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A SIMPLE ROUTE TO 3-FURANYLTRIMETHYLSILANE VIA HYDROMAGNESIATION

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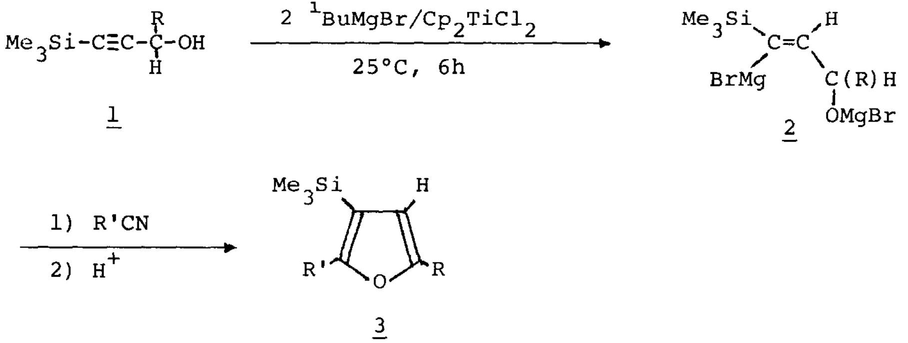
Summary: Hydromagnesiation of 3-trimethylsilylprop-2-yn-1-ols with isobutylmagnesium bromide in the presence of a catalytic amount of Cp_2TiCl_2 followed by treatment of the resulting (Z)-vinyl Grignard reagents with nitriles affords 3-furanyltrimethylsilanes.

We report here a facile one-pot route to 3-furanyltrimethylsilanes 3, which is based on hydromagnesiation of 3-trimethylsilylprop-2-yn-1-ols 1 to (Z)-vinyl Grignard reagents 2 [1] and the following reaction with nitriles.[2]



A catalytic amount of Cp_2TiCl_2 (0.12 g, 0.48 mmol) was added to a solution of isobutylmagnesium bromide in ether (43 ml of 0.40 M solution, 17 mmol) under argon at 0°C. After 5 min stirring, 3-trimethylsilylprop-2-yn-1-ol (0.88 g, 6.8 mmol) was added, and the mixture was stirred for 6 h at 25°C. To this solution was added propionitrile (0.48 g, 8.8 mmol), and the mixture was stirred for 2 h at room temperature. The reaction mixture was quenched with 2N-hydrochloric acid and the product was extracted with ether repeatedly. The combined ether layers were dried, concentrated in vacuo, and the oil remained was subjected to column chromatography on silica gel to afford 3-trimethylsilyl-2-ethylfuran (0.94 g, 82% yield). Additional experimental results are summarized in Table 1.

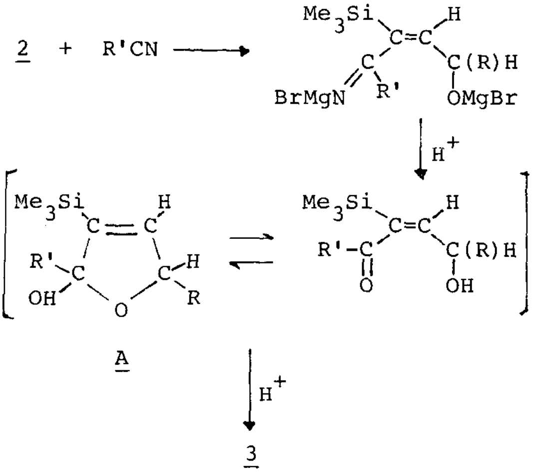
The reaction can be rationalized by the mechanism shown in Scheme 1. It is well known that the reaction between nitriles and Grignard reagents leads to ketones via a ketimine stage.[3] The intermediary hemiacetal A has been shown to be dehydrated spontaneously under acidic conditions.[4]

Table 1. Yields of 3

R in 1	R' in R'CN	Yield of 3[a] %
H	C_2H_5	82
H	$CH(CH_3)_2$	85
H	C_6H_5	88
$n-C_3H_7$	CH_3	38
$n-C_3H_7$	C_2H_5	86

[a] Isolated by column chromatography, based on 1

Scheme 1



The reaction of 2 with acyl halides or acid anhydrides also affords the corresponding 3-furanyltrimethylsilane 3, however, the yields of 3 were lower than the reaction with nitriles. Thus, the reaction of 2 (R = H) with isopropyonyl chloride or isopropyonyl anhydride afforded 3 (R = H, R' = $CHMe_2$) in 58 or 28% yield, respectively.

References

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3. In our hands, however, the (E)-vinyl Grignard reagents obtained by Cp_2TiCl_2-catalyzed hydromagnesiation of silylacetylenes ($R-C\equiv C-SiMe_3$)[5] or prop-2-ynylic alcohols ($R-C\equiv C-CH_2OH$)[6] did not afford the corresponding ketones in more than 5% yield.
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