

การเตรียมโบรมไฮโดรไซด์จากไฮโดรไฮโดรเจนโดยใช้โบรมีนเนทิงเอเจนต์

นางสาวภัทรสุภา ศรีธนกฤต

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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

PREPARATION OF BROMOSILANE FROM HYDROSILANE USING  
BROMINATING AGENTS

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A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science Program in Petrochemistry and Polymer Science  
Faculty of Science  
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ภัทรสุภา ศรีชนกฤช: การเตรียมโบรโมไซเลนจากไฮโดรไซเลนโดยใช้โบรมิเนทิงเอเจนต์.  
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ได้พัฒนาวิธีการเตรียมโบรโมไซเลนจากไฮโดรไซเลน 2 วิธี ระบบที่ 1 ประกอบด้วยเอทิล  
ไทรโบรโมอะซิเตต ( $\text{Br}_3\text{CCOOEt}$ ) และ  $\text{PdCl}_2$  ปริมาณตัวเร่งปฏิกิริยาที่อุณหภูมิห้องของ  
เทตระไฮโดรฟูราน สามารถเปลี่ยนไฮโดรไซเลนเป็นโบรโมไซเลนได้ในปริมาณสูงภายใน 15  
นาที ได้เสนอกลไกการเกิดปฏิกิริยาของระบบนี้ว่าเกิดขึ้นจากการทำปฏิกิริยาระหว่างโบรมิเนทิง  
เอเจนต์กับ  $\text{Pd}(0)$  โดยปฏิกิริยาออกซิเดทีฟแอคชัน ตามด้วยปฏิกิริยารีดักทีฟอิลิมิเนชัน สำหรับ  
ระบบที่ 2 สามารถใช้เตรียมโบรโมไซเลนปริมาณสูงได้โดยใช้เฮกซะโบรโมอะซิโตน  
( $\text{Br}_3\text{CCOCBr}_3$ ) ร่วมกับยูวี (254 นาโนเมตร, 6 วัตต์) ภายใน 45 นาที เชื่อว่ากลไกการเกิดปฏิกิริยา  
เกิดผ่านแรดิคอล โดยมีหลักฐานสนับสนุนจากการทดลองแทรีปปีง นอกจากนี้ได้ศึกษาความ  
ว่องไวของโบรมิเนทิงเอเจนต์สำหรับการสังเคราะห์โบรโมไซเลน พบว่า  $\text{Br}_3\text{CCOOEt}$  มีความ  
ว่องไวมากที่สุด วิธีที่ได้พัฒนานี้สามารถประยุกต์สำหรับการสังเคราะห์ไซลิลอีเทอร์และไซลิลเอส  
เทอร์ได้ในปริมาณสูงแบบวันพอด

สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ปลายมือชื่อนิสิต.....  
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Two methodologies for the preparation of bromosilane from hydrosilane have been developed. The first system comprising of ethyl tribromoacetate ( $\text{Br}_3\text{CCOOEt}$ ) with a catalytic amount of  $\text{PdCl}_2$  at reflux THF, could convert hydrosilane to bromosilane in high yield within 15 min. The mechanism of this system was proposed to occur *via* the interaction of brominating agent with  $\text{Pd}(0)$  by oxidative addition, followed by reductive elimination. For the second system, high yield of bromosilane could be achieved by using hexabromoacetone ( $\text{Br}_3\text{CCOCBr}_3$ ) in the presence of UV irradiation (254 nm, 6W) within 45 min. The mechanism was believed to occur *via* a radical pathway supporting by the evidence of trapping experiment. In addition, the relative reactivity of brominating agent towards the synthesis of bromosilane was studied.  $\text{Br}_3\text{CCOOEt}$  revealed the highest reactivity. These developed methodologies could further be applied for the synthesis of silyl ethers and silyl esters in high yield by one-pot reaction.

Field of Study: Petrochemistry and Polymer Science Student's Signature .....

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%	percent
°C	degree of Celsius
br s	broad singlet (NMR)
$\delta$	chemical shift
<i>J</i>	coupling constant (NMR)
d	doublet (NMR)
dd	doublet of doublet (NMR)
eq	equivalent (s)
g	gram (s)
h	hour (s)
Hz	hertz
m.p.	melting point
mmol	millimole (s)
min	minute (s)
m	multiplet (NMR)
nm	nanometer
NMR	nuclear magnetic resonance
ppm	part per million
q	quartet (NMR)
RT	room temperature
s	singlet (NMR)
t	triplet (NMR)
TLC	thin layer chromatography
UV	ultraviolet
W	watt
$\alpha$	alpha
conc.	concentration
$\mu\text{L}$	microliter (s)
quant	quantitative
N	normal

## CHAPTER I

### INTRODUCTION

Halosilanes are of important starting materials or reagents in the field of organosilicon chemistry [1] such as silicone and polymer chemistry as well as in synthetic organic chemistry [2] as a protecting group, hydrosilylating agent or deoxygenating agent. Among halosilanes, chlorosilanes are well known and widely useful for the synthesis of organosilicon compounds or polymer, materials in paint industries. Various synthetic methods for chlorosilanes have thus been developed and reported. Considering the reactivity between chloro- and bromosilanes, the latter should be of higher reactivity than the former and should be more versatile for the utilization in organic synthesis. Nevertheless, up to date, a few methods for the preparation of bromosilanes have been addressed since not many brominating agents are readily available [3-4].

