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Tandem Photochemical or Thermal [1,5]-H, Thermal [1,5]-Si Migrations of Vinyl Silanes

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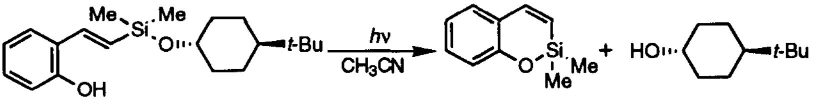
Key word: sigmatropic reaction.

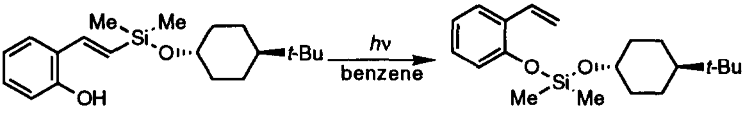
Abstract: *The irradiation or thermolysis of o-hydroxystyryl vinylsilanes results in migration of the silyl group to the phenolic oxygen via consecutive [1,5]-H and [1,5]-Si shifts.*

We have recently reported on the photochemistry of two (hydroxystyryl)dialkylsilyl ethers useful as photochemically-removable protecting groups.[2] While irradiation of **1** at 254 nm (Rayonet) in acetonitrile resulted in the desired ring closure and freeing of the alcohol (eq 1), in benzene an unusual rearrangement (eq 2), producing the dialkoxysilane **3**.[3] The mechanism of this process is the subject of this Letter.



(1)

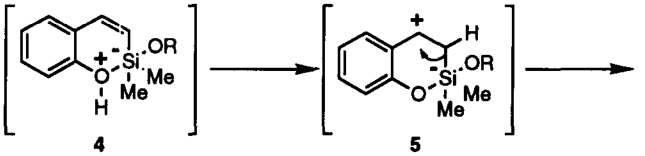
1 **2**



(2)

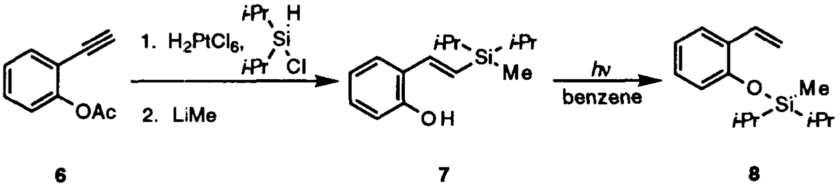
1 **3**

Our working hypothesis for the deprotection shown in eq 1 is *trans-cis* isomerization to produce betaine **4**, followed by elimination of alcohol. It was therefore reasonable to consider paths by which **4** could also serve as a precursor to **3**. One possibility is proton transfer to the vinyl silane moiety (eq 3), giving as an intermediate the β-silyl benzylic cation **5** that eliminates to give **3**. The rearrangement product might also derive from photoacid generation from the phenol followed by protiodesilylation of the vinyl silane, with trapping of the silyl moiety within a solvent cage. However, a common, charged intermediate in both deprotection and rearrangement pathways would make it difficult to explain the solvent effect. Furthermore, **5** does not possess the optimum geometry for stabilization of the cationic center or for the elimination reaction.



(3)

This intramolecular rearrangement is a reasonably general process, since **8**[4] is obtained (86 %) when **7** (obtained by treatment of the hydrosilation product of **6** with MeLi) is irradiated in benzene (eq 4), and the diisopropylsilyl ether **9** is converted (eq 5) to **10**[5] (89%).



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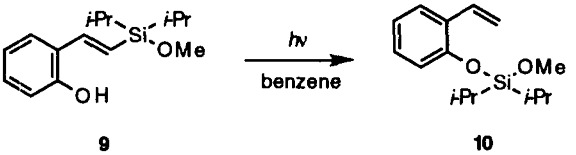
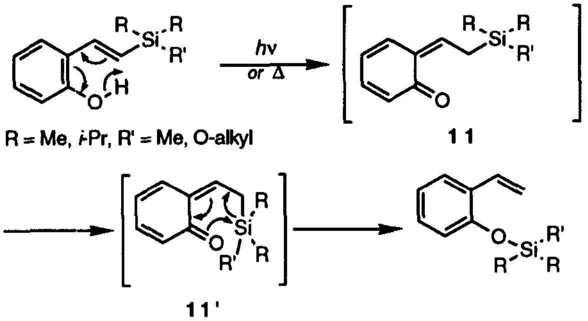
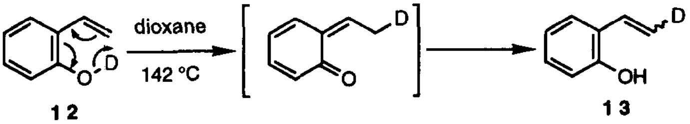


