Journal of Organometallic Chemistry, 446 (1993) C9–C11

JOM 23256PC

Preliminary Communication

Rearrangements from the reactions of silenes with trimethylsilylketene

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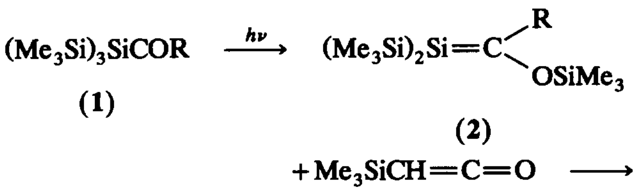
(Received August 5, 1992; in revised form September 28, 1992)

Abstract

Silenes of the family $(Me_3Si)_2Si{=}C(OSiMe_3)R$ (R = Ad, ${}^tBu$) react with $Me_3SiCH{=}C{=}O$ to give non-cyclic acylsilane adducts which result from major skeletal rearrangement of a postulated [2+2] initial adduct.

In the recent past we have studied the cycloaddition reactions of the relatively stable silenes $(Me_3Si)_2Si{=}C(OSiMe_3)R$, **2**, (R = Ad, ${}^tBu$) with dienes and alkenes where [2 + 2] cycloadditions were prominent [1], with carbonyl compounds where siloxetanes were formed as a result of [2 + 2] cycloaddition with the carbonyl group [2], and with various α,β-unsaturated carbonyl compounds where [2 + 4] cycloadditions with both possible regiochemistries were the main products observed [3,4]. We have now investigated the dark reactions of the silenes with the stable ketene trimethylsilylketene **3**, anticipating [2 + 2] cycloaddition to either the C=C or C=O group. To our surprise the silenes gave rise exclusively to compounds having the structures **4** with *E* geometry (eqn. (1)), indicating that bonding has occurred between the sp^2-hybridized silicon atom of the silene and the terminal carbon atom of the silylketene, but where skeletal rearrangements have subsequently occurred.

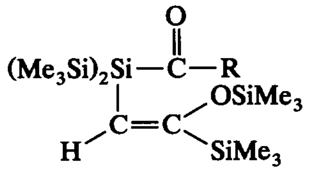


$$(Me_3Si)_3SiCOR \xrightarrow{h\nu} (Me_3Si)_2Si{=}C\begin{matrix}R\\OSiMe_3\end{matrix}$$

(1) (2)

$$+\,Me_3SiCH{=}C{=}O \longrightarrow$$

(3)



(1)

(4)

(R = Ad, ${}^tBu$)

In a typical experiment 0.32 g (0.78 mmol) of the acylsilane **1**, R = Ad, in 0.8 ml of C_6D_6 in a sealed NMR tube was photolyzed with ≥ 360 nm radiation for 65 h. A ^1H NMR spectrum indicated 83% of the silene **2** and 17% of unconsumed acylsilane **1**, due to the photostationary state resulting from reversion of the silene back to acylsilane [5]. To the solution was added 89 mg (0.78 mmol) of the silylketene **3**, and the reaction was followed by NMR spectroscopy. The mildly exothermic reaction, accompanied by some fading of the initial yellow color, was complete in about 2 h. The solvent was removed under reduced pressure, also removing unconsumed silylketene, and the residual oil, which failed to crystallize, was redissolved in C_6D_6. NMR spectra [6] indicated the presence only of product **4**, formed quantitatively from the initially formed silene **2**, and the unconsumed acylsilane **1**. Chromatography of the solution containing **4** on silica gel failed to remove it from the residual acylsilane **1**. Cophotolysis of the acylsilane **1** with the silylketene failed as an alternative route to **4** due to the formation of numerous other by-products, presumably because **4**, which is itself an acylsilane, also underwent photochemical reactions.

^{29}Si NMR spectroscopy established that **4** contained three different types of Me_3Si groups in the ratio 2:1:1. For **4**, R = Ad, the signal representing the two equivalent groups had a characteristic chemical shift at −14.8 ppm representative of two Me_3Si groups attached to a central silicon atom [7], which itself was unusually shielded ($\delta = -41.9$ ppm), and inconsistent with a siloxetane structure arising from [2 + 2] addition across the C=O group (δ typically +40 to 60 ppm [2]) or a silacyclobutane from [2 + 2] addition across the C=C bond (δ typically −16 to −30 ppm [1] for compounds bearing similar substituents). The single Me_3Si groups had chemical shifts characteristic of a $OSiMe_3$ group ($\delta = 14.8$ [7]), and of a Me_3Si group attached to carbon, at −12.3 ppm (which showed splitting to a

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* Dedicated to Professor M.G. Voronkov in recognition of his many important contributions to the development of Organosilicon Chemistry.