This research thus devotes to the synthesis of bromosilane from hydrosilane using brominating agent under mild conditions. Further application for the synthesis of silyl ether and silyl ester in one-pot fashion is also investigated.

#### **1.1 Introduction of Bromosilanes**

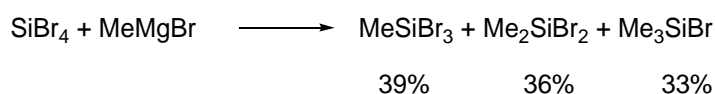
Halosilanes are important reagents towards the synthesis of organosilicon compounds. Among halosilanes, bromosilanes exhibit high reactivity and Lewis acidity that permit the interaction with C-O and C=O bonds occur smoothly, unlike fluoro- and chlorosilanes [5]. So, bromosilanes should be appropriate reagents to use as protecting agents for alcohols and carboxylic acids affording silyl ethers and silyl esters, respectively.

#### **1.2 Classical Methods for the Preparation of Bromosilanes**

Bromosilane can be prepared by simple substitution reaction using organometallic reagent such as Grignard reagent reacting with silicon tetrabromide

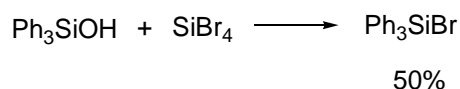
(SiBr<sub>4</sub>), redistribution of SiBr<sub>4</sub> with silicon tetrachloride (SiCl<sub>4</sub>) and the reaction of aluminium tribromide (AlBr<sub>3</sub>) with hydrosilane.

The classical method for the preparation of bromosilane was addressed by the reaction of SiBr<sub>4</sub> and CH<sub>3</sub>MgBr [6]. The disadvantage of this method is less selective producing providing a mixture of product such as di- or tri-bromosilanes which was difficult to separate and gave low yield of product.

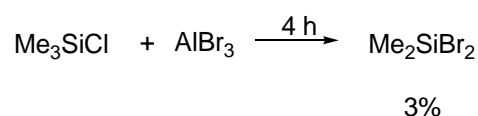
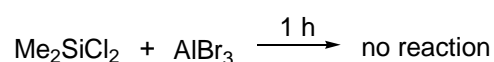
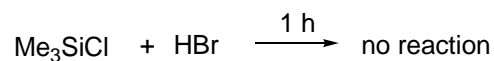


The reaction of Grignard reagents with SiBr<sub>4</sub> is suitable in general for the preparation of mono and dibromosilanes where the boiling points of the products are not too close to one another.

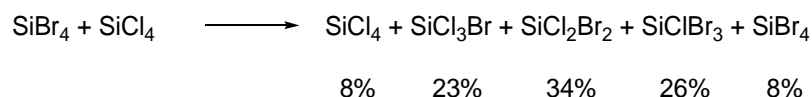
In addition, the reaction of siloxanes and SiBr<sub>4</sub> could be possible for the preparation of bromosilanes [6]. This method gave 50% yield of the desired product. The advantage of this method is high specificity in producing of target product, but in moderate yield.



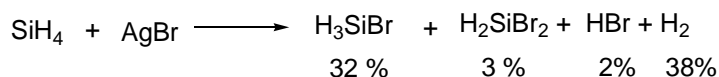
Another method to prepare bromosilane was accomplished by converting chlorosilanes to bromosilanes with brominating agents such as AlBr<sub>3</sub> or HBr [6]. This method took place when the condition was performed under high temperature and long reaction time.



Redistribution of  $\text{SiCl}_4$  with  $\text{SiBr}_4$  could be used to prepare bromosilane (7). The desired product was achieved in low yield and occurred in random distribution. Therefore, the desired product needed to be separated with difficulty.



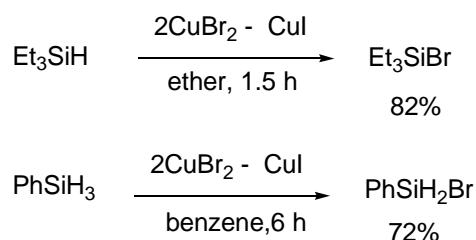
Hydrosilane could be converted to bromosilane by the gas-solid phase reaction between silane and silver bromide ( $\text{AgBr}$ ) [8]. The drawback for this method was that a mixture of product such as mono- or di-bromosilanes was obtained in low yield and unpleasant by-product such as  $\text{HBr}$  was invariable generated.



Other methods for the preparation of bromosilane reported in literatures included the cleavage of  $\text{Si-O}$  bonds with  $\text{PBr}_3$  [9], cleavage of  $\text{Si-Ph}$  bonds [10] or  $\text{Si-Si}$  bonds [11] with  $\text{Br}_2$ , bromination of polysilane with  $\text{Br}_2$  [12],  $\text{HBr}$  [13],  $\text{HgBr}_2$  [14] or  $\text{NBS}$  [15]. Those reported methods could be accomplished by employing toxic brominating agents, high reactivity of brominating agent, severe conditions with unpleasant by-products such as  $\text{HBr}$  or  $\text{Br}_2$ .

