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A Rearranged Acetylene from an E1 Solvolysis of a Substituted α-Trimethylsilylvinyl System

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Summary: The reaction of $\mathrm{Mes_2C{=}C(OH)SiMe_2R}$ ($\mathrm{R{=}Me, SiMe_3}$) with $\mathrm{SOCl_2}$ gives the rearranged elimination product $\mathrm{MesC{\equiv}CMes}$, presumably via β-mesityl participation in the solvolysis of the derived OSOCl derivative, followed by "$\mathrm{Me_3Si^+}$" loss from the rearranged ion $\mathrm{MesC(Me_3Si){=}\overset{+}{C}\text{-}Mes}$. Under the same conditions, the carbon analogue $\mathrm{Mes_2C{=}C(OH)Bu\text{-}t}$ gives the ketone $\mathrm{Mes_2CHCOBu\text{-}t}$ and benzofurans via non-solvolytic reactions.

An α-$\mathrm{R_3Si}$ substituent destabilizes a trigonal cation compared with the analogous α-$\mathrm{R_3C}$ group, whereas a β-$\mathrm{R_3Si}$ stabilizes it much more than a β-$\mathrm{R_3C}$.[1] In $\mathrm{S_N1}$ vinylic solvolysis, an α-$\mathrm{Me_3Si}$ was suggested to be deactivating compared with α-t-Bu[2], although reconsideration of the same data led to an opposite conclusion.[3a,b] MO calculations indicate that in the gas phase α-$\mathrm{Me_3Si}$ stabilizes a carbonium ion similarly[3a] or more[3b] than t-Bu and that $\mathrm{SiH_3}$ and Me are similarly activating.[3c] Calculated vinylic carbocation stabilization by β-$\mathrm{R_3Si}$ is much larger than by β-$\mathrm{R_3C}$[3c,d], e.g. a β-$\mathrm{H_3Si}$ is 20 kcal $\mathrm{mol^{-1}}$ more stabilizing than β-Me.[3c]

The expected large driving force for an α-silylvinyl cation → β-silylvinyl cation rearrangement raises the question whether the solvolysis of a β-aryl-α-silylvinyl system proceeds at all via the β-aryl-α-silylvinyl cation and does it differ from the solvolysis of the t-Bu analogue, where the driving force for rearrangement is smaller. The availability of enols **1a**,[4a,b], **2a**[4b] and **3a**[4c] suggests their use for preparation of solvolysis precursors in order to investigate these questions.

If the solvolysis of **1-3**, X=nucleofuge, initially gives the unrearranged cations **4a-c**, the

$\mathrm{Mes_2C{=}C(X)SiMe_3}$	$\mathrm{Mes_2C{=}C(X)SiMe_2SiMe_3}$	$\mathrm{Mes_2C{=}C(X)Bu\text{-}t}$	$\mathrm{Mes_2C{=}\overset{+}{C}\text{-}R}$
1a: X=OH	**2a**: X=OH	**3a**: X=OH	**4a**: $\mathrm{R{=}Me_3Si}$
1b: X=OTf	**2b**: X=Cl	**3b**: X=Cl	**4b**: $\mathrm{R{=}Me_3SiMe_2Si}$
1c: X=Cl			**4c**: R=t-Bu
1d: X=OSOCl			

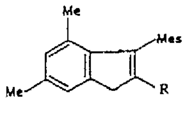
Dedicated to Prof. M. Hanack on the occasion of his 60th birthday.

$\mathrm{MesC(R)=\overset{+}{C}\text{-}Mes}$ $\quad$ $\mathrm{Mes_2C=C(Me)\overset{+}{Si}Me_2}$ $\quad$ $\mathrm{Mes_2C=\overset{+}{C}\text{-}Mes}$

5a: $\mathrm{R=Me_3Si}$ $\quad$ **6** $\quad$ **7**

5b: $\mathrm{R=Me_3SiMe_2Si}$

5c: R=t-Bu $\quad$ Mes=Mesityl



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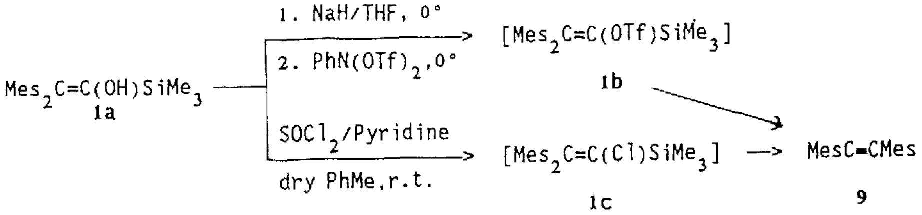
latter can react by four different routes. (a) Capture by nucleophile. (b) β-Mesityl rearrangement to form the doubly stabilized α-mesityl-β-alkylvinyl cations **5a-c**, which can be captured or eliminate R^+. (c) β-Me migration from R, e.g. to form the silicenium ion **6** from **4a**[5]. (d) Cyclization on a β-mesityl-Me to form **8** in analogy with the formation of **8**, R=Mes from **7**.[6]

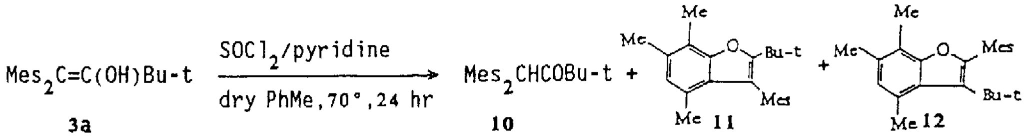
Assuming that the solvolysis of **1**-derivatives will be slow[7], we tried to prepare the triflate **1b** from the enolate of **1a** with aniline N,N-bistriflate. Several products, including dimesitylacetylene **9** were formed. The high reactivity suggested the use of a poorer nucleofuge. Reaction of **1a** with thionyl chloride and pyridine in toluene at room temperature for 4 hrs did not give the expected chloride **1c**, but the only product isolated (>80% by NMR) was the acetylene **9** (equation 1). It was identified by its mp (127-8°, lit.[8] 127.5-128.5°), the three singlets in the ^{1}H NMR spectrum, the seven signals in the ^{13}C NMR spectrum including one for C≡C at 92.5 ppm, a Raman absorption at 2200 cm^{-1} and a base peak at m/z 262.17 in the high resolution mass spectrum.



