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Novel Syntheses of 1, 2-Diarylacetylenes and α-Silylalcohols from Acylsilanes Mediated by Ytterbium Metal

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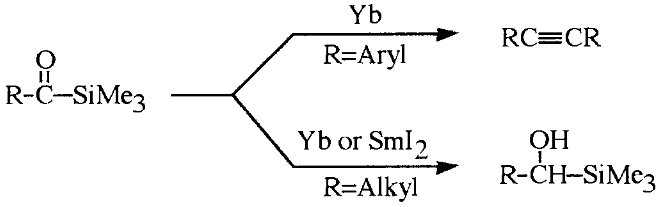
Aromatic acylsilanes such as benzoyltrimethylsilane react with ytterbium metal to give symmetrical 1, 2-diarylacetylenes in good yields. Aliphatic acylsilanes are reduced with lanthanoid reagents such as Yb metal and SmI_2 to afford α-silylalcohols.

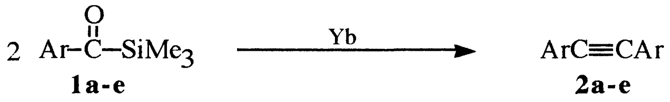
Recently, we reported that reaction of lanthanoid metals (Yb, Sm) with diaryl ketones such as benzophenone produced the corresponding dianion complexes that react easily with a variety of electrophiles like ketones, esters, epoxides, nitriles, carbon dioxide, and acetylenes producing adducts.1) We have succeeded in isolating and structurally characterizing the ytterbium(II)-benzophenone dianion complex.2) In continuing studies on exploring lanthanoid mediated synthetic reactions, we investigated the reaction of acylsilanes (**1a-e**) with Yb metal and SmI_2, and found that aromatic acylsilanes (**1a-e**) give the corresponding homocoupling products, 1, 2-diarylacetylenes (**2a-e**) and aliphatic acylsilanes give the reduction products, α-silylalcohols, when they were treated with Yb or SmI_2 under mild conditions (Scheme 1). In this communication we wish to report these results.



Scheme 1.

A mixture of Yb metal (40 mesh, 173 mg, 1 mmol) and benzoyltrimethylsilane (**1a**) (178 mg, 1 mmol) in THF (4 mL) - HMPA (1 mL) was stirred at -10 °C for 20 min to give diphenylacetylene (**2a**) in 67 % yield along with benzyl phenyl ketone (**3**, 19%).3) In marked contrast to the above reaction, the use of lithium metal in lieu of Yb metal did not give **2a**, the corresponding coupling adduct, but afforded **3**, benzil and benzoin in 52, 25 and 22% yields, respectively. This indicates that the reaction of acylsilanes with Yb metal becomes a convenient synthetic method for symmetric acetylenes, which uses neutral conditions. Table 1 summarizes the results of the reaction of various aromatic acyltrimethylsilanes (**1a-e**) with Yb metal, and shows that the reaction of acyltrimethylsilanes with electron-donating substituents on phenyl group (**1a-d**) give the corresponding 1, 2-diarylacetylenes (**2a-d**) in high yields (entries 1-4), while the reaction of *p*-chlorobenzoyltrimethylsilane (**1e**) having an electron-withdrawing group (Cl) gives acetylene **2e** in low yield because of the complex side-reactions (entry 5). The possible mechanism of the reaction of **1a** with Yb is shown in Scheme 2. The intermediate **B** would react with another molecule of **1a** to give intermediates **C** and/or **C'** which undergo the Peterson olefination to give intermediates **D** and/or **D'**. The intermediate **D** (**D'**) would give rise to the acetylene.