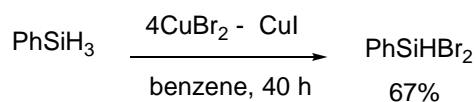
### 1.3 Literature Reviews on the Conversion of Hydrosilanes to Halosilanes

Kunai and Oshita reported the synthesis of bromosilanes from hydrosilanes in high yield by the reaction of hydrosilane with 2 eq of  $\text{CuBr}_2$  in the presence of a catalytic amount of  $\text{CuI}$  [16].

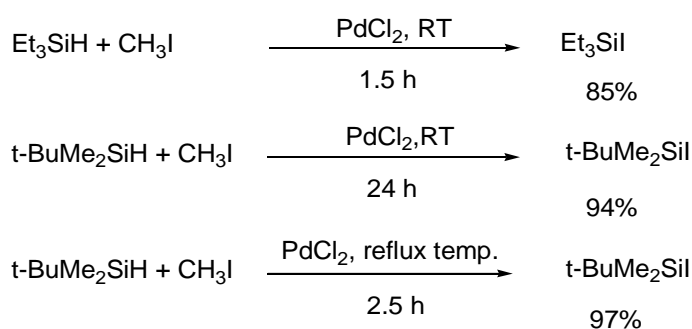




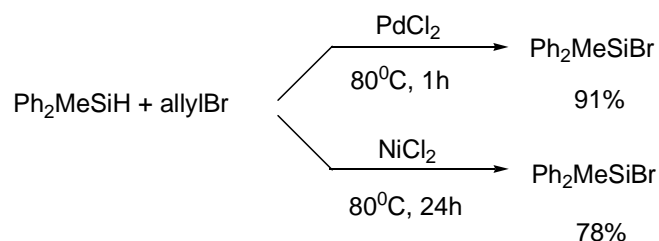
PhSiHBr<sub>2</sub> was prepared by using 4 eq of CuBr<sub>2</sub>-CuI reagent for 40 h. This method could not be applicable for the preparation of tribromosilanes, even though required long reaction time.



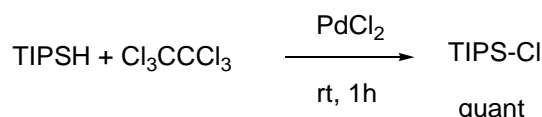
Kunai and coworkers addressed the reaction of hydrosilanes and alkyl iodides in the presence of a catalytic amount of PdCl<sub>2</sub> [17] affording iodasilane in high yield with long reaction time. This method revealed that hydrosilanes bearing a bulky substituent on the silicon atom required reflux temperature (~ 60°C).



PdCl<sub>2</sub> and NiCl<sub>2</sub> were screened as a proper catalyst to prepare bromosilane from the reaction of hydrosilane with brominating agent such as allyl bromide, ethyl bromide, *n*-propyl bromide in the presence of a catalytic amount of PdCl<sub>2</sub> [18]. PdCl<sub>2</sub> was disclosed to be the appropriate one whereas allyl bromide was found to be a suitable brominating agent. The limitation of this method is the selection of brominating agent which needed to be compatible with the substance. The advantage of this route was the high yield of bromosilane with none of by-product detected.



Pongkittiphan and coworkers addressed the chlorination of triisopropylsilane (TIPS-H) using hexachloroethane ( $\text{Cl}_3\text{CCCl}_3$ ) in the presence of a catalytic amount of  $\text{PdCl}_2$  [19] affording triisopropylchlorosilane (TIPS-Cl) in quantitative yield under mild reaction and short reaction time.



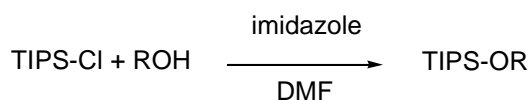
## 1.4 Introduction of Silyl Derivatives

The role of silyl groups is important in organic chemistry both analytical and synthetic point of view, especially as protecting group. The reaction involves a variety of organic compound including alcohols or organic acids being attacked by a nucleophile. A few applications of polysilyl esters are in the cotton textile industry to protect water repellency [20] and polysiloxanes bearing silyl ester end groups have also been used as protecting agent in anionic polymerization [21].

### 1.4.1 Preparation of Silyl Ethers and Silyl Esters

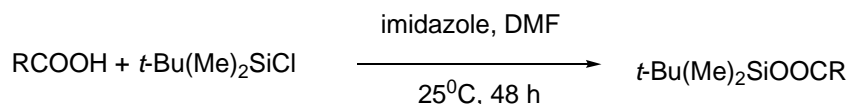
Generally, the method for the preparation of silyl ethers could be carried out by treatment of alcohols with silyl chlorides or silyl triflates in the presence of base [22].

