



Synthesis of novel ferrocenyl silyl ethers via dehydrocoupling reactions under Karstedt catalyst



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ABSTRACT

(4-Ferrocenylbutyl)dimethylsilane is prepared by a Grignard reaction from 4-chlorobutylferrocene and chlorodimethylsilane in THF. The Si–H group reacts with primary and secondary alcohols at room temperature to give good yields of (4-ferrocenylbutyl)dimethylsilyl ethers with Karstedt catalyst in THF. Ferrocenyl groups in pendant side chain are attached to cellulose acetate butyrate via alcoholysis at room temperature with Karstedt catalyst.

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1. Introduction

Derivatives of ferrocene continue to attract attention 60 years after its discovery [1–3]. The sustained interest is in part due to the rich chemistry of the iron (II) center and the variety of synthetic methods available for functionalizing the cyclopentadienyl-ligands [4,5]. The role of the ferrocene groups as a three-dimensional metal-containing equivalent of benzene has prompted the synthesis of novel air-stable compounds.

Derivatives of ferrocene are widely used in catalysis and materials science [6]. They are starting materials in both organic and organometallic chemistry [7,8]. They have shown a broad variety of applications in materials [9,10], medicine [11–13], organic synthesis [14,15], organometallic polymers [16], dendritic macromolecules [17,18] and liquid crystals [19,20]. Ferrocene derivatives are a well-known class of one-electron donors which exhibit well established reversible redox couples. As a consequence, ferrocene derivatives, particularly those possessing functionalized tethers, have emerged as strong candidates for molecular electronic devices, electro-optical materials, multielectron redox catalysts and electrode surface modifiers [21,22]. Numerous ferrocene

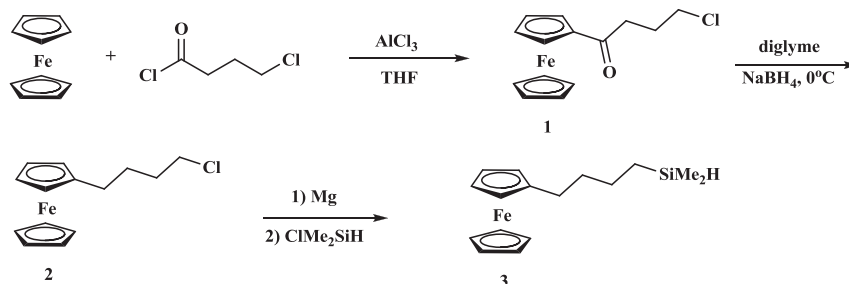
derivatives are used as catalyst for asymmetric synthesis of a large number of optically active organic compounds [3,23].

Organosilicon reagents and compounds are valuable in organic synthesis, so methods to synthesize them have become of considerable importance. Examples are silyl ethers and silyl ketals [24]. A special feature of hydrosilanes is their ability to undergo alcoholysis leading to alkoxy silanes and gaseous hydrogen (dehydrocondensation). The rate of dehydrocondensation significantly depends on the extent of Si–H bond polarization in the silane, and the reaction occurs in the presence of either nucleophilic or electrophilic catalysts [25,26].

Over the years, there have been significant developments in silyl ether synthesis and their applications to organic chemistry. Silyl ethers are important in organic synthesis due to their versatility, compatibility with a wide range of reaction conditions, safety, and the ease of usage. They are used in the areas of tethering reactants for stereospecific intramolecular reactions [27,28], protecting agents for many functional groups [29], anchoring reagents, substrates for solid support synthesis, organic synthesis [30] and multistep synthesis [31,32]. They have an important role in inorganic synthesis as precursor in the preparation of sol gel and other condensed siloxane materials [33] and in the preparation of prodrugs for drug delivery [34].

We recently reported the formation of functionalized polymers with dehydrocoupling reactions with Karstedt catalyst [35]. The

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Scheme 1. Synthesis of (4-ferrocenylbutyl)dimethylsilane.

development of environmentally friendly polymers based on renewable materials is of great interest. Indeed, requirements for ecological safety constantly increase and renewable polymers show considerable economic promise for manufacture of industrially advanced polymers. The attraction of easily available functional cellulose derivatives provides strong motivation to validate synthetic methods with respect to their potential for the preparation of new polymers based on renewable raw materials. In particular, cellulose derivatives bearing ionic, electro- or photochromic, redox- or catalytically active side groups are of interest.

