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SHORT COMMUNICATION

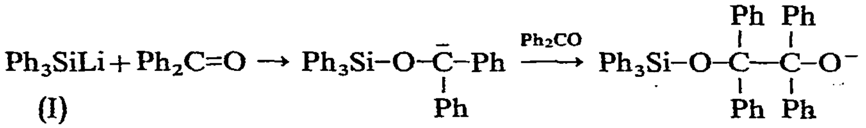
The reaction of triphenylsilyllithium with methyl pivalate: 2,2,5,5-tetramethyl-4-(triphenylsiloxy)-3-hexanone

Very little has been reported on the reaction of triphenylsilyllithium, (I), with esters. With ethyl acetate Gilman and Peterson[1] reported two products, 1,1-bis(triphenylsilyl)ethanol, (II) (5%), and 1-(triphenylsiloxy)-1-(triphenylsilyl)ethane, (III) (6%), and with ethyl benzoate Gilman and Trepka[2] found triphenylethoxysilane, (IV) (8%), and benzoin, (V) (4%). Although the isolation of (II) and (III) were readily accounted for they failed to account for the formation of (IV) and (V) and for the major portion of the product in both cases.

We wish to report a study of the reaction of (I) with methyl pivalate*. When (I) was added to a large excess of methyl pivalate, followed by acid workup and distillation, two products were obtained. The first was triphenylmethoxysilane, (VI) (43%), and the second was identified as 2,2,5,5-tetramethyl-4-(triphenylsiloxy)-3-hexanone, (VII) (46%).

The structure of (VII) was assigned on the following basis. It was in agreement with the carbon-hydrogen analysis, the infrared, NMR and mass spectra. Addition of deuterium oxide with trifluoroacetic acid to an NMR sample failed to exchange any protons. The treatment of the anion of pivaloin with triphenylchlorosilane gave (VII). The ultraviolet absorption spectrum of (VII) had a λ_{max} at 318 mμ considerably longer than those in pivaloin (305 mμ) or methoxyacetone (282 mμ)[3]. Treatment of pivaloin with hexamethyldisilazane gave an analogous trimethylsiloxy ketone, (VIII), with a λ_{max} at 318 mμ. Finally the formation of (VII) can be rationalized on the basis of the reaction sequence shown in Scheme 1.

The steps up to the formation of (IX) find direct analogy in the work of Brook and Schwartz[4] on the reaction of (I) with benzophenone:



$$\underset{\text{(I)}}{Ph_3SiLi} + Ph_2C{=}O \rightarrow Ph_3Si{-}O{-}\underset{Ph}{\overset{-}{C}}{-}Ph \xrightarrow{Ph_2CO} Ph_3Si{-}O{-}\underset{Ph}{\overset{Ph}{C}}{-}\underset{Ph}{\overset{Ph}{C}}{-}O^-$$

The reaction of (IX) with methoxide to give the two products observed, (VI) and (VII), is an example of a β-elimination[5].

Even when only one equivalent of pivalate was added to (I), (VII) was still the major product isolated.

It seems probable that such diaddition reactions are also of importance in other systems such as the reaction of (I) with anhydrides and acid chlorides where low overall yields have been reported[1].

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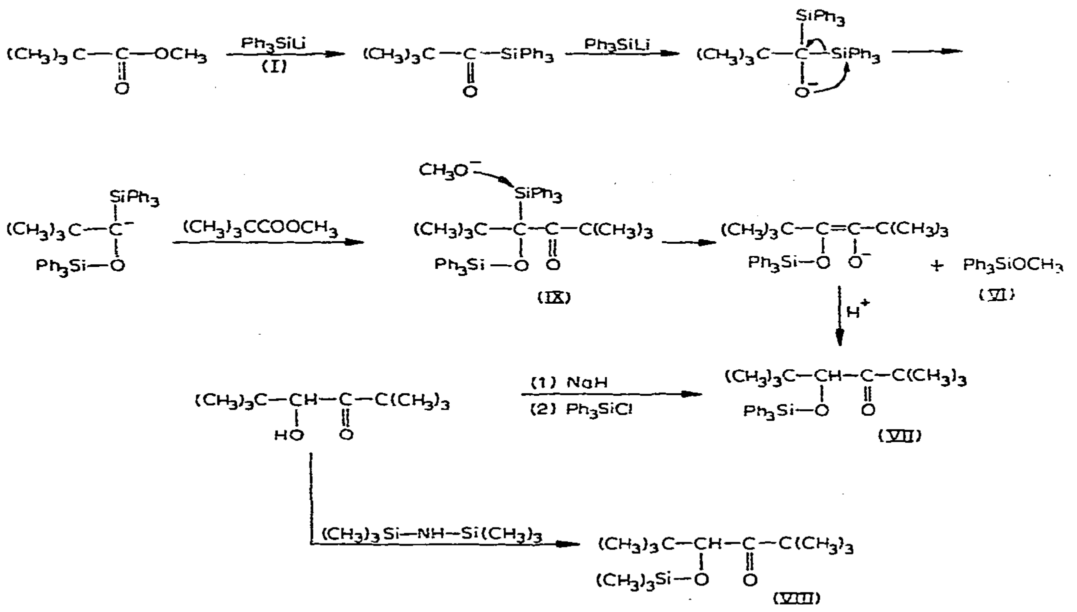
* Pivalic acid = 2,2-dimethylpropionic acid.