A number of hindered triorganosilyl groups employed for the marking hydroxyl functions such as *tert*-butyldimethylsilyl (TBDMS) [23], *tert*-butyldiphenylsilyl (TBDPS) [24], triisopropylsilyl chloride (TIPS-Cl) [25] and bases were used as catalyst including imidazole or 4-dimethylaminopyridine (DMAP).

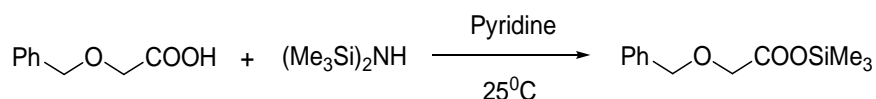


TIPS group was a proper hydroxyl-protecting moiety because of its low cost, greater stability of TIPS over TBDMS ethers and more facial acidic deprotection of TIPS over TBDPS derivatives.

For the synthesis of silyl ester, the same reagents could be applied for silyl ethers. For example, TBDMS ester could be prepared by using carboxylic acid with TBDMS chloride in the presence of imidazole in DMF [26]. The drawback is long reaction time required, but this method gave the desired product in high yield under mild condition.

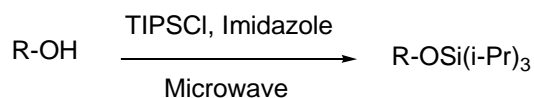


Aminosilanes as silylating agents have been reported to use in the conversion of the carboxyl group to the silyl ester in high yield; nonetheless, certain by-product such as  $\text{NH}_3$  or amine was generated [27].

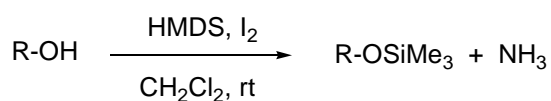


#### 1.4.2 Literature Review on the Synthesis of Silyl Derivatives

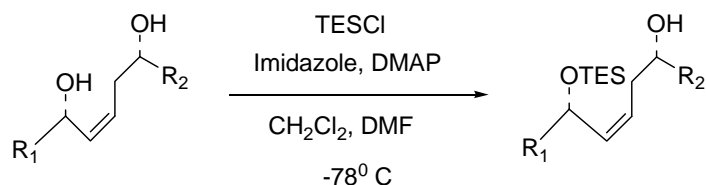
Khalafi-Nezhad and Alamdari [28] reported the efficient method for the protection of 1°, 2°, 3° alcohols and phenols using triisopropylsilyl chloride/imidazole under microwave irradiation. This method is very simple and offers high yields of the silylated products under short time reaction (not more than 3 min).



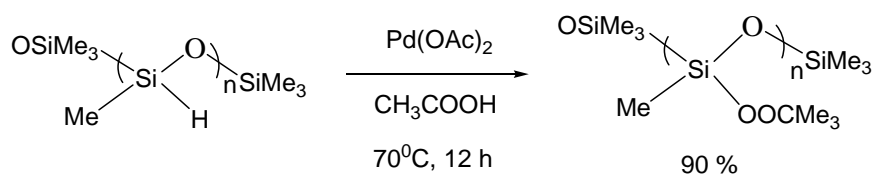
Karimi and Golshani [29] presented the protocol for converting 1°, allylic, benzylic alcohols to silyl ether using hexamethyldisilazane (HMDS) and a catalytic amount of iodine. The reaction produced silyl ether in high yield (> 90%) under mild condition at room temperature and short reaction time. The drawback of this method is the occurrence of ammonia by-product.



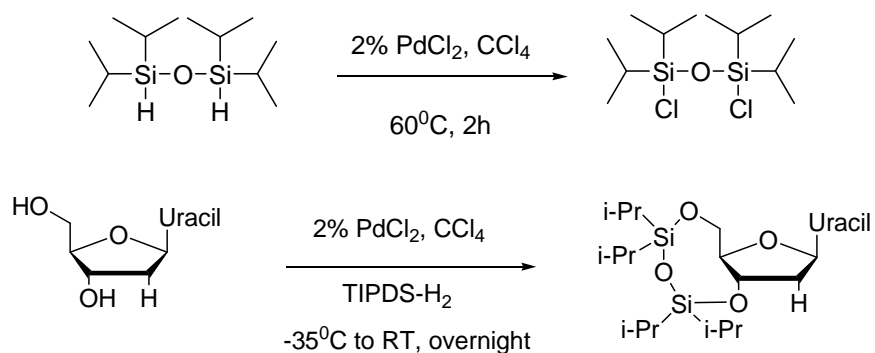
Hicks and co-workers [30] described the silylation of 2° allylic alcohol using triethylchlorosilane, imidazole and DMAP. This method proceeded with high selectivity for various substrates including allylic/homoallylic alcohols providing allylic triethylsilyl ethers in high yields (61-81%); nevertheless, the reaction was quite difficult to handle due to the low temperature required.



Chauhan and co-workers [31] addressed the route for conversion of silanes and polysiloxane to the corresponding silyl esters in high yields. This reaction was achieved under mild reaction condition in the presence of  $\text{Pd}(\text{OAc})_2$ , but long reaction time was necessary.



