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AN IMPROVED SYNTHESIS OF BIS(TRIMETHYLSILYL)-CHLOROMETHANE. (U)

MAR 81 A H COWLEY, R A KEMP

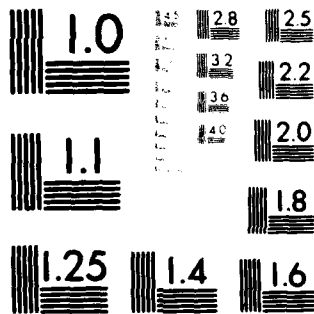
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AN IMPROVED SYNTHESIS OF BIS(TRIMETHYLSILYL)CHLOROMETHANE

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ABSTRACT

A new "one pot" synthesis of the important intermediate, $(\text{Me}_3\text{Si})_2\text{CHCl}$, is described. The method involves the reaction of CH_2Cl_2 , Me_3SiCl , and $n\text{-BuLi}$ in a mixed solvent system. The overall yield of $(\text{Me}_3\text{Si})_2\text{CHCl}$ based upon the CH_2Cl_2 consumed is 78%. Apart from the obvious advantage of being a single step procedure, the method also has the advantage of utilizing relatively inexpensive starting materials. Moreover, the method can be scaled up without significant diminution of the yield.

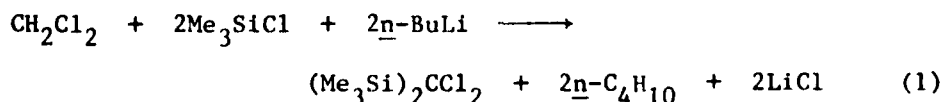
INTRODUCTION

Use of the bis(trimethylsilyl)methyl ligand has permitted the isolation of several novel transition metal and main group compounds.¹ The most common method for the introduction of the bis(trimethylsilyl)methyl ligand is by treatment of $(\text{Me}_3\text{Si})_2\text{CHLi}$ with an active halide. The precursor for the preparation of the lithio derivative is the chloride, $(\text{Me}_3\text{Si})_2\text{CHCl}$. Several methods of preparation of this key compound have now appeared in the literature. The present paper describes an improved "one pot", inexpensive synthesis of $(\text{Me}_3\text{Si})_2\text{CHCl}$.

DISCUSSION

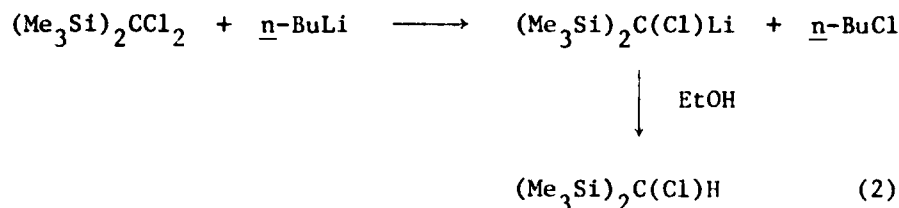
Two general approaches have been taken to the synthesis of $(\text{Me}_3\text{Si})_2\text{CHCl}$. One involves the prior synthesis of $(\text{Me}_3\text{Si})_2\text{CCl}_2$ starting with either CH_2Cl_2 ^{2,3} or $\text{ClMe}_2\text{SiCHCl}_2$.⁴ In turn, the $(\text{Me}_3\text{Si})_2\text{CCl}_2$ is converted into $(\text{Me}_3\text{Si})_2\text{CHCl}$ by reaction of the former with $n\text{-BuLi}$ at low temperature followed by a protic quench of the anion. The second approach involves the deprotonation of $\text{Me}_3\text{SiCH}_2\text{Cl}$ with $s\text{-BuLi}$ followed by treatment with Me_3SiCl .^{5,6} All of these preparative methods have drawbacks. The disadvantage of the first approach is that the yield of the intermediate dichloride, $(\text{Me}_3\text{Si})_2\text{CCl}_2$, is only moderate (50-65%).^{2,3} Even though the conversion of $(\text{Me}_3\text{Si})_2\text{CCl}_2$ to $(\text{Me}_3\text{Si})_2\text{CHCl}$ proceeds in higher yield, the overall yield of the desired compound is small. One of the problems with the second approach is that the reaction is difficult to scale up to the quantities of $(\text{Me}_3\text{Si})_2\text{CHCl}$ needed for our work. Furthermore, in our hands the reaction of $\text{Me}_3\text{SiCH}_2\text{Cl}$ with $s\text{-BuLi}$ was difficult to reproduce with or without TMEDA activation.