Table 1. Reaction of aromatic acyltrimethylsilanes with Yb leading to acetylenes a)

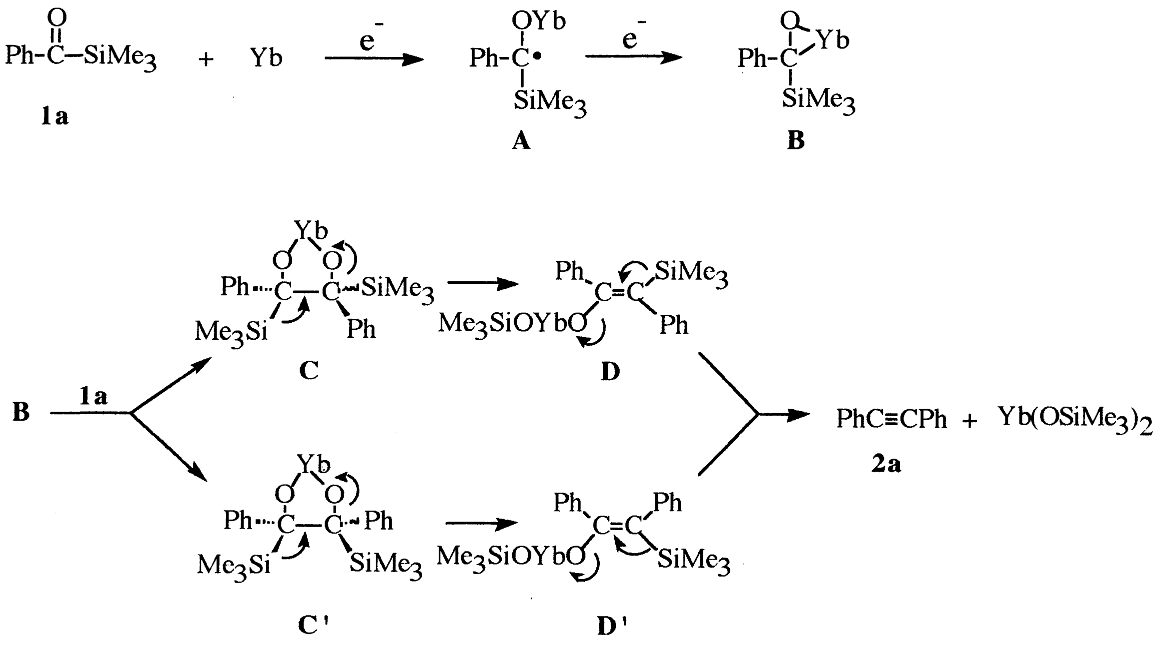


$$2\ \text{Ar}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{SiMe}_3 \xrightarrow{\text{Yb}} \text{ArC}\equiv\text{CAr}$$

1a-e **2a-e**

Entry		Ar	Yield of Alkyne (%) b)
1	**1a**	Ph	67
2	**1b**	*p*-MeC_6H_4	91
3	**1c**	*m*-MeC_6H_4	82
4	**1d**	*p*-MeOC_6H_4	84
5	**1e**	*p*-ClC_6H_4	31

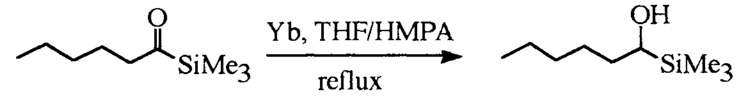
a) **1** 1 mmol, Yb 1 mmol, THF 4 ml, HMPA 1 ml, -10 °C, 20 min.
b) GC yield based on **1**.



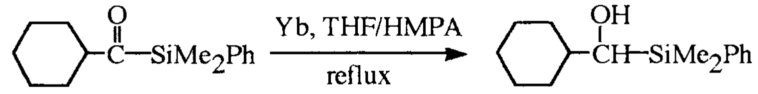
Scheme 2.

Interestingly, the similar reaction of **1a** with 3 equiv. of SmI_2 in THF, which is a powerful single electron reductant, resulted in the formation of α-trimethylslilylbenzylalcohol (**4a**) in 62% yield.