Ferreri and co-workers [32] demonstrated the synthesis of dichloride product ( $\text{TIPDS-Cl}_2$ ) from siloxane ( $\text{TIPDS-H}_2$ ). This reaction was succeeded by using  $\text{CCl}_4$  in the presence of  $\text{PdCl}_2$  under mild conditions; nevertheless, the long reaction time required. These systems could be applied in one-pot silylation of nucleosides in high yield but the reaction condition was hard to control because of the low temperature needed.



## 1.5 Recent Halogenating Agents

$\text{Br}_3\text{CCOOEt}$ , another effective brominating agent was addressed by Jang and co-workers [33] for the preparation of acid bromides from carboxylic acid at room temperature under neutral condition. Aromatic aldehydes with electron-donating group were found to be more reactive than those with electron-withdrawing group and aliphatic aldehydes under reaction conditions. The acid bromides generated could be applied for the preparation of amide in one-pot fashion.

Jang and co-workers [34] addressed the conversion of aromatic aldehyde into acid bromide using benzoyl peroxide as initiator and  $\text{Br}_3\text{CCOOEt}$  as brominating agent in high yield. The aromatic aldehyde with electron-donating group was more reactive than those with electron-withdrawing group and aliphatic aldehydes.

Tongkate [35] described the method for bromination of alcohols by  $\text{PPh}_3/\text{Br}_3\text{CCOOEt}$  and  $\text{PPh}_3/\text{Br}_3\text{CCOCBr}_3$ . Various alcohols could be converted to alkyl bromides in high yield under mild conditions and short reaction time. The study on the reactivity of brominating agents for the synthesis of alkyl bromide revealed that  $\text{Br}_3\text{CCOCBr}_3$  was the most efficient brominating agent, compared with other brominating agents studied.

## 1.6 Limitations of Previous Works

From literature reviews, most bromosilanes could be synthesized in moderate yield. The limitations from those previous protocols could be summarized as: long reaction time, use toxic brominating agents, low efficiency, and the reaction being hard to handle.

## 1.7 The Objective of This Research

The objective of this research is to develop the methodology for the conversion of hydrosilanes to bromosilanes using brominating agent. Two approaches involve the use of brominating agent coupled with  $\text{PdCl}_2$  as a catalyst and using  $\text{Br}_3\text{CCOCBr}_3$  and UV irradiation in place of a catalyst. This developed methodology was further applied for the preparation of silyl derivatives in one-pot reaction.

## CHAPTER II

### EXPERIMENTAL

#### 2.1 Instruments and Equipment

All reactions were performed under an atmosphere of N<sub>2</sub>. The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were performed in CDCl<sub>3</sub> with tetramethylsilane (TMS) as an internal reference on Varian nuclear magnetic resonance spectrometer, model Mercury plus 400 NMR spectrometer which operated at 399.38 MHz for <sup>1</sup>H and 100.54 MHz for <sup>13</sup>C nuclei. The chemical shifts are assigned by comparison with residue solvent proton. Yields of products were determined by <sup>1</sup>H-NMR technique using toluene as an internal standard.

Thin layer chromatography (TLC) was performed on aluminum sheets pre-coated with silica gel (Merck's, Kieselgel 60 PF<sub>254</sub>) and column chromatography was performed on silica gel (Merck's silica gel 60 G Art 7734 (70-230 mesh)).

#### 2.2 Chemicals

All solvents were purified by standard methodology before use except for those which were reagent grades. The reagents used for synthesis were purchased from Fluka or Sigma-Aldrich chemical company and used without further purification.

#### 2.3 Preparation of Brominating Agents

##### **Ethyl tribromoacetate [36]**

One mL of conc H<sub>2</sub>SO<sub>4</sub> was cautiously added to the mixture of Br<sub>3</sub>COOH 1 eq (40 mmol, 11.87 g) and EtOH 4.5 mL. The mixture was refluxed for 3-6 h and then poured into 100 mL of water in a separatory funnel. The upper layer of crude ester was removed and washed with 50 mL of water, saturated aqueous NaHCO<sub>3</sub> and water respectively, then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>.

*Ethyl tribromoacetate*: colorless oil (65%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ (ppm): 1.36 (3H, t,  $J = 7.2$  Hz,  $\text{CH}_2\text{CH}_3$ ) and 4.46 (2H, q,  $J = 7.2$  Hz,  $\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ (ppm): 13.7, 29.5, 65.7 and 161.9.

### **Hexabromoacetone [37]**

Anhydrous NaOAc 7 g was mixed with 20 mL of glacial acetic acid. The reaction mixture was stirred and heated to  $60^\circ\text{C}$ , acetone 1.4 mL was added; followed by dropwise addition of  $\text{Br}_2$  5 mL over a 10 min period with stirring. The mixture was then heated to  $95^\circ\text{C}$  for 3-6 h. After which it was cooled to RT and mixed with 100 mL of water to precipitate the desired product as white solid. After air drying, the pure product was obtained upon recrystallization from hexane.

*Hexabromoacetone*: white solid (60%).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 24.5 and 173.5.

