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Preliminary Communication

A new trialkoxysilylation reaction, the cross-coupling of (tri-isopropyloxysilyl)methyl grignard reagent with organic halides *

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Abstract

The reaction of tri-isopropyloxy(chloromethyl)silane with magnesium led to stable THF solutions of the Grignard reagent. The latter underwent coupling reactions with organic bromides to give high yields of trialkoxysilylated compounds.

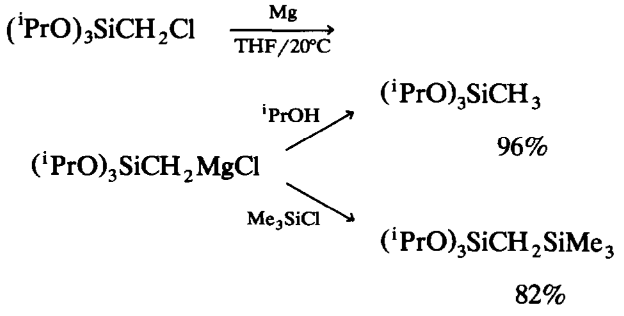
Inorganic-organic hybrid polymers are an interesting new class of materials which can be produced by sol-gel polymerisation [1] of organically substituted alkoxides such as $RSi(OR')_3$ [2-4] (eqn. (1)). The resulting

$$nRSi(OR')_3 \xrightarrow[(-R'OH)]{H_2O} \longrightarrow (RSiO_{1.5})_n \qquad (1)$$

silsesquioxanes $(RSiO_{1.5})_n$ are models for silica surfaces and particles, and have been used as ceramic precursors and to anchor metal complexes moieties to a silicate matrix [5]. Our current interest in the control of the morphology of a material at the molecular level has led us to study inorganic-organic hybrid gels, with various structural features, prepared from trimethoxysilylated precursors $RSi(OMe)_3$ [4]. Whereas silylated compounds can be prepared by a variety of trimethylsilylation reactions [6], the hydrosilylation reaction [7] constitutes the only general method for the preparation of trialkoxysilylderivatives. The reactions of $ClSi(OMe)_3$ also allowed the preparation of trimethoxysilyl derivatives [3,4] *via* silylation of organometallic intermediates or *via* an extension of the Calas–Dunogues silylation reaction [8]. Other methods of preparation of trifunctional silicon-containing molecules include silylation with $HSiCl_3/Et_3N$ [9], silylation with $SiCl_4$ in the presence of disilanes [10], and nickel catalysed reactions of disilanes [11,12]. In order to obtain some new general routes to trialkoxysilylated organic compounds, we explored the possible preparation of new functional nucleophilic reagents for trialkoxysilation reactions.

α-Silyl organometallic compounds such as (trimethylsilyl)methyl magnesium chloride are stable nucleophilic reagents widely used in the Peterson olefination reaction [13]. When functional groups are attached to silicon, the compounds X_3SiCH_2MgCl undergo intermolecular coupling to give a highly branched polycarbosilane [14]. However, stable functional Grignard reagents ($Me_2(X)SiCH_2MgCl$, X = H or ^iPrO) [15,16] were formed with a functional group of a low reactivity. Our search for new trifunctional silylated reagents led us to study the preparation of Grignard reagents from trialkoxysilyl derivatives. We wish to report here the preparation and some reactions of a (tri-isopropyloxysilyl)methyl Grignard reagent.

We found that the room temperature reaction of tri-isopropyloxy(chloromethyl)silane [17*] with magnesium in THF led to solutions of the required Grignard reagent (eqn. (2)).



$$\begin{tikzcd}
(^{i}PrO)_3SiCH_2Cl \arrow[r, "Mg", "THF/20^{\circ}C"'] & {} & \\
 & & (^{i}PrO)_3SiCH_3 \quad 96\% \\
(^{i}PrO)_3SiCH_2MgCl \arrow[urr, "^{i}PrOH"] \arrow[drr, "Me_3SiCl"'] & & \\
 & & (^{i}PrO)_3SiCH_2SiMe_3 \quad 82\%
\end{tikzcd}$$

(2)

THF solutions of the bulky (tri-isopropyloxysilyl)-methyl Grignard were stable for several days at room

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* Reference number with asterisk indicates a note in the list of references.