Scheme 1. Formation of 2,2,5,5-tetramethyl-4-(triphenylsiloxy)-3-hexanone(VII).

Experimental

General. All reactions were carried out under an atmosphere of prepurified nitrogen. Melting points are uncorrected. Elemental analyses were by Galbraith Laboratories, Inc., Knoxville, Tennessee. Mass spectra, infrared spectra, ultraviolet spectra and NMR data were determined on Metropolitan-Vickers MS-9, Perkin Elmer 421, Perkin Elmer 202 and Varian Associates A-60 spectrometers, respectively.

Reaction of triphenylsilyllithium with methyl pivalate. (a). A solution of triphenylsilyllithium prepared from 7.4 g (0.025 mole) of triphenylchlorosilane and 0.7 g (0.1 g-atom) of lithium in 50 ml of THF was added to 25 ml of methyl pivalate cooled in a dry ice/acetone bath. The resultant mixture was allowed to warm to room temperature and then added to ethyl ether, ice and dilute hydrochloric acid. The ether layer was dried with sodium sulfate and concentrated under reduced pressure. The resultant oil was distilled to obtain 3.1 g (43 %) of triphenylmethoxysilane, b.p. 160–170° (0.05 mm), m.p. 50–54°, and 4.9 g (46%) of (VII), b.p. 200–215° (0.05 mm) m.p. 98–113°. Recrystallization of (VII) from heptane gave 4.1 g (38%), m.p. 118–121°. (Found: C, 78.0; H, 7.99. $C_{28}H_{34}O_2Si$ calcd.: C, 78.1; H, 7.96%.)

The NMR spectrum (CCl_4) consisted of singlets at τ 9.18, 9.07 and 5.64 ppm and a multiplet τ 2.3–2.8 ppm with relative areas of 9 : 9 : 1 : 15 respectively.

The infrared absorption spectrum (CCl_4) had a ν_{max} at 1712 cm^{-1} and the ultraviolet absorption spectrum had λ_{max} 318 (ε 26, heptane) and λ_{max} 315 (ε 30, ethanol).

The mass spectrum did not show a parent but had fragments of mass 345 (33 %) $[M - (CH_3)_3CCO]$ and 353 (3 %) $[M - C_6H_5]$. The other major peaks were 276.0970 (55%), 259 (72%), 199 (100%), 122 (31 %) corresponding to Ph_3SiOH^+, Ph_3Si^+, Ph_2SiOH^+ and $PhSiOH^+$, respectively.

(*b*). A solution of 2.9 g (0.025 mole) of methyl pivalate was added to a rapidly stirring solution of triphenylsilyllithium (100 ml, 0.05 mole) in THF. Workup as above gave a light yellow oil, from which 2.9 g (54%) of (VII) was obtained by crystallization with heptane and with methanol.

Reaction of the pivaloin with triphenylchlorosilane. A solution of 1.7 g (0.01 mole) of pivaloin in 100 ml of THF was stirred for 48 h with 0.24 g (0.01 mole) of sodium hydride. Following addition of 2.9 g (0.01 mole) of triphenylchlorosilane the resultant mixture was stirred for 70 h. Workup as above and recrystallization from heptane gave 3.2 g (74%) of (VII) identical in all respects with that previously prepared.

Reaction of pivaloin with hexamethyldisilazane. A mixture of 0.85 g (0.005 mole) of pivaloin, 10 ml of hexamethyldisilazane and a few drops of trimethylchlorosilane was stirred for 84 h. The solid present was filtered off, the filtrate was concentrated under reduced pressure and the resultant oil was crystallized from ethanol to obtain 0.46 g (39%) of (VIII), m.p. 37–39°. (Found: C, 63.7; H, 11.33. $C_{13}H_{19}O_2Si$ calcd.: C, 63.9; H, 11.54%.)

The NMR spectrum (CCl_4) consisted of singlets at τ 9.85, 9.06, 8.83 and 5.76 ppm with relative areas of 9:9:9:1, respectively.

The infrared absorption spectrum (CCl_4) had a ν_{max} at 1712 cm^{-1} and the ultraviolet absorption spectrum had a λ_{max} 318 (ε 27, heptane).

The mass spectrum did not show a parent but had fragments of mass 159 (93%) $[M - (CH_3)_3CCO]$ and 229 (1%) $[M - CH_3]$. The only other major fragment was mass 73 (100%), $[Me_3Si^+]$.

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