The reaction of aliphatic acylsilanes such as *n*-hexanoyltrimethylsilane (**1f**) with Yb metal under the above reaction conditions did not take place, but the reaction at reflux for 20 h gave 1-trimethylsilylhexan-1-ol (**4f**), the reduction product in 67% yield (Eq. 1). Similarly, the reaction of **1f** with an equimolar amount of SmI_2 in THF at room temperature for 18 h afforded **4f** in 56% yield.[4] Reaction of sterically hindered cyclohexanecarbonyldimethylphenylsilane (**1g**) gave the reduction product, cyclohexyldimethylphenylsilylmethanol (**4g**) in only 24% yield (Eq. 2). The formation of these reaction products would be explained best by a Yb-oxametallacycle intermediate like **B** which is generated by double electron-transfer from Yb metal[1,2]; acetylenes would be formed from the reaction of **B** with **1**, and α-silylalcohols from hydrogen abstraction of **B** from the solvent.

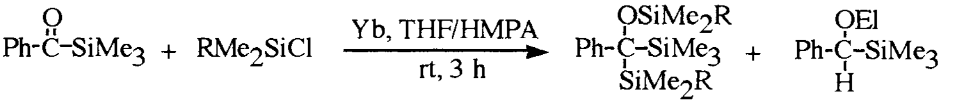


1f **4f** (67%) (1)



1g **4g** (24%) (2)

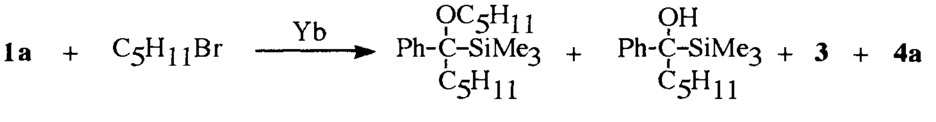
The formation of the Yb-oxametallacycles **B** was proved by the following trapping experiments using several electrophiles such as silyl chlorides and *n*-pentyl bromide. In the case of the reaction of **1a** with silyl chlorides (**5a,b**), C,O-disilylation adducts **6a** and **6b** were obtained in 80 and 28% yields along with α-silylalcohol derivatives **4a** (20%) and **7** (25%) in each reaction, respectively (Eq. 3).[5] With excess of *n*-pentyl bromide there were obtained C,O-dialkylation adduct **8** (16%) and C-alkylation adduct **9** (28%) along with **3** (32%) and **4a** (15%) (Eq. 4). These results clearly indicate that the Yb-acylsilane dianion complex **B** is readily formed. Therefore, Yb metal can act as a double electron reductant forming the oxametallacycle intermediacy.



$$\mathrm{Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}SiMe_3 + RMe_2SiCl \xrightarrow[\text{rt, 3 h}]{\text{Yb, THF/HMPA}} Ph\text{-}\underset{SiMe_2R}{\overset{OSiMe_2R}{C}}\text{-}SiMe_3 + Ph\text{-}\underset{H}{\overset{OEl}{C}}\text{-}SiMe_3} \quad (3)$$

1a **5a** ($R=CH_3$) **6a** ($R=CH_3$, 80%) **4a** (El=H, 20%)

5b ($R=Bu^t$) **6b** ($R=Bu^t$, 28%) **7** ($El=SiMe_2Bu^t$, 25%)



$$\mathrm{1a + C_5H_{11}Br \xrightarrow{Yb} Ph\text{-}\underset{C_5H_{11}}{\overset{OC_5H_{11}}{C}}\text{-}SiMe_3 + Ph\text{-}\underset{C_5H_{11}}{\overset{OH}{C}}\text{-}SiMe_3 + 3 + 4a} \quad (4)$$

8 (16%) **9** (28%) (32%) (15%)

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References

1) Z. Hou, K. Takamine, O. Aoki, H. Shiraishi, Y. Fujiwara, and H. Taniguchi, *J. Org. Chem.*, **53**, 6077 (1988); K. Takaki and Y. Fujiwara, *Appl. Organomet. Chem.*, **4**, 297 (1990).

