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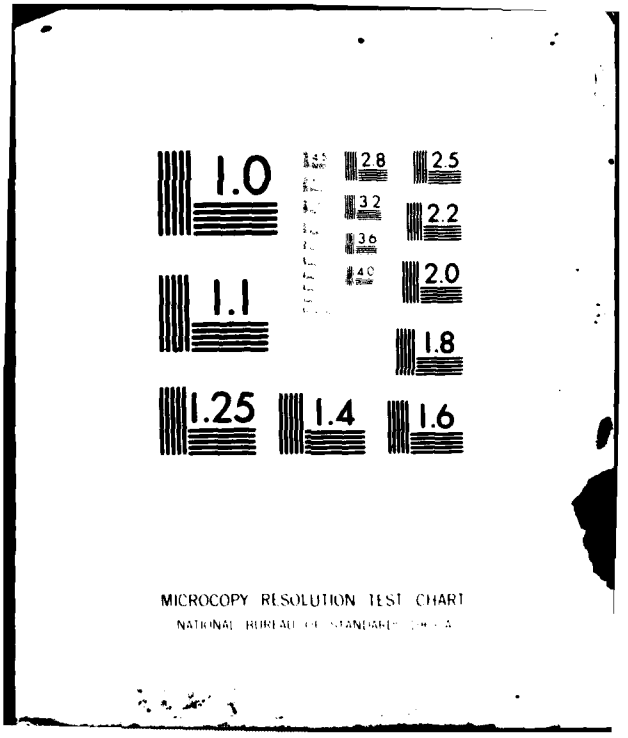
AN IMPROVED SYNTHESIS OF BIS(TRIMETHYLSILYL)-CHLOROMETHANE.(U)
MAR 81 A H COWLEY, R A KEMP N00014-76-C-0577
UNCLASSIFIED TR-81-01 NL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REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: 81-01	2. GOVT ACCESSION NO.: AD-A097210
3. RECIPIENT'S CATALOG NUMBER:	
4. TITLE (and Subtitle): An Improved Synthesis of Bis(Trimethylsilyl)-Chloromethane	5. TYPE OF REPORT & PERIOD COVERED: Technical Report 1981
6. PERFORMING ORG. REPORT NUMBER: TR-81-01	
7. AUTHOR(s): A. H. Cowley* and R. A. Kemp	8. CONTRACT OR GRANT NUMBER(s): N00014-76-C-0577
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE: Mar[illegible]81
	13. NUMBER OF PAGES: 5
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release: Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Prepared for publication in Synthesis and Reactivity in Inorganic and Metal-organic Chemistry

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

synthesis

bulky ligands

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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S/N 0102-014-6601

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

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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.

OFFICE OF NAVAL RESEARCH

Contract N00014-76-C-0577

Task No. NR 053-612

TECHNICAL REPORT NO. 81-01

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Prepared for Publication

in

SYNTHESIS AND REACTIVITY IN

INORGANIC AND METAL-ORGANIC CHEMISTRY

Department of Chemistry
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March 11, 1981

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ABSTRACT

A new "one pot" synthesis of the important intermediate, $(Me_3Si)_2CHCl$, is described. The method involves the reaction of CH_2Cl_2, Me_3SiCl, and n-BuLi in a mixed solvent system. The overall yield of $(Me_3Si)_2CHCl$ 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 $(Me_3Si)_2CHLi$ with an active halide. The precursor for the preparation of the lithio derivative is the chloride, $(Me_3Si)_2CHCl$. 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 $(Me_3Si)_2CHCl$.

DISCUSSION

Two general approaches have been taken to the synthesis of $(Me_3Si)_2CHCl$. One involves the prior synthesis of $(Me_3Si)_2CCl_2$ starting with either CH_2Cl_2 [2,3] or $ClMe_2SiCHCl_2$.[4] In turn, the $(Me_3Si)_2CCl_2$ is converted into $(Me_3Si)_2CHCl$ by reaction of the former with n-BuLi at low temperature followed by a protic quench of the anion. The second approach involves the deprotonation of Me_3SiCH_2Cl with s-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, $(Me_3Si)_2CCl_2$, is only moderate (50-65%).[2,3] Even though the conversion of $(Me_3Si)_2CCl_2$ to $(Me_3Si)_2CHCl$ 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 $(Me_3Si)_2CHCl$ needed for our work. Furthermore, in our hands the reaction of Me_3SiCH_2Cl with s-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 $(Me_3Si)_2CHCl$. A key feature of our synthetic procedure is that it is not necessary to isolate the intermediate, $(Me_3Si)_2CCl_2$. 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-BuLi at -110°C in a THF/Et_2O/n-pentane mixed solvent system (eq. 1).

$$CH_2Cl_2 + 2Me_3SiCl + 2n\text{-}BuLi \longrightarrow (Me_3Si)_2CCl_2 + 2n\text{-}C_4H_{10} + 2LiCl \qquad (1)$$

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-BuLi, followed by quenching with 95% EtOH (eq. 2).

$$(Me_3Si)_2CCl_2 + \text{n-BuLi} \longrightarrow (Me_3Si)_2C(Cl)Li + \text{n-BuCl}$$

$$\downarrow \text{EtOH}$$

$$(Me_3Si)_2C(Cl)H \qquad (2)$$

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-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 4Å molecular sieves, and CH_2Cl_2 and n-pentane were each distilled from P_4O_{10} immediately prior to use.

Synthesis of $(Me_3Si)_2CHCl$

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-pentane (40 ml) held at -110°C was added dropwise a pre-cooled solution (-78°C) of n-BuLi (453 ml of 1.6 M solution, 725 mmol) via a double-tipped needle. The addition of the n-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-BuLi (219 ml of 1.6 M solution, 350 mmol). The light tan color characteristic of the $[(Me_3Si)_2CCl]^-$ 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 $(Me_3Si)_2CHCl$ as a pale yellow liquid. Fractional vacuum distillation, bp 68-80°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 $(Me_3Si)_2CHCl$ was made on the basis of ^1H NMR spectroscopy.

ACKNOWLEDGMENT

The authors are grateful to the Office of Naval Research (Contract N00014-76-C-0577, Task No. NR 053-612) for generous financial support.

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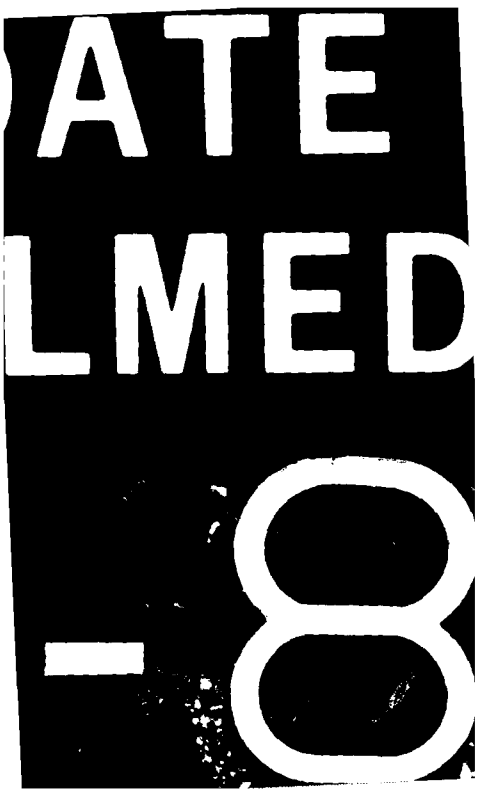
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