## **2.4 General Procedure for Conversion of Hydrosilane to Bromosilane**

### **2.4.1 General Procedure for the Preparation of Bromosilanes Using Pd(II) Catalyst**

A stirred solution of  $\text{PdCl}_2$  (1% mmol, 1.8 mg) and 1.25 eq (1.25 mmol, 185 $\mu\text{L}$ ) of brominating agents in THF 0.25 mL was successively added hydrosilane 1 eq (1.0 mmol, 205 $\mu\text{L}$ ) at reflux THF under  $\text{N}_2$  atmosphere for 15 min. After 15 min, the crude mixture was analyzed by  $^1\text{H-NMR}$  with the addition of toluene 1 eq (1.0 mmol, 106  $\mu\text{L}$ ) as an internal standard.

### **2.4.2 General Procedure for the Preparation of Bromosilanes Using UV Irradiation Condition**

A stirred solution of  $\text{Br}_3\text{CCOCBr}_3$  (0.3 mmol, 15.8 mg) in THF 0.25 mL was successively added hydrosilane 1 eq (1.0 mmol, 205 $\mu\text{L}$ ) under the radiation of UV (254 nm, 6W) under  $\text{N}_2$  atmosphere for 45 min. The crude mixture was then analyzed by  $^1\text{H-NMR}$  with the addition of toluene 1 eq (1.0 mmol, 106  $\mu\text{L}$ ) as an internal standard.

## 2.5 Conditions Optimization for the Synthesis of Bromosilanes by Using Pd(II) Catalyst

### 2.5.1 Effect of Brominating Agents

The conversion of triisopropylhydrosilane (TIPS-H) into triisopropylsilylbromide (TIPS-Br) was carried out using the reaction conditions described in the general procedure. Eight diverse brominating agents including tetrabromomethane ( $\text{CBr}_4$ ), allyl bromide ( $\text{CH}_2=\text{CHCH}_2\text{Br}$ ), tribromoacetic acid ( $\text{Br}_3\text{CCOOH}$ ), ethyl tribromoacetate ( $\text{Br}_3\text{CCOOEt}$ ), bromoform ( $\text{CHBr}_3$ ), dibromoacetic acid ( $\text{Br}_2\text{CHCOOH}$ ), ethyl dibromoacetate ( $\text{Br}_2\text{CHCOOEt}$ ) and bromoethane ( $\text{CH}_3\text{CH}_2\text{Br}$ ) were utilized.

### 2.5.2 Effect of Solvent

The general reactions performed using various solvents (0.25 mL) including tetrahydrofuran (THF), 1,4-dioxane, acetonitrile ( $\text{CH}_3\text{CN}$ ) and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) were carried out.

### 2.5.3 Effect of Type of Pd(II) Catalyst and Amount of $\text{PdCl}_2$

Three different types of Pd(II) catalyst namely  $\text{PdCl}_2$ ,  $\text{PdBr}_2$  and Pd(0) on charcoal were selected to compare their effects on the reaction efficiency. The amount of  $\text{PdCl}_2$  catalyst (0.5 and 1.0% mmol) was explored for the synthesis of TIPS-Br from TIPS-H.

### 2.5.4 The Variation of Reaction Conditions

The optimum condition was investigated under different circumstances, *i.e.*, under refluxing and sonication conditions compared with that carried out at room temperature.

### 2.5.5 Effect of the Amount of $\text{Br}_3\text{CCOOEt}$

Various amounts of  $\text{Br}_3\text{CCOOEt}$  (1.00, 1.25, 1.50 mmol) were varied for the bromination of TIPS-H.



## 2.6 General Procedure for the Preparation of Bromosilanes Using $\text{Br}_3\text{CCOOCBr}_3$ and UV Irradiation Condition

### 2.6.1 The Effect of Reaction Conditions

The reactions were performed under different reaction conditions, *i.e.*, refluxing, sonication and UV radiation conditions compared with that carried out at RT.

### 2.6.2 Effect of Solvent

The general reactions were performed using various solvents (0.25 mL) including THF, 1,4-dioxane,  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$ .

### 2.6.3 Effect of the Amount of $\text{Br}_3\text{CCOOCBr}_3$

In general procedure, the amount of  $\text{Br}_3\text{CCOOCBr}_3$  (0.25, 0.30, 0.35 mmol) was varied for the bromination of TIPS-H.

### 2.6.4 Effect of Reaction Time

The reaction time was varied as follows: 30, 45 and 60 min under UV light.

## 2.7 The Application of the Developed Procedure for the Synthesis of Bromosilanes

The bromination of various hydrosilanes (1 mmol) was carried out using the developed procedures either using  $\text{PdCl}_2$  1%mmol (1.8 mg) and  $\text{CBr}_3\text{COOEt}$  as a brominating agent at refluxing THF for 15 min or using  $\text{CBr}_3\text{COOCBr}_3$  as a brominating agent in THF under UV radiation (254 nm, 6W) for 45 min. The quantity of bromosilane in the crude mixture was determined by  $^1\text{H-NMR}$  using toluene as an internal standard.

