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Preliminary communication

Reactions of triethylsilyl thiophenoxide with ketones having an electron-withdrawing group on the α-carbon

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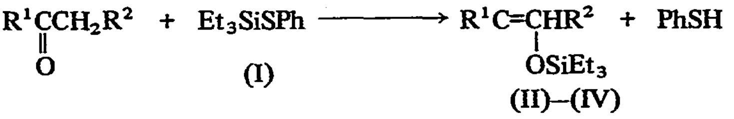
SUMMARY

Triethylsilyl thiophenoxide has been found to react with easily enolizable ketones to give silyl enol ethers; these have also been synthesized by a Rh^{I} complex catalysed reaction of triethylsilane with enolizable ketones in the presence of a small amount of silyl thioether or thiophenol.

Many studies have been made of the synthesis and spectroscopy of silyl thioethers[1], but their reactions with carbonyl compounds seem not to have been examined. The corresponding reactions of silylamines have been studied to some extent[2,3,4], and thus, for example, it is known that disilazanes react with ketones to give imines[3] and that silylamines react with ketones to give enamines[4]. We describe below the reactions of triethylsilyl phenyl thioether (I) with enolizable ketones bearing an electron-withdrawing group on the α-carbon.

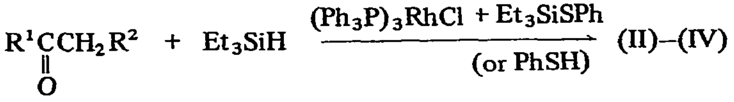
The reaction of the silyl thioether (I) with benzoyl acetonitrile is a typical example. In this, an equimolar mixture of benzoyl acetonitrile and the silyl thioether (I) was heated under reflux in xylene for 7 h under nitrogen. Distillation under reduced pressure gave 2-cyano-1-triethylsiloxystyrene (II) (b.p. 127°/0.25 mm, *cis/trans* 50/50) in 90% yield. Likewise, the silyl thioether (I) reacted smoothly with methyl acetoacetate and acetylacetone to give, respectively, methyl-1-triethylsiloxycrotonate (III) (b.p. 60°/0.7 mm) in 82% yield after 10 h at 120° and 2-triethylsiloxypent-2-en-3-one (IV) (b.p. 76°/1 mm) in 75% yield after 12 h at 100°.



$$R^1\underset{\underset{O}{\|}}{C}CH_2R^2 + \underset{(I)}{Et_3SiSPh} \longrightarrow \underset{(II)\text{–}(IV)}{R^1C{=}\underset{\underset{OSiEt_3}{|}}{C}HR^2} + PhSH \qquad (1)$$

(II: $R^1 = Ph$, $R^2 = CN$; III: $R^1 = Me$, $R^2 = COOMe$; IV: $R^1 = Me$, $R^2 = COMe$)

$$Et_3SiH + PhSH \xrightarrow{(Ph_3P)_3RhCl} Et_3SiSPh + H_2 \qquad (2)$$



$$R^1\underset{\underset{O}{\|}}{C}CH_2R^2 + Et_3SiH \xrightarrow[\text{(or PhSH)}]{(Ph_3P)_3RhCl\ +\ Et_3SiSPh} (II)\text{–}(IV) \qquad (3)$$

Investigation of dehydrogenative condensation between an easily enolizable ketone and triethylsilane followed from consideration of reaction (1) and of the recently reported reaction of hydrosilanes with thiophenol (2) [5]. A combination of reaction (1) and (2) could provide a catalysed version of reaction (3), proceeding though a mechanism involving the silyl thioether or thiophenol as a chain carrying intermediate. A necessary condition for reaction (3) to be observed is that the dehydrogenative condensation of triethylsilane must be faster than the hydrosilylation of the ketone, and when this be the case it is possible to synthesize silyl enol ethers II–IV selectively from the appropriate ketone and triethylsilane in the presence of a small amount of the silyl thioether or thiophenol.

Thus, when mixtures of triethylsilane and these enolizable ketones in the presence of 1/20 equivalent of the silyl thioether or thiophenol and 0.1 mol% of $(Ph_3P)_3RhCl$ were refluxed in benzene for 12–24 h, the silyl enol ethers II, III and IV were obtained in 98, 61 and 92% yields, respectively. Since silyl enol ethers are versatile reagents for many useful synthetic reactions, this new method of preparation should have considerable application in synthetic organic chemistry.

The Rh^I complex catalysed reactions of triethylsilane with benzoyl acetonitrile, methyl acetoacetate and acetylacetone in the absence of the silyl thioether I gave a mixture of the products of hydrosilylation and dehydrogenative condensation in fair yield (for benzoyl acetonitrile: silyl ether/silyl enol ether 50/50; for methyl acetoacetate 80/20; for acetylacetone 2/98). It should be noted that ordinary ketones were hydrosilylated selectively by the same catalyst without any dehydrogenative condensation [6].

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