(1)

Enol **2a** has an additional β-$\mathrm{Me_3Si}$ group which should stabilize the initially formed **4b**. Reaction of **1b** with $\mathrm{SOCl_2}$/pyridine in toluene was qualitatively slower than that of **1a** and gave only traces of **9** after 16 hrs at 20°C. After additional 12 hrs at 30-35°C unreacted **2a** was still present together with **9** and another compound which gave $\mathrm{C_{22}H_{28}SiCl}$ and $\mathrm{C_{22}H_{28}SiClO}$ fragments in the mass spectrum. Tentatively the OH or $\mathrm{Me_3Si}$ were replaced by Cl, but the unavailability of the compound prevented further study.

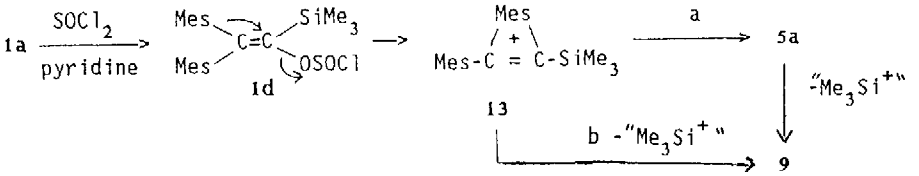
Reaction of the t-butyl analogue **3a** was much slower. With $\mathrm{SOCl_2}$/pyridine most of **3a** was recovered after 24 hrs at 30°C. After additional 24 hrs at 70°C the two main products were ketone **10** [9] and benzofuran **11**. Schmittel and Baumann obtained **11** from electrochemical or from one-electron oxidation of **3a**.[10,11] Two other products were formed: an isomer of **11** (m/z 334) was tentatively identified as **12** (equation 2), and a compound formed in 2% yield which showed m/z 320.



(2)

Five mechanistic points emerge from the data. First, the product from the β-silyl derivatives is **9**, which is most likely derived by loss of a "Me_3Si^+" entity from the rearranged ion **5a.**[12] Loss of a "β-Me_3Si^+" entity from trigonal carbocations is common[13a] and similar eliminations from vinyl cations were also reported[13b]. A persistent β-silylvinyl cation $R\overset{+}{C}=CHSiR_3$ was recently observed by NMR from the low temperature protonation of $RC \equiv CSiR_3$ with FSO_3H/SbF_5.[14] Second, if **1c** is rapidly formed, its solvolysis is much faster than that of the stable trimesitylvinyl chloride whose solvolysis in 80% EtOH requires Ag^+-catalysis.[8] Third, the reaction of the α-Me_3Si-vinyl system is much faster than that of the α-t-Bu-vinyl system which is incomplete at 70°C after 24 hrs. Fourth, product formation from **2a** seems slower than that from **1a**, in spite of opposite expectations due to the presence of a β-Me_3Si group.[15] Finally, the main reaction products of **3a** seem to arise from a non-solvolytic cation route.

The faster overall reaction of **1a** than of **2a**, **3a** or trimesitylvinyl chloride could result from faster formation of **1c** or **1d** or from a faster formation the free ion **4a** than of the free ion **7**, followed by the well known β-aryl rearrangement.[16a] However, even if α-Me_3Si is slightly more activating than α-t-Bu, the known data on substituent effects in vinylic S_N1 solvolysis indicate that **1c** should be formed more slowly than trimesitylvinyl chloride.[1] If the solvolysis step is rate determining, β-aryl participation which was observed in the solvolysis of β-aryl-α-alkylvinyl triflates,[16b] should be most favorable in the solvolysis of **1**, X=nucleofuge (e.g. in **1d**) where the positive charge is delocalized in the transition state by the strongly electron-donating mesityl groups as well as by an "incipient" β-Me_3Si group. Opening of **13** to **5a** followed by loss of Me_3Si and a positive charge (marked by "Me_3Si^+"without mechanistic



(3)

implications) (equation 3, route a) or direct loss of "Me_3Si^+" from **13** (route b) will then give **9**. According to this suggestion, neither **1c** nor **4a** are formed at all.

The two main products from **3a** are formed by known non-solvolytic reactions. Ketone **10** is thermodynamically more stable than enol **3a** and the thermal **3a** → **10** isomerization was studied.[4c] However, **1a** is more stable than its isomeric ketone.[4a] Schmittel's scheme for formation of the benzofuran **11** via oxidation of **3a** to Mes$_2$C=C(Bu-t)O$^+$ which then cyclizes[10] is also applicable in our system. The likely oxidant is thionyl chloride and precendents to oxidations by SOCl$_2$ are known.[17] If the assigned structure of **12** is correct, this requires formation of the rearranged ion **5c**, possibly as in equation 3, capture of **5** by an oxygen nucleophile and cyclization. The details of this process, and the reason for the slower reaction of **2a** than of **1a** are unknown.

A clearer picture of these reactions is expected from future kinetic studies of more defined precursors **1-3**, X=nucleofuge.

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