*Triisopropylbromosilane*: (quant),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.11 (18H, d,  $J = 7.2$  Hz,  $\text{Si}(\text{CH}(\underline{\text{C}}\text{H}_3)_2)_3$ ) and 1.26 (3H, m,  $\text{Si}(\underline{\text{C}}\text{H}(\text{CH}_3)_2)_3$ ).

*Triethylbromosilane*: (70-72%),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.83 (9H, t,  $J = 7.8$  Hz,  $\text{Si}(\text{CH}_2\underline{\text{C}}\text{H}_3)_3$ ) and 1.02 (6H, q,  $J = 7.8$  Hz,  $\text{Si}(\underline{\text{C}}\text{H}_2\text{CH}_3)_3$ ).

*Triphenylbromosilane*: (91%-quant),  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 7.35 (9H, m, Ar-H) and 7.72 (6H, d,  $J = 6.5$  Hz, Ar-H).

*tert-Butyldimethylbromosilane*: (61-67%),  $^1\text{H}$ -NMR( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.52 (6H, s,  $\text{Si}(\text{CH}_3)_2$ ) and 1.01 (9H, s,  $\text{SiC}(\text{CH}_3)_3$ ).

*Diphenylbromosilane*: (64-70%),  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 5.78 (1H, s,  $\text{Ph}_2\text{Si-BrH}$ ), 7.48 (6H, m, Ar-H) and 7.70 (4H, d,  $J = 6.7$  Hz, Ar-H).

## 2.8 One-pot Synthesis of Silyl Derivatives

The general method for the one-pot synthesis of silyl derivatives can be divided into 2 steps.

**Step 1** The synthesis of bromosilane

Method 1 Using catalyst: TIPS-H 1 eq (2.0 mmol) as a substrate, brominating agent 1.25 eq (2.5 mmol) and 1%PdCl<sub>2</sub> (3.6 mg) in dry THF (0.5 mL) for 15 min at refluxing temperature.

Method 2 In the absence of catalyst: TIPS-H 1 eq (2.0 mmol) as a substrate and Br<sub>3</sub>CCOOCBr<sub>3</sub> 0.3 eq (0.6 mmol) in dry THF (0.5 mL) under UV radiation (254 nm, 6W) for 45 min.

**Step 2** The transformation of bromosilane to silyl derivatives

The *in situ* reaction from step 1 was further reacted with selected alcohols or carboxylic acids (1 mmol), imidazole 1.5 mmol and DMAP 0.5 mmol. The reaction was followed by TLC until the completion.

### 2.8.1 Synthesis of Silyl Ether Derivatives

Different chosen alcohols (1.0 mmol): geraniol, *trans*-cinamyl alcohol and benzyl alcohol were examined. After the reaction was finished, the quantity of silyl ethers in the crude mixture was determined by  $^1\text{H}$ -NMR using toluene as an internal standard or purified by alumina column.

*Triisopropyl(phenethoxy)silane*: colorless oil (86%),  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.05 (21H, d,  $J = 5.1$  Hz,  $\text{Si}(\text{CH}(\text{CH}_3)_2)_3$ ), 2.86 (2H, t,  $J = 7.2$  Hz,  $\text{PhCH}_2\text{-CH}_2\text{OSi}$ ), 3.88 (2H, t,  $J = 7.2$  Hz,  $\text{PhCH}_2\text{CH}_2\text{OSi}$ ) and 7.25 (5H, m, Ar-H).

*trans*-(3,7-dimethylocta-2,6-dienyloxy)triisopropylsilane: (quant),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.05 (21H, d,  $J = 4.8$  Hz,  $\text{Si}(\text{CH}(\text{CH}_3)_2)_3$ ), 1.59 (1H, s,  $\text{CH}_3\text{CCH}_2$ ), 1.64 (1H, s,  $\text{CH}_3\text{CCH}_3$ ), 2.00 (2H, t,  $J = 6.9$  Hz,  $\text{CHCH}_2\text{CH}_2\text{CCH}_3$ ), 2.07 (2H, t,  $J = 7.2$  Hz,  $\text{CHCH}_2\text{CH}_2\text{CCH}_3$ ), 5.09 (1H, t,  $J = 6.5$  Hz,  $\text{CH}=\text{CCH}_3$ ) and 5.32 (1H, t,  $J = 5.7$  Hz,  $\text{C}=\text{CHCH}_2\text{OSi}$ ).

*Benzyloxytriisopropylsilane*: (quant),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.05 (21H, d,  $J = 4.8$  Hz,  $\text{Si}(\text{CH}(\text{CH}_3)_2)_3$ ), 4.82 (2H, s,  $\text{PhCH}_2\text{OSi}$ ), 7.16 (1H, t,  $J = 8.3$  Hz, Ar-H), 7.25 (2H, t,  $J = 7.9$  Hz, Ar-H) and 7.38 (2H, d,  $J = 8$  Hz, Ar-H).