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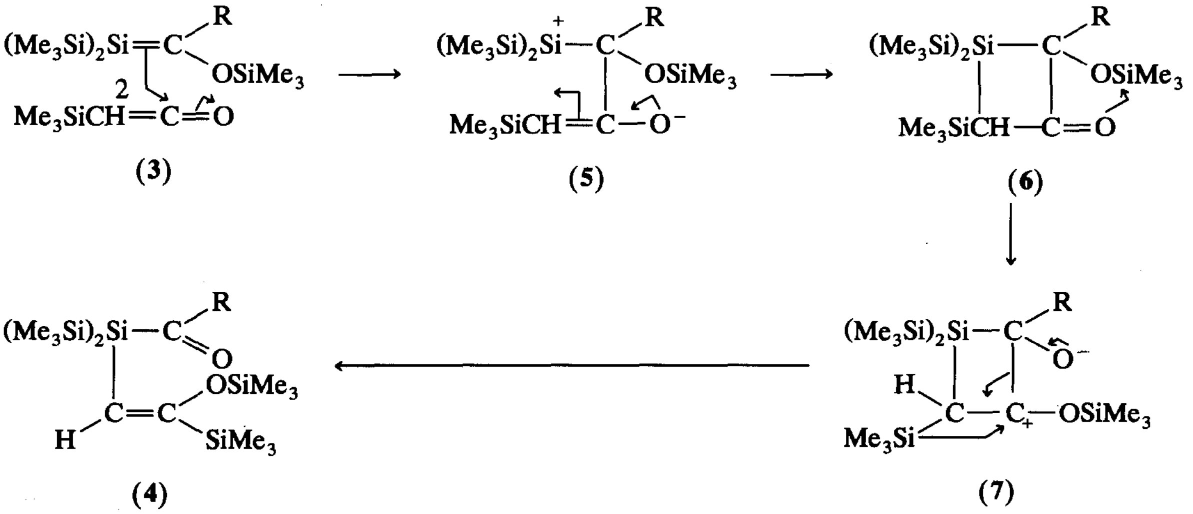

(R = Ad, ^{t}Bu)

Scheme 1.

doublet of decets due to an adjacent hydrogen in the ^{29}Si–^{1}H coupled spectra). The ^{13}C NMR spectrum showed a signal at about 247 ppm characteristic of the carbonyl carbon of an acylsilane [7]. In addition, there were two sp^2-hybridized carbon resonances, one at 128.7 ppm (with H attached, shown by the APT [8] spectrum) and one at 170 ppm (no H attached). These features, and all other spectroscopic properties, are accounted for by the proposed structure **4** for the products. The *E* geometry was demonstrated for **4**, R = ^{t}Bu, by a NOE experiment which indicated interaction between the =CH proton signal at δ 5.24 with the Me_3Si group having its ^{1}H NMR signal at 0.24 ppm (but not the signal at δ 0.30). A HETCOR experiment showed that the ^{1}H NMR signal at $\delta = 0.24$ correlated with the ^{29}Si NMR signal at -12.30 ppm, which belongs to the Me_3Si group on carbon and not the $OSiMe_3$ group. Hence the H and Me_3Si groups attached to the C=C bond in **4** must be *cis*-related.

A possible explanation for the formation of **4** involves the initial (probably stepwise) [2 + 2] cycloaddition of the silene with the C=C bond of the ketene leading via **5** to the apparently unstable intermediate **6** (Scheme 1). This then undergoes a 1,4 silyl migration from oxygen-to-oxygen, a previously observed rapid process [9,10] which would nominally yield the dipolar intermediate **7**. This unstable species would be expected to rearrange, by migration of the Me_3Si group to the β-carbocationic site, to yield the observed product **4**. At this time it is not known whether **5**, **6**, and **7** are discrete intermediates, or whether the overall conversion to **4** is an essentially concerted process. Attempts to show the presence of any intermediate by running the reaction at low temperature failed. At -78°C, -30°C, or -15°C, NMR spectra showed only the presence of unreacted starting materials. At temperatures near 10°C the reagents appeared to be converted directly (but slowly) to product **4** with no evidence for the accumulation of any intermediate.

When bis-trimethylsilylketene was employed as the ketene no reaction with the silene was observed over several days. Further studies are underway.

Acknowledgments

We are indebted to Professor T. Tidwell for a gift of starting material for preparation of the ketenes, and to Nick Plavac for assistance with the NOE and HETCOR experiments.

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6 Spectroscopic properties of 4 (R = Ad): ^{1}H NMR (C_6D_6): δ 0.21, 0.30 (each 9H, s, Me_3Si), 0.31 (18H, s, 2 Me_3Si), 1.58–1.91 (15H, m, Ad), 5.21 (1H, s, =CH). ^{13}C NMR: δ 0.51 (Me_3Si), 1.01 (2 Me_3Si), 2.09 ($OSiMe_3$), 28.57 (Ad CH), 37.07, 38.05 (Ad CH_2), 51.55 (Ad quat C), 128.68 (=CH), 170.25 (=*C*-$SiMe_3$), 246.92

(C=O). ^{29}Si NMR: δ 14.78 ($OSiMe_3$), -12.26 ($Me_3Si{-}C$), -14.68 ($(Me_3\mathit{Si})_2Si$), -41.92 ($(Me_3Si)_2\mathit{Si}$). IR (KBr): 1622 cm^{-1} (C=O). 3 (R = ^{t}Bu): δ 0.24, 0.30 (each 9 H, s, Me_3Si), 0.31 (18 H, s, $2Me_3Si$), 1.09 (9H, s, Me_3C), 5.24 (1H, s, =CH). ^{13}C NMR: δ 0.48 (Me_3Si), 0.81 (2 Me_3Si), 2.01 ($OSiMe_3$), 25.92 (Me_3C), 48.93 ($Me_3\mathit{C}$), 128.58 (=CH), 170.20 ($=C{-}SiMe_3$), 246.99 (C=O). ^{29}Si NMR: δ 14.96 ($OSiMe_3$), -12.30 $Me_3Si{-}C$), -14.63 ($(Me_3\mathit{Si})_2Si$), -41.73 ($(Me_3Si)_2\mathit{Si}$). IR (KBr): 1619 or 1631 cm^{-1} (C=O).

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