(5)

These results drew our focus to processes such as concerted reactions which are favored in non-polar solvents. An initial [1,5]-H shift to produce the quinone methide **11** followed by conformational change to **11'** and a [1,5]-Si shift (eq 6) would yield the observed products. Such a process is suggested by the known thermal isotopic exchange of the terminal vinylic protons and stereoisomerization in 2-vinylphenols, which occur by thermal [1,5]-H shift to produce the quinone methide followed by reversion (eq 7).[6]

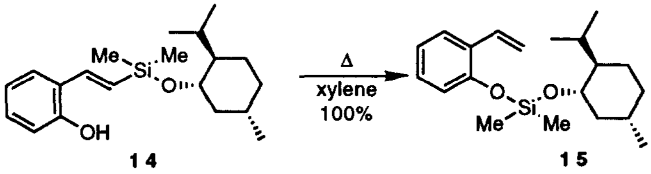


(6)

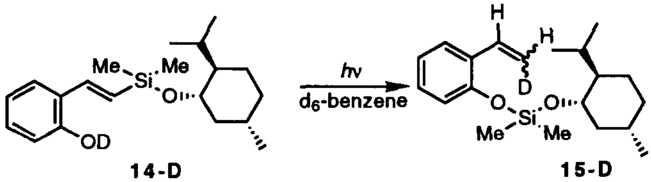


(7)

The vinylphenol precedent suggested that the rearrangement of the silyl ethers could be accomplished thermally, as was readily demonstrated with reactant **14**, which under reflux in xylene for 4 h produces **15**[7] quantitatively (eq 8). The pathway of the photochemical rearrangement of **14** was studied by isotopic incorporation experiments. Irradiation in d$_6$-benzene leads to **15** without detectable deuteration. When the phenolic hydrogen is exchanged for deuterium to produce **14-D**, its irradiation produces **15-D**[8] as a 1:1 mixture of stereoisomers. A crossover experiment between **1** and **14-D** establishes that the rearrangement is intramolecular. Attempts to intercept the intermediate quinone methide by a [4 + 2] cycloaddition with a polar alkene such as vinyl acetate or dihydrofuran were unsuccessful due to the inefficiency of the bimolecular processes in competition with the intramolecular rearrangement.



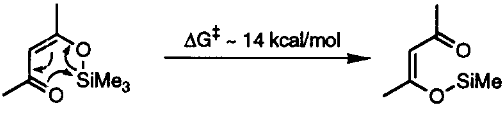
(8)



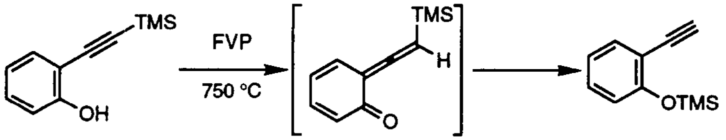
(9)

The results summarized above are consistent with the initial step in the rearrangement of these (hydroxystyryl)dialkylsilyl ethers being a precedented [1,5]-H shift to produce the quinone methide **11**. This process can be promoted either thermally or photochemically and, for the latter, the reactive excited state should be the singlet. Because **11** must then undergo a [1,5]-Si migration, precedents for this process are important. Though not a sigmatropic reaction, a thermal decarboxylation with 1,5-silyl transfer has been reported by Coates.[9] The silyl migration in **11'** is also the vinylog of the thermal [1,3]-Si migration in α-silylketones to form silyl enol ethers.[10] The bond-switching of β-diketone silyl ethers (eq 10) is one prototype for the silyl migration in **11'**.[11] The major difference is the formation of an aromatic ring in the latter case, which should provide significant thermodynamic and kinetic advantages. It is interesting that the known [1,3]- and [1,5]-Si migrations occur with retention of configuration at silicon, implying formation of a pentavalent silicon intermediate that undergoes pseudorotation before cleaving to give the product. Finally, the thermolytic rearrangement of *o*-(trimethylsilyl)ethynylphenol to the *o*-ethynylphenyl(trimethylsilyl)ether reported by Barton[12] (eq 11) is very analogous to the process proposed here.

The data in this report are consistent with a mechanism for the photochemical and thermal conversion of (hydroxystyryl)silanes to the (hydroxystyryl)silyl ethers involving concerted [1,5]-H shift followed by [1,5]-Si shift. Because these processes show little charge separation in the transition state, they are favored in non-polar solvents. Polar solvents must therefore be used for the photochemical deprotection reaction.



(10)



(11)

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References and Notes.