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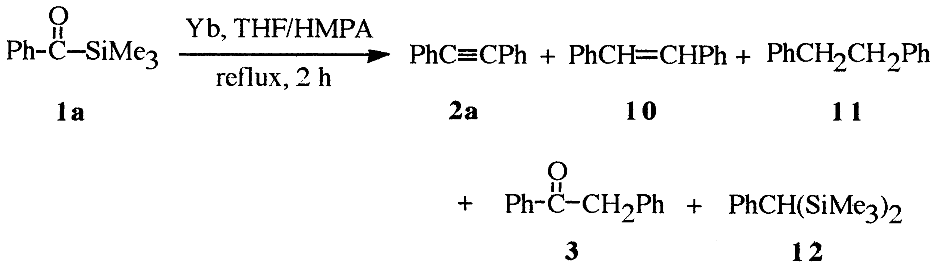
3) The similar reaction at reflux temperature gave several products such as diphenylacetylene (**2a**), (*E*)-stilbene (**10**), 1,2-diphenylethane (**11**), **3** and bis(trimethylsilyl)phenylmethane (**12**) in 12, 11, 25, 20 and 32% yields, respectively. Control experiments revealed that **10** and **11** were formed *via* reduction of **2a** by Yb metal.[6]



$$\underset{\textbf{1a}}{\mathrm{Ph{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}SiMe_3}} \xrightarrow[\text{reflux, 2 h}]{\text{Yb, THF/HMPA}} \underset{\textbf{2a}}{\mathrm{PhC{\equiv}CPh}} + \underset{\textbf{10}}{\mathrm{PhCH{=}CHPh}} + \underset{\textbf{11}}{\mathrm{PhCH_2CH_2Ph}} + \underset{\textbf{3}}{\mathrm{Ph{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_2Ph}} + \underset{\textbf{12}}{\mathrm{PhCH(SiMe_3)_2}}$$

4) Since even with 3 molar amounts of SmI_2 to **1f**, silylalcohol **4f** was obtained in a similar yield (54%), it seems that this SmI_2 mediated reaction proceeds *via* the radical anion such as **A** (Scheme 1) derived from single electron-transfer from SmI_2.

5) Interestingly, the reaction of acylsilane **1a** with Yb metal in the presence of an equimolar amount of trimethylsilyl bromide gave 1,2-bis(4-trimethylsilylphenyl)-1,2-bistrimethylsilylethene (**13**) in 26% yield along with **2a** (12%). **13**; mp 187.7-189.2 °C (hexane) as colorless needles. IR (Nujol) 1274 cm^{-1}, Mass (70 eV), m/e 468(M^+, 20%), 453(M^+-CH_3, 16%), 73(TMS^+, 100%); ^{1}H NMR ($CDCl_3$) δ -0.38 (s, 18 H), -0.37 (s, 18 H), 7.01 (d, J = 7.3 Hz, 4 H), 7.42 (d, J = 7.3 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ -0.95, 0.25, 127.5, 132.5, 137.1, 146.3, 148.6; ^{29}Si NMR ($CDCl_3$) δ -4.7, -7.4; Anal. Found: C, 66.53; H, 9.39%. Calcd for $C_{26}H_{44}Si_4$: C, 66.58; H, 9.45%. Diphenylacethylene (**2a**) was also reduced by Yb metal in the presence of 10 equiv. of trimethylsilyl chloride at -10 °C for 20 min to afford **10**, **11**, **13** and 1,2-bis(trimethylsilyl)-1,2-diphenylethene (**14**) in 4, 7, 8 and 30% yields, respectively.

6) 1,2-Diphenylacetylene (**2a**) was reduced with 3 equiv. of Yb metal in THF-HMPA to give stilbenes (**10**) (*E/Z*=2:1) and 1,2-diphenylethane (**11**) in 31 and 47% yields, respectively. The olefin **10** was also transformed into **11** quantitatively under the same conditions. See also; Z. Hou, H. Taniguchi, and Y. Fujiwara, *Chem. Lett.*, **1987**, 305 and Z. Hou, Y. Fujiwara, T. Jintoku, N. Mine, K. Yokoo, and H. Taniguchi, *J. Org. Chem.*, **52**, 3524 (1987).

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