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Novel Deoxygenative Acylation of Diaryl Ketones with Acylsilanes Mediated by Lanthanoid Metals

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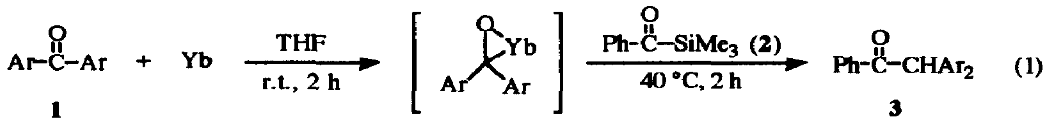
Abstract: *The reaction of diaryl ketones and benzoyltrimethylsilane is mediated by lanthanoid metals such as ytterbium to give the deoxygenatively acylated product, 1,1-diarylacetophenones in good yields. In the reaction with acetylsilane, the corresponding silyl enol ether was obtained in a moderate yield.*

Lanthanoid mediated reactions have played an important role in organic synthesis because of their unique properties.[1] Recently, we reported that the reaction of lanthanoid metals (Yb, Sm) with diaryl ketones produced the corresponding dianionic complexes, which reacted easily with a variety of electrophiles like ketones, esters, epoxides, nitriles, carbon dioxide, and acetylenes to give the corresponding adducts.[2] We have succeeded in isolating and structurally characterizing the ytterbium(II)-benzophenone dianionic complex.[3] We also found that reaction of acylsilanes using this carbonyl reduction system led to symmetric acetylenes.[4] In continuing studies on exploring lanthanoid mediated synthetic reactions, we investigated the ytterbium mediated reaction of diary ketones (**1**) with benzoylsilane (**2**) to afford 1,1-diarylacetophenones (**3**) under mild conditions (Eq. 1). In this communication we wish to report these results.

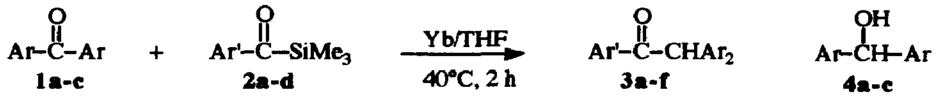


(1)

The representative results for the deoxygenative acylation of diaryl ketones are summarized in Table 1. In this reaction, 1,1-diarylacetophenones were obtained in good yields along with trace amounts of diarylmethanols. The preparation of 1,1-diphenylacetophenone is a typical example (entry 1, Table 1): A mixture of Yb metal (40 mesh, 173 mg, 1 mmol), benzophenone (**1a**) (182 mg, 1 mmol) and methyl iodide (3 μL) in THF (5 mL) was stirred at room temperature for 2 h under argon. Benzoyltrimethylsilane (**2a**) (178 mg, 1 mmol) was added by a syringe to the mixture. The mixture was stirred at 40 °C for 2 h. Usual work-up followed by column chromatography (SiO_2, hexane-ethyl acetate) gave 1,1-diphenylacetophenone (**3a**) (0.166 g, 61%), which gave satisfactory IR, NMR, Mass spectral data and elemental analysis. Diphenylmethanol (**4a**) was obtained in 20 % yield as a byproduct. An addition of a polar solvent such as HMPA is not effective. Samarium metal causes the similar reaction.

In the case of the reaction of aliphatic acylsilanes, such as acetyltrimethylsilane (**2e**) with the Yb-benzophenone complex at 0 ~ 40°C for 3 days, **4a** was formed quantitatively. This suggests that high basicity

Table 1. Ytterbium Mediated Reaction of Diaryl Ketones with Acyltrimethylsilanes[a)]

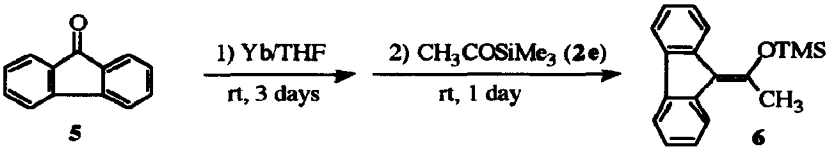


$$\underset{\mathbf{1a\text{-}c}}{\mathrm{Ar{-}C(=O){-}Ar}} + \underset{\mathbf{2a\text{-}d}}{\mathrm{Ar'{-}C(=O){-}SiMe_3}} \xrightarrow[40^\circ\mathrm{C},\ 2\ \mathrm{h}]{\mathrm{Yb/THF}} \underset{\mathbf{3a\text{-}f}}{\mathrm{Ar'{-}C(=O){-}CHAr_2}} \quad \underset{\mathbf{4a\text{-}c}}{\mathrm{Ar{-}CH(OH){-}Ar}}$$

Entry	Diary Ketone (Ar)	Acylsilane (Ar')	Product and Yield (%)[b)]	
1	Ph (**1a**)	Ph (**2a**)	**3a**, 68 (61)[c)]	**4a**, 29 (20)[c)]
2	**1a**	p-MeC$_6$H$_4$ (**2b**)	**3b**, 78	**4a**, 22
3	**1a**	m-MeC$_6$H$_4$ (**2c**)	**3c**, 71	**4a**, 22
4	**1a**	p-ClC$_6$H$_4$ (**2d**)	**3d**, 51	**4a**, 43
5	p-MeC$_6$H$_4$ (**1b**)	**2b**	**3e**, 83	**4b**, trace
6	p-MeOC$_6$H$_4$ (**1c**)	**2b**	**3f**,(37%)[c,d)]	**4c**,(27)[c,d)]

a) **1** (1 mmol), **2** (1 mmol), Yb (1 mmol), THF (5 mL), 40 °C, 2 h. b) GC yield based on **1**.
c) Numbers in parentheses are isolated yileds. d) **1c** (17%) was recovered.

of the Yb-benzophenone dianionic complex causes the α- hydrogen abstraction of acetylsilane. On the contrary, the reaction of fluorenone (**5**) with **2a** gave 9-fluorenyl phenyl ketone in only 30% yield along with 9-fluorenol (34%). Interestingly, in the reaction of **5** with **2e** at room temperature for 4 days, non-aqueous work-up followed by SiO$_2$ column chromatography gave the corresponding silyl enol ether **6** in 36% isolated yield (Eq. 2).



5 **6** (2)

Further mechanistic study and synthetic application are under investigation.

ACKNOWLEDGMENT

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