample.

The column was then eluted with 100 ml of chloroform/benzene 1 : 1 to yield 1.71 g (91 %) of desoxybenzoin, m.p. 59–60° after recrystallization from ethanol, identified by comparison of the mixed melting point and infrared spectrum with an authentic sample.

Finally, chloroform elution of the column gave 0.73 g of triphenylphosphine oxide, m.p. 157–158.5°, (total yield 1.10 g, 47 %), identified by mixed melting point.

α-(Triphenylgermyl)styrene

To 0.0025 mole of methylenetriphenylphosphorane was added 1 g (0.0025 mole) of benzoyltriphenylgermane in 25 ml of ether. The yellow colour due to both reagents was rapidly discharged and a flocculent white precipitate was formed. After being stirred overnight, workup gave a solid on removal of the solvent which was recrystallized from methanol to yield 0.71 g (72 %) of α-(triphenylgermyl)styrene, m.p. 120.5–122.5° (lit.[18] 119–120°). The infrared spectrum showed bands at 6.96 and 9.15 μ (Ge–Ph): ultraviolet spectrum, λ_{max} (methanol) 248 (8,500) mμ.

An alternative synthesis was effected by the addition of 1 mmole of methylmagnesium bromide to an ethereal solution of 274 mg (0.685 mmole) of benzoyltriphenylgermane. The yellow colour of the benzoyltriphenylgermane was discharged rapidly. Workup gave an oil which was dissolved in 10 ml of benzene and added to a mixture of 0.75 ml of concentrated sulphuric acid and 1 ml of water. The mixture was stirred rapidly for 24 h and then poured into 50 ml of water. The organic phase was separated, dried over anhydrous magnesium sulphate and the solution was evaporated under reduced pressure to yield a white solid which was recrystallized from methanol to yield 129 mg (48 %) of α-(triphenylgermyl)styrene which was identical to the above in all respects.

Reaction of benzoyltriphenylgermane with ethylidenetriphenylphosphorane

To 0.001 mole of ethylidenetriphenylphosphorane was added 0.410 g (0.001 mole) of benzoyltriphenylgermane in 25 ml of ether over a period of 30 min. The yellow colours of the two reagents faded over the time of the addition and a white precipitate was formed. The reaction mixture was stirred for 4 h and then was hydrolyzed with 10 % hydrochloric acid and worked up. The ether extracts were evaporated under reduced pressure and the pale yellow oil crystallized from absolute ethanol to give

0.33 g (81 %) of α-(triphenylgermyl)-*trans*-β-methylstyrene, m.p. 89–91.5°. The infrared spectrum showed bands at 6.96 and 9.15 μ (Ge–Ph) and the NMR spectrum showed a three-proton doublet (*J* 7 Hz) at 1.64 ppm and a one-proton quartet (*J* 7 Hz) at 6.54 ppm assigned to the methyl group and the vinyl proton respectively: ultraviolet spectrum, λ_{max} (cyclohexane); 245 (5,300) mμ. (Found: C, 76.88; H, 5.90. $C_{27}H_{24}Ge$: C, 77.03; H, 5.71 %.)

Reaction of acetyltriphenylsilane with butylidenetributylphosphorane

To a solution of 0.003 mole of butylidenetributylphosphorane [prepared from 1.16 g (0.003 mole) of tetra-n-butylphosphonium iodide and n-butyllithium] in dry ether were added 0.91 g (0.003 mole) of acetyltriphenylsilane in 30 ml of ether. A white precipitate formed and the solution slowly turned orange over a period of several days. At the end of a week the solution was still orange but the precipitate had virtually disappeared. The solution was filtered, and the solvents were removed under reduced pressure to yield a brown oil which was chromatographed on a silica gel column. The column was eluted with 100 ml of hexane to yield 0.31 g of a brown solid whose NMR spectrum showed a number of ill-defined peaks centred at 4.5 ppm. The column was then eluted with 100 ml of carbon tetrachloride to yield 0.49 g (82 %) of tributylphosphine, $n_D^{19°}$ 1.4679 (authentic sample 1.4683). The column was then eluted with 200 ml of benzene to yield 0.40 g (50 %) of triphenylsilanol, m.p. 150–152°.

The unknown was re-chromatographed on a $\frac{1}{2} \times 3''$ silica gel column. Elution with 100 ml portions of hexane and carbon tetrachloride gave no product. The column was then eluted with 100 ml of benzene to yield 191 mg (39 %) of triphenylsilanol. The total yield of triphenylsilanol was thus 89 %.