1. Postdoctoral fellow of the Korea Science and Engineering Foundation.
2. Pirrung, M. C.; Lee, Y. R. *J. Org. Chem.*, in press.
3. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.24 (s, 6H), 0.81(s, 9H), 0.93-1.93 (m, 9H), 3.72 (m, 1H), 5.21 (dd, J = 11.4, 1.2 Hz, 1H), 5.69 (dd, J = 17.4, 1.2 Hz, 1H), 6.92 (m, 2H), 6.99 (dd, J = 17.4, 11.4 Hz, 1H), 7.11 (ddd, J = 8.1, 7.5, 1.8 Hz, 1H), 7.46 (dd, J = 7.5, 1.8 Hz, 1H). IR (neat): 2946, 2867, 1598, 1552, 1484, 1452, 1255, 1088, 927, 801, 754 cm^{-1}· MS (m/z, CI): 333 (M^++1). HREIMS: Calcd. for $C_{20}H_{32}O_2Si$, 332.2171; Found, 332.2168.
4. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.19 (s, 3H), 1.02 (d, J = 3.5 Hz, 6H), 1.04 (d, J = 3.5 Hz, 6H), 1.10 (m, 2H), 5.20 (dd, J = 11.5, 1.5 Hz, 1H), 5.67 (dd, J = 17.5, 1.5 Hz, 1H), 6.77 (d, J = 8.5 Hz, 1H), 6.90 (dd, J = 8.5, 7.5 Hz, 1 H), 7.04 (dd, J = 17.5, 11.5 Hz, 1H), 7.09 (ddd, J = 7.5, 7.5, 2.0 Hz, 1H), 7.46 (dd, J = 7.5, 2.0 Hz, 1H). IR (neat): 2946, 2867, 1598, 1552, 1483, 1452, 1255, 1088, 927, 801, 753 cm^{-1}. MS (m/z, CI): 249(M^++1). HREIMS: Calcd. for $C_{15}H_{24}OSi$, 248.1596; Found, 248.1597.
5. ^{1}H NMR (300 MHz, benzene-d_6): δ 1.09 (d, J = 2.5 Hz, 12H), 1.03 - 1.15 (m, 2H), 3.45 (s, 3H), 5.22 (d, J = 11.1 Hz, 1H), 5.69 (d, J = 18.0 Hz, 1H), 6.83 - 7.47 (m, 4H), 7.37 (dd, J = 18.0, 11.1Hz, 1H). IR (neat): 2947, 2868, 1599, 1482, 1451, 1257, 1069, 924, 885, 754 cm^{-1}.
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7. ^{1}H NMR (500 MHz, benzene-d_6): δ 0.23 (s, 3H), 0.25 (s, 3H), 0.78 (d, J = 7.0 Hz, 3H), 0.79 (d, J = 6.0 Hz, 3H), 0.92 (d, J = 7.5 Hz, 3H), 1.45 - 2.35 (m, 9H), 3.65 (m, 1H), 5.21 (dd, J = 11.1, 1.5 Hz, 1H), 5.71 (dd, J = 18.0, 1.5 Hz, 1H), 6.83 (dd, J = 7.5 , 7.5 Hz, 1H), 7.02 (ddd, J = 8.0, 7.5, 1.5 Hz, 1 H), 7.07 (d, J = 8.0 Hz, 1H), 7.32 (dd, J = 18.0, 11.1 Hz, 1H), 7.45 (dd, J = 8.0 Hz, 1.5 Hz, 1H). IR (neat): 2956, 2923, 2870, 1599, 1485, 1462, 1256, 1102, 1093, 1059, 998, 928, 884, 832, 799, 753 cm^{-1}. MS (m/z, EI): 332 (M^+). HREIMS: Calcd. for $C_{20}H_{32}O_2Si$, 332.2171; Found, 332.2159.
8. ^{1}H NMR (500 MHz, benzene-d_6): δ 0.23 (s, 3H), 0.25 (s, 3H), 0.78 (d, J = 7.0 Hz, 3H), 0.79 (d, J = 6.0 Hz, 3H), 0.92 (d, J = 7.2 Hz, 3H), 1.45 - 2.35 (m, 9H), 3.65 (m, 1H), 5.19 (d J = 11.0 Hz, 0.5H), 5.69 (d, J = 17.5 Hz, 0.5H), 6.83 - 7.46 (m, 4H), 7.29 (d, J = 11.0 Hz, 0.5 H), 7.30 (d, J = 17.5 Hz, 0.5 H). IR (neat): 2956, 2923, 2870, 1600, 1463, 1452, 1372, 1258, 1100, 1093, 1069, 1052, 981, 929, 884, 831, 800, 752 cm^{-1}. MS (m/z, EI): 333 (M^+). HREIMS: Calcd. for $C_{20}H_{31}DO_2Si$, 333.2234; Found, 332.2233.
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