Among cellulose derivatives, ester-modified celluloses such as cellulose acetate butyrate are known as good film-forming materials with high scratch resistance, and are commercially available in different grades, at reasonable prices. Polymers using ferrocene in pendant side chains have been emphasized and their special properties have been illustrated. Functionalization of celluloses backbone with ferrocene derivatives has been recently reported in the literature [36,37]. The reported methods usually require severe conditions and multistep reactions. Here we report a very simple and one-pot reaction for the modification of cellulose acetate butyrate with ferrocenyl groups and formation of ferrocenyl silyl ethers with various alcohols under mild conditions by the use of the Karstedt catalyst at room temperature.

2. Results and discussion

We have recently reported the synthesis of silyl ether derivatives of Calixarenes and tris(alkoxydimethylsilyl)methanes via the reaction of tris(dimethylsilyl)methane and Calixarenes having Si–H group with various alcohols in the presence of the Karstedt catalyst under mild conditions [38,39]. In continuous of our work on silyl ethers we extended the procedure to include coupling of alcohols with Si–H groups functionalized with ferrocenyl groups. A few articles reporting the synthesis of (4-ferrocenylbutyl)dimethylsilane are found in the literature [40–42]. Due to interesting properties of ferrocene derivatives we decided to use our methodology to attach the (4-ferrocenylbutyl)dimethylsilyl side chain to a polymer backbone.

(4-Ferrocenylbutyl)dimethylsilane is synthesized from 4-chlorobutylferrocene via a Grignard reaction in THF [40–42]. 4-Chlorobutyrylferrocene was prepared by Friedel–Crafts acylation of ferrocene with 4-chlorobutyryl chloride in dichloromethane in the presence of AlCl_3 as catalyst (Scheme 1) [43,44]. 4-Chlorobutyrylferrocene was reduced to 4-chlorobutylferrocene by NaBH_4 in diglyme [44]. We examined several ether solvents such as THF, 1,4-dioxane, diethyl ether and diglyme for this reduction. The best result (85%) obtained in diglyme at 0°C .

As reported in literature [24], (4-ferrocenylbutyl)dimethylsilane is an air sensitive and unstable compound that decomposes on exposure to air, but we found that this compound is stable to air and moisture and does not decompose at room temperature.

For dehydrocoupling reaction of alcohols with Si–H group, we started with the reaction of compound **3** with a primary alcohol, methanol, at room temperature and THF as a solvent under Karstedt catalyst (Scheme 2).

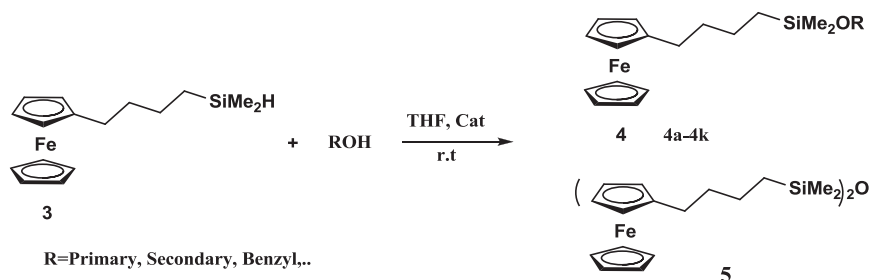
The reaction was tracked by FT-IR spectroscopy and stopped when the Si–H stretching bond frequency is disappeared in FT-IR spectrum after 2 h (Entry 1, Table 1).

Refluxing of the reaction decreased the yield of the desired silyl ether products and (4-ferrocenylbutyl)dimethylsiloxane **5** was formed as the main product.

Long chain primary alcohols show lower reactivity than methanol. As shown in Table 1 (4e and 4f) the yields decreased respectively to about 82% and 80% with increasing alcohol chain length. Secondary alcohols reacting with compound **3** to give desired silyl ethers in good yield (Table 1, 4g, 4h). Aromatic alcohols such as benzyl alcohol produced the desired silyl ether in high yields (4j, 93%) and showed higher reactivity than the aliphatic alcohols, but the phenolic silyl ether could not be obtained from the reaction of phenol with compound **3** (4k, Table 1).

Cellulose derivatives such as cellulose acetate butyrate (CAB) are commercially available in different grades. The hydroxyl groups on the cellulose acetate butyrate backbone are good candidates for dehydrocoupling reactions.

Our synthetic procedure was applied to cellulose acetate butyrate containing freely accessible hydroxyl functional side groups,



Scheme 2. Reaction of ferrocene compound **3** with various alcohols.

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