Reaction of phenacyltriphenylsilane with methylenetriphenylphosphorane

To 158 mg (0.413 mmole) of phenacyltriphenylsilane dissolved in 20 ml of ether was added dropwise an ethereal solution of methylenetriphenylphosphorane until a faint permanent yellow colour persisted. A dense white precipitate formed during the course of the addition. The reaction mixture was stirred overnight and then was hydrolyzed with dilute hydrochloric acid. The organic layer was extracted, dried over anhydrous magnesium sulphate and the ether was removed under reduced pressure. The remaining oil was chromatographed on silica gel using benzene to yield 101 mg (87.5 %) of triphenylsilanol, m.p. and mixed melting point 150.5–152°. The column was then eluted with 100 ml of chloroform to yield 21 mg (68 %) of acetophenone, $n_D^{20°}$ 1.5339 (lit.[19] 1.5342) whose infrared spectrum was identical with that of an authentic sample.

Reaction of phenacyltriphenylgermane with methylenetriphenylphosphorane

To 112 mg (0.25 mmole) of phenacyltriphenylgermane in 20 ml of ether was added dropwise an ethereal solution of methylenetriphenylphosphorane. A dense white precipitate was observed to form and the addition was continued until the solution was a faint permanent yellow colour. The reaction mixture was stirred overnight and then was hydrolyzed with hydrochloric acid. The organic layer was extracted, dried and the solvents removed under reduced pressure. The pale yellow oil so obtained was chromatographed on a silica gel column and eluted with chloroform to yield 21 mg (66 %) of acetophenone, $n_D^{20°}$ 1.5341, whose infrared spectrum was identical to that of an authentic sample.

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SUMMARY

The Wittig reactions of several silyl and germyl ketones have been investigated. Benzoylsilanes were found to yield siloxyalkenes exclusively, whereas benzoylgermanes, and alkyl silyl ketones gave normal Wittig reactions. Phenacyltriphenylsilane and phenacyltriphenylgermane underwent β-elimination reactions with methylenetriphenylphosphorane.

REFERENCES

1 A. G. BROOK, *J. Org. Chem.*, 25 (1960) 1072.
2 A. G. BROOK AND N. V. SCHWARTZ, *J. Org. Chem.*, 27 (1962) 2311.
3 A. G. BROOK, W. W. LIMBURG, D. M. MACRAE AND S. A. FIELDHOUSE, *J. Am. Chem. Soc.*, 89 (1967) 704.
4 C. D. GUTSCHE, in *Organic Reactions, Vol.* 8, Wiley, New York, 1954, p. 364.
5 A. G. BROOK AND W. W. LIMBURG, *J. Am. Chem. Soc.*, 85 (1963) 832.
6 A. G. BROOK, G. E. LEGROW AND D. M. MACRAE, *Can. J. Chem.*, 45 (1967) 1231.
7 D. SEYFERTH AND S. O. GRIM, *J. Am. Chem. Soc.*, 83 (1961) 1610.
8 A. MAERKER, *Organic Reactions*, Vol. 14, Wiley, New York, 1965, p. 270.
9 J. A. POPLE, W. G. SCHNEIDER AND H. J. BERNSTEIN, *High Resolution Nuclear Magnetic Resonance*, McGraw Hill, New York, 1959, p. 238.
10 L. M. JACKMAN, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon Press, New York, 1964, p. 61.
11 E. ELIEL, *Stereochemistry of Carbon Compounds*, McGraw Hill, New York, 1962, p. 138.
12 H. GILMAN AND G. D. LICHTENWALTER, *J. Am. Chem. Soc.*, 80 (1958) 2680.
13 C. EABORN, *Organosilicon Compounds*, Butterworths, London, 1960, p. 133–139.
14 A. G. BROOK, R. KIVISIKK AND G. E. LEGROW, *Can. J. Chem.*, 43 (1965) 1175.
15 H. GILMAN AND L. S. MILLER, *J. Am. Chem. Soc.*, 73 (1951) 865.
16 A. I. VOGEL, *Practical Organic Chemistry*, Longmans, London, 1959, p. 743.
17 A. G. BROOK AND J. B. PIERCE, unpublished studies.
18 A. L. ALLRED, *Inorg. Chem.*, 4 (1965) 1752.
19 *Handbook of Chemistry and Physics*, The Chemical Rubber Publishing Co., Cleveland, Ohio, 44th Ed., p. 780.