Solution Phase Photochemical Hydrosilylation of Silylacetylenes

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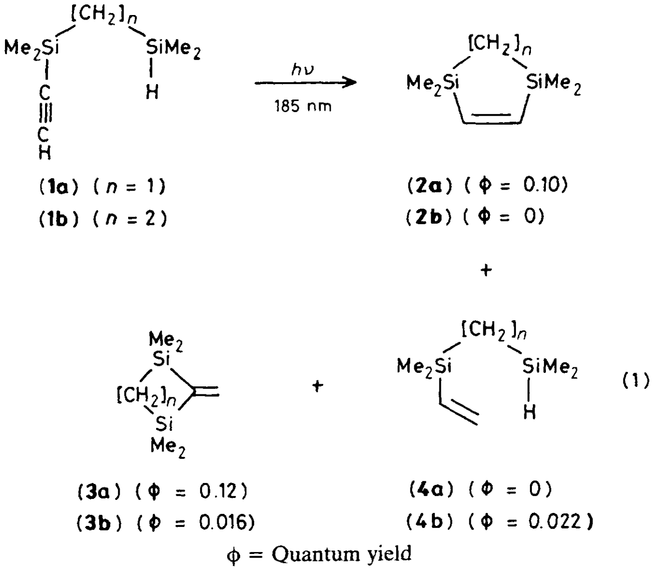
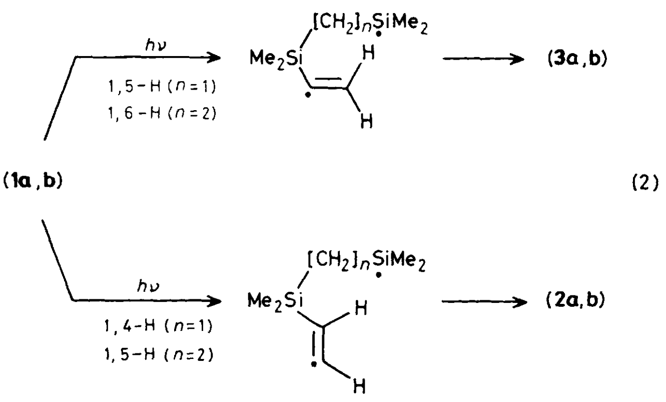
Intramolecular addition of silanes to silylacetylenes in competition with reduction of the triple bond by solvent can be effected photochemically (185 nm).

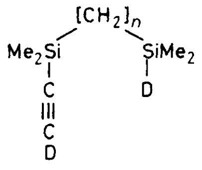
Photoreduction to alkenes usually occurs when simple acyclic mono- and di-alkylacetylenes are photolysed at 185 nm in hydrocarbon solvents such as pentane.[1] Intramolecular abstraction of a secondary hydrogen from an alkyl substituent by photoexcited acetylene and cyclization of the resultant diradical has only been observed with cyclononyne, which gives bicyclo[4.3.0]non-1-ene (ϕ = 0.25) in addition to (E,Z)-cyclononenes (ϕ = 0.16).[1] We report herein that acyclic silylacetylenes bearing a remote silane hydrogen donor group, *i.e.*, $HMe_2Si–[CH_2]_n–SiMe_2C{\equiv}CH$, produce disilacycloalkenes. A potential hydrogen abstraction mechanism requires both 1,5-H and 1,4-H transfer to form products when n = 1, whereas 1,6-H transfer is needed when n = 2. Crossover experiments indicate that the cyclic products are formed intramolecularly and not *via* potential free-radical chain mechanisms.



(1)



(2)



$[^2H_2]$ (**1a, b**)

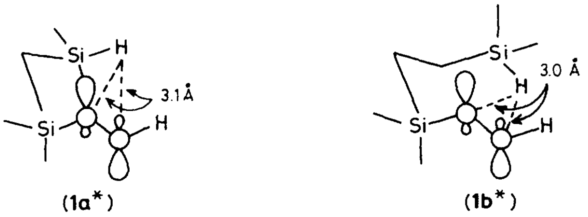


Figure 1

Direct photolyses of 10^{-2} M solutions of 2,4,4-trimethyl-2,4-disilahex-5-yne (**1a**)[2] in deoxygenated pentane in which only the 185 nm component of a low pressure mercury lamp (185 + 254 nm) was absorbed[†] produced 1,1,3,3-tetramethyl-1,3-disilacyclopentene (**2a**)[2–4] and 2-methylene-1,1,3,3-tetramethyl-1,3-disilacyclobutane (**3a**)[2,5] in absolute yields of 8% each at 34% conversion, as determined by g.c. At <12% conversions (**2a**) plus (**3a**) accounted for 94% of reacted (**1a**). Similarly, 2,5,5-trimethyl-2,5-disilahept-6-yne (**1b**)[‡] gave maximum yields of 3% of 2-methylene-1,1,3,3-tetramethyl-1,3-disilacyclopentane (**3b**),[4] no detectable 1,1,4,4-tetramethyl-1,4-disilacyclohexene (**2b**),[4] and 4% of 2,5,5-trimethyl-2,5-disilahept-6-ene (**4b**)[‡] at >15% conversions. No other volatile products were detected in the photolysates of (**1a**) or (**1b**) by g.c. After preparative g.c., the photoproducts of (**1a**) and (**1b**) were identified by comparison of spectral data and g.c. retention times with authentic samples of (**2a**,**b**), (**3a**,**b**), and (**4b**). Quantum yields obtained at <4% conversions by *cis*-cyclo-octene actinometry[6,7] are summarized in equation (1).