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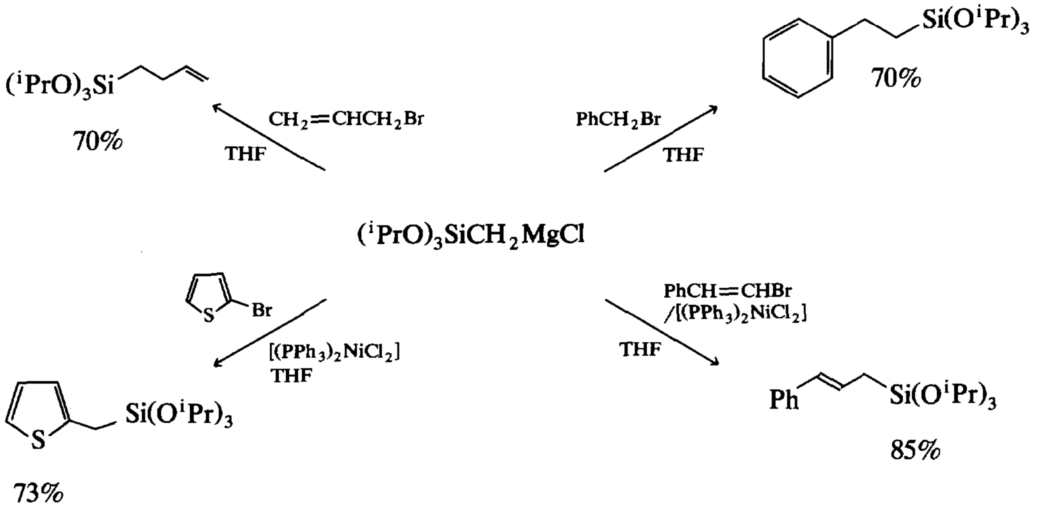
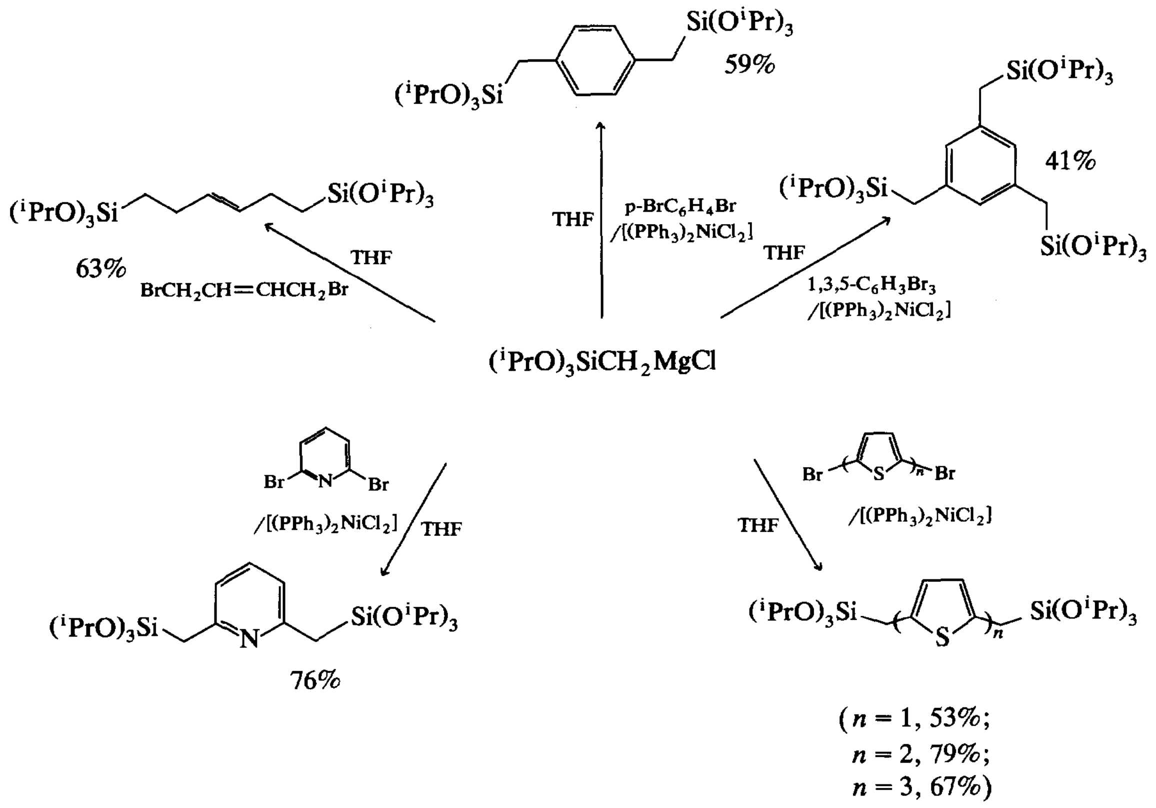


