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REMARKABLE STABILIZING EFFECTS OF SILYL GROUP ON FURFURYL CHLORIDES AND FURFURYL GRIGNARD REAGENTS

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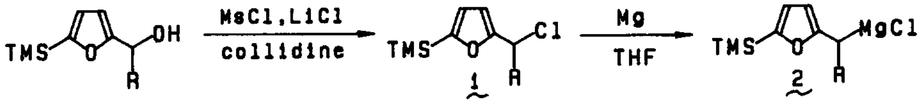
Summary: By introducing a silyl group on their 5-position, furfuryl chlorides and the Grignard reagents have been stabilized remarkably and the Grignard reagents have exhibited unusual ambident behavior toward several electrophiles.

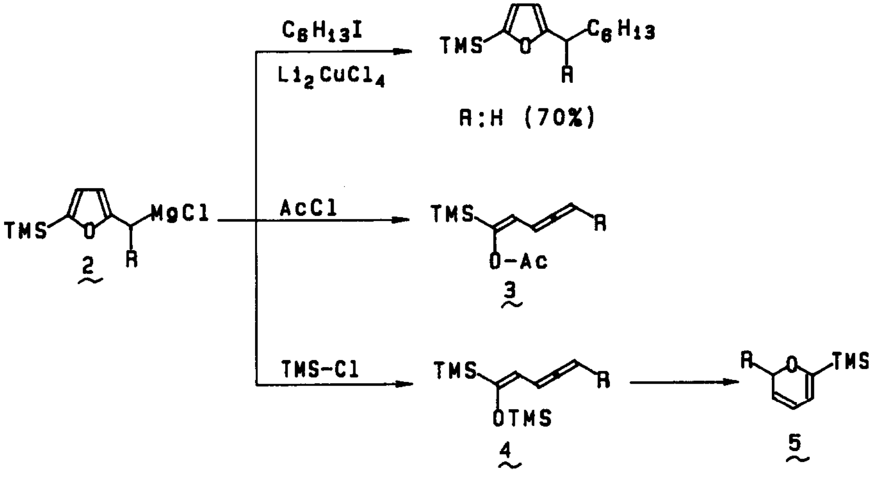
Different from other organic halides, furfuryl chlorides are usually quite unstable and difficult to manipulate for synthetic purposes.[1] Extreme lability of such halides has also made it impossible to use furfuryl Grignard reagents for organic synthesis. However, even if the Grignard reagents may be prepared from the halides, they are expected to undergo a ring opening reaction readily and their use in a usual manner may be almost impossible as suggested from behaviors of furfurylcarbanions.[2] In connection with our approach to use furans as butenolide equivalents, we attempted to find certain stabilized furfurylcarbanionic nucleophiles, and recently reported that introduction of a silyl group on their 5-position has brought about a remarkable stabilizing effect on lithiated furfuryl phenyl sulfides which can be employed as useful nucleophiles.[3] In this paper, we describe similar stabilizing effects of a silyl group on both furfuryl chlorides and furfuryl Grignard reagents.

α-Anion stabilizing as well as α-cation destabilizing effects[4] of silyl groups have been well demonstrated and these characteristic features have been utilized for several synthetic transformations. Such effects are expected not to be limited on α-position only, but have also similar influence on γ- and ε-positions of a conjugate system. Furfuryl group appears to be most appropriate to test such assumptions, considering its high labilities both as cationic and anionic species. Accordingly, we have examined a preparation of the chloride bearing a silyl group on 5-position of furan ring to estimate the stabilizing effects. 5-(Trimethylsilyl)furfuryl alcohol was treated with MsCl and collidine in the presence of LiCl, and the furfuryl chloride 1 (R = H) could be isolated in 90% yield as a stable distillable liquid. On treatment with benzenethiolate anion it acted as an electrophile to afford the furfuryl sulfides almost quantitatively.

By using the chloride 1 (R = H) furfurylmagnesium chloride 2 (R = H) can be prepared in a usual manner (Mg in THF), and as expected, the resulting reagent 2 is as stable as usual Grignard reagents. Interestingly, α-alkyl-substituted furfuryl chlorides **1** can also be prepared in good yield (R = CH_3 80%, C_4H_9 73%) and converted similarly to the corresponding Grignard reagents **2**.



In the reactions with several electrophiles, the Grignard reagents **2** have exhibited rather anomalous behaviors, depending on reagents used. An alkyl halide reacted with 2 on its furfuryl site in the presence of Li_2CuCl_4, whereas an acyl chloride added on the oxygen of furan exclusively, accompanied with a ring opening, to give the corresponding acyclic enol ester 3 (R = H, 65%). A chlorosilane also showed similar behavior toward 2 to yield siloxytriene **4** (R = H, CH_3, C_4H_9) in ca. 80% yield. On hydrolytic workup, **4** (R = CH_3, C_4H_9) afforded the 2-silyldihydropyran **5** in ca. 60% yield as a sole product in place of the expected dienoylsilane. Thus, behavior of **2** has made a good contrast to that of lithiated furfuryl sulfide,[3] and such reactivities may be understood in a similar way with those of enolate anions.



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