Given the hydrogen donating ability of trialkylsilane groups [D(Si–H) = 377 kJ mol^{-1}][8] compared with secondary alkyl hydrogens [D(C–H) = 397 kJ mol^{-1}],[8] the enhanced intramolecular reactivity of (**1a**) and (**1b**) relative to previously studied acyclic alkylacetylenes[1] is reasonably explained by the hydrogen transfer mechanism of equation (2). An alternative, radical chain mechanism involving intramolecular addition of a silyl radical centre to the ground state acetylene was ruled out by the lack of significant crossover forming monodeuteriated products when isotopic mixtures containing 47.0% non-deuteriated (**1a**) + 2.62% $[^2H_1]$(**1a**) + 50.1% $[^2H_2]$(**1a**) or 41.0% non-deuteriated (**1b**) + 2.01% $[^2H_1]$(**1b**) + 54.9% $[^2H_2]$(**1b**) were photolysed to 30—40% conversions and analysed by g.c.–mass spectrometry. The photolysates contained the following isotopic distributions: unreacted (**1a**) (49.3% non-deuteriated, 4.38% $^2H_1$, 45.9% $^2H_2$), (**2a**) (54.6% non-deuteriated, 4.92% $^2H_1$, 40.1% $^2H_2$), and (**3a**) (50.1% non-deuteriated, 3.30% $^2H_1$, 46.5% $^2H_2$); unreacted (**1b**) (43.4% non-deuteriated, 5.45% $^2H_1$, 50.4% $^2H_2$), (**3b**) (41.7% non-deuteriated, 7.10% $^2H_1$, 48.8% $^2H_2$), and (**4b**) (40.4% non-deuteriated, 8.69% $^2H_1$, 46.2% $^2H_2$).

The higher efficiencies observed for (**1a**) compared with (**1b**) are consistent with (**1a**) having a larger fraction of excited molecules in favourable cyclic conformations for intramolecular hydrogen transfer by the equation (2) mechanism. Furthermore, (**1b**) has one additional rotation to 'freeze-out' in achieving a cyclic transition state.

Shown in Figure 1 are MM2 calculated[10] initial geometries for 1,4-H and 1,5-H transfer in which the excited state acetylenic group is modelled by a bent, *trans* structure[11,12] such that the transferring hydrogen has an in- or out-of-plane approach. The out-of-plane approach *via* a chair geometry mitigates the in-plane distance advantage (2.6 Å) for 1,5-H transfer *via* the half-chair and potentially accounts for the lack of preference of (**1a**) for 1,5-H over 1,4-H transfer, which otherwise rarely occurs.[13] Given arguments[11] suggesting that acetylene excited states are electrophilic above and below the σ plane, the out-of-plane approach might be favoured over in-plane transfer, as shown, if the hydrogen is nucleophilic owing to the electropositive nature of silicon. Some flattening of the MM2 calculated chair geometry would be needed to bring the transferring hydrogen and acetylenic p orbitals within the sum of the van der Waals radii (2.9 Å)[14] for reaction to occur. An additional factor involving stabilization of β *vs.* α

[†] U.v. (pentane) λ 185 nm (ε 1290), 193 (1100), 198 (661), and 254 (<1). See ref. 2 for the synthesis of (**1a**) in a study of the photochemistry of (**2a**).

[‡] The elemental analysis of (**1b**) and exact mass of the parent ion (high resolution mass spectra) of (**4b**) were satisfactory. Spectral data will be reported in our full paper.

odd-electron density, as has been established for silyl-substituted alkyl radicals,[15] possibly makes 1,4-H transfer competitive with the 1,5 mode of (**1a**).

As with (**1a**), the MM2 calculated[10] initial chair geometry of (**1b**) shows both carbons of the excited acetylene approximately equidistant from the transferring hydrogen. However, exceptionally close approach of hydrogen to the terminal acetylenic carbon is effected through slight flattening of the chair. Stereoelectronic requirements, as discussed for abstraction by carbon of enones,[14] then become ideal for 1,6-H transfer, since the vector defined by the hydrogen and abstracting carbon is nearly perpendicular to its projection within the plane of the bent acetylenic skeleton and within 10° of perpendicular to the axis of the acetylenic carbons.

Additional studies are underway to determine whether (**2a**) is produced by a divergent mechanism involving 1,2-Si shift across the triple bond followed by SiH insertion of a vinylidene intermediate similar to certain thermal rearrangements of terminal or trimethylsilyl-substituted acetylenes.[9]

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