Scheme 1. Reactions of $(^iPrO)_3SiCH_2MgCl$.

temperature. Upon quenching with ^iPrOH or Me_3SiCl good yields of the methyl and [(trimethylsilyl)methyl]-tri-isopropyloxysilanes, respectively, were obtained.

The trifunctional Grignard reacts with various electrophilic reagents (Scheme 1) leading to trialkoxysilyl derivatives. Good yields of isolated products were obtained upon reaction of activated halides such as allyl and benzyl bromides. The nickel-catalysed cross-coupling reaction [18] allowed (silyl)methylation of 2-bromothiophene and 2-bromostyrene in 73 and 85% yields, respectively. The (tri-isopropoxysilyl)methyl Grignard is stable under these reaction conditions.

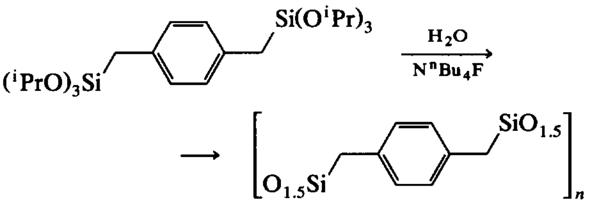
The preparation of polysilylated compounds was also achieved easily (Scheme 2). Yields ranging from 40 to 69% were obtained upon condensation with 1,4-dibromobut-2-ene, as well as with aromatic di- or tri-



Scheme 2. Synthesis of polysilylated derivatives.

bromides. The reaction of heteroaromatic dibromides led to disilylated pyridine and oligothiophenes in 53 to 79% yield.

The reactions of this (trialkoxysilyl)methyl Grignard reagent therefore offers a quite general method for the preparation of a variety of polyfunctional organosilicon compounds. It involves the use of readily accessible starting materials such as chloromethyltrichlorosilane. A variety of inorganic-organic hybrid gels are accessible upon hydrolysis and polycondensation of the trialkoxysilated precursors. The hydrolysis of 1,4 bis[(triisopropyloxysilyl)methyl]benzene (eqn. (3)) under nucleophilic catalysis [19,20] by fluoride ion quantitatively led to a new hydrid gel. The resulting solid exhibited characteristics similar to those reported for related hybrid materials [4]. ^{13}C and ^{29}Si CP MAS NMR [21*] clearly established that the structure of the molecular precursor was retained within the gel. No silicon-carbon bond cleavage occured during polymer formation.



(3)

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21 ^{13}C CP MAS NMR: 133.5, 129.3 (aromatic carbon atoms), 21.4 ppm (CH$_2$Si); ^{29}Si CP MAS NMR: −54.7, −63.0, −70.1 ppm corresponding respectively to T_1:C*Si*(OR)$_2$(OSi), T_2:C*Si*(OR)(OSi)$_2$ and T_3:C*Si*(OSi)$_3$ substructures.