In view of the foregoing, it became highly desirable to develop an inexpensive, reproducible, high yield synthesis of $(\text{Me}_3\text{Si})_2\text{CHCl}$. A key feature of our synthetic procedure is that it is not necessary to isolate the intermediate, $(\text{Me}_3\text{Si})_2\text{CCl}_2$. The "one pot" reaction is conducted in two distinct stages and controlled by the temperature and sequence of reagent addition. In the first stage, CH_2Cl_2 is treated with two equivalents of Me_3SiCl and $n\text{-BuLi}$ at -110°C in a $\text{THF}/\text{Et}_2\text{O}/n\text{-pentane}$ mixed solvent system (eq. 1).



This stage of the reaction is completed by warming briefly to room temperature as evidenced by the precipitation of LiCl .

After re-cooling the reaction mixture to -110°C , the second stage of the reaction is conducted by addition of one equivalent of $n\text{-BuLi}$, followed by quenching with 95% EtOH (eq. 2).



Overall reproducible yields of 78% are obtained based upon the CH_2Cl_2 consumed, and the reaction can be conducted on at least a one mole scale.

EXPERIMENTAL

Materials and General Procedures

Until the EtOH quench, all manipulations were performed under anhydrous, oxygen-free conditions. Chlorotrimethylsilane and $n\text{-BuLi}$ were procured commercially and used without subsequent purification. All solvents were dried rigorously. Tetrahydrofuran was freshly distilled from CaH_2 , Et_2O was distilled from LiAlH_4 and stored over $4\text{\AA}$ molecular sieves, and CH_2Cl_2 and $n\text{-pentane}$ were each distilled from P_4O_{10} immediately prior to use.

Synthesis of $(\text{Me}_3\text{Si})_2\text{CHCl}$

To a solution of CH_2Cl_2 (22.4 ml, 350 mmol), Me_3SiCl (92.2 ml, 725 mmol) in THF (250 ml), Et_2O (90 ml), and $n\text{-pentane}$ (40 ml) held at -110°C was added dropwise a pre-cooled solution (-78°C) of $n\text{-BuLi}$ (453 ml of 1.6 M solution, 725 mmol) via a double-tipped needle. The addition of the $n\text{-BuLi}$ solution took approximately 40 minutes. Following this addition, the reaction mixture was allowed to warm to room temperature, during

which time the precipitation of LiCl was clearly in evidence. The reaction mixture was then re-cooled to -110°C , and the second stage of the synthesis was accomplished by dropwise addition of a pre-cooled (-78°C) solution of $n\text{-BuLi}$ (219 ml of 1.6 M solution, 350 mmol). The light tan color characteristic of the $[(\text{Me}_3\text{Si})_2\text{CCl}]^-$ anion became apparent during the addition. After stirring for 45 minutes at -100°C , the reaction mixture was treated with 100 ml of 95% EtOH. Following this, the reaction vessel and its contents were allowed to warm slowly from -100°C . When the temperature reached -40°C , 100 ml of 6 N HCl solution was added in order to quench the LiOEt which had formed in the previous step of the reaction. After warming to room temperature the aqueous layer was separated from the organic layer and extracted twice with 75 ml portions of n -hexane. After combination of the organic solutions, the solvents were removed by means of a rotary evaporator, leaving $(\text{Me}_3\text{Si})_2\text{CHCl}$ as a pale yellow liquid. Fractional vacuum distillation, bp $68\text{--}80^{\circ}\text{C}/25$ torr, afforded 52.8 g (272 mmol) of pure material. The overall yield based upon the consumption of CH_2Cl_2 is thus 78%. Identification of $(\text{Me}_3\text{Si})_2\text{CHCl}$ was made on the basis of ^1H NMR spectroscopy.

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