*trans*-Cinnamyloxytriisopropylsilane: colorless oil (72%),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.08 (21H, d,  $J = 6.0$  Hz,  $\text{Si}(\text{CH}(\text{CH}_3)_2)_3$ ), 4.43 (2H, d,  $J = 3.3$  Hz,  $\text{CHCH}_2\text{OSi}$ ), 6.29 (1H, m,  $J = 15.9$ , 4.7 Hz,  $\text{CHCHCH}_2\text{OSi}$ ), 6.63 (1H, d,  $J = 15.9$  Hz,  $\text{PhCHCH}$ ) and 7.34 (5H, m, Ar-H).

## 2.8.2 Synthesis of Silyl Ester Derivatives

Three selected carboxylic acids (1.0 mmol): *trans*-cinnamic acid, 3-methoxybenzoic acid and benzoic acid were examined for the scope of this developed one-pot reaction. After the reaction was completed, the quantity of silyl esters in the crude mixture was determined by  $^1\text{H-NMR}$  using toluene as an internal standard.

*Triisopropylsilyl benzoate*: (quant),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.16 (18H, d,  $J = 7.0$  Hz,  $\text{Si}(\text{CH}(\text{CH}_3)_2)_3$ ), 1.41 (3H, m,  $J = 7$  Hz,  $-\text{Si}(\text{CH}(\text{CH}_3)_2)_3$ ), 7.44 (2H, t,  $J = 8.0$  Hz, Ar-H), 7.55 (1H, t,  $J = 8.0$  Hz, Ar-H) and 8.08 (2H, d,  $J = 8.0$  Hz, Ar-H).

*Triisopropylsilyl-3-methoxybenzoate*: (quant),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.15 (18H, d,  $J = 7.5$  Hz,  $\text{Si}(\text{CH}(\text{CH}_3)_2)_3$ ), 1.41 (3H, m,  $J = 7.0$  Hz,  $-\text{Si}(\text{CH}(\text{CH}_3)_2)_3$ ), 3.85 (3H, s, Ar-OCH<sub>3</sub>), 7.12 (1H, d,  $J = 8.3$  Hz, Ar-H), 7.35 (1H, t,  $J = 7.9$  Hz, Ar-H), 7.62 (1H, s, Ar-H) and 7.67 (1H, d,  $J = 7.6$  Hz, Ar-H).

*Triisopropylsilyl cinnamate*: (quant),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.15 (18H, d,  $J = 7.5$  Hz,  $\text{Si}(\text{CH}(\text{CH}_3)_2)_3$ ), 1.41 (3H, m,  $J = 7.0$  Hz,  $-\text{Si}(\text{CH}(\text{CH}_3)_2)_3$ ), 6.42 (1H, d,  $J = 15.6$  Hz), 7.15 (1H, t,  $J = 8.3$  Hz, Ar-H), 7.37 (2H, t,  $J = 7.9$  Hz, Ar-H), 7.58 (2H, d,  $J = 8.0$  Hz, Ar-H) and 7.63 (1H, d,  $J = 15.6$  Hz,  $\text{PhCHCH}$ ).

## 2.9 Comparative Reactivity Study of Brominating Agents for Conversion of TIPS-H to TIPS-Br

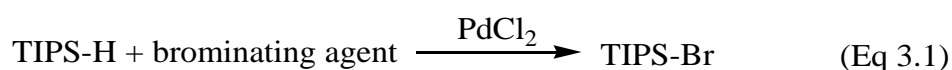
The reactivity of  $\text{Br}_3\text{CCOOEt}$  and other brominating agents was studied using a competitive reaction between brominating and chlorinating agents towards hydrosilane. The reactivity of selected brominating agent was rationalized by the obtained yield ratio of bromosilane and chlorosilane.

TIPS-H 1 eq (1mmol, 205  $\mu\text{L}$ ) was added to mixture of  $\text{Cl}_2\text{CHCOOEt}$  1.25 eq (1.25 mmol, 154  $\mu\text{L}$ ) and selected brominating agent 1.25 eq (1.25 mmol) in dry THF (0.25 mL). After 30 min, the crude reaction was determined by  $^1\text{H}$ - NMR using toluene as an internal standard.

## CHAPTER III

### RESULTS AND DISCUSSION

Halosilanes have been reported as one of important reagents in the field of organosilicon chemistry and synthetic organic chemistry. Among halosilanes, bromosilane is an efficient protecting agent for alcohols and carboxylic acids affording ether and ester derivatives, respectively [5]. Even though, the reactivity of bromosilanes are comparatively higher than chlorosilanes, their availability in commercial was limited mainly due to brominating agents being not readily available. Thus, in this research the methodology for the synthesis of bromosilanes using two new brominating agents including ethyl tribromoacetate ( $\text{Br}_3\text{CCOOEt}$ ) and hexabromoacetone ( $\text{Br}_3\text{CCOCBr}_3$ ) has been developed. The optimal conditions for the synthesis of bromosilanes utilizing these brominating agents are examined using two different protocols. The first one employs  $\text{PdCl}_2$  as a catalyst whereas the second approach utilizes UV to initiate the bromination. The general equations are presented below (Equations 3.1 and 3.2).



The application of this new protocol to manipulate silyl ethers and silyl esters in one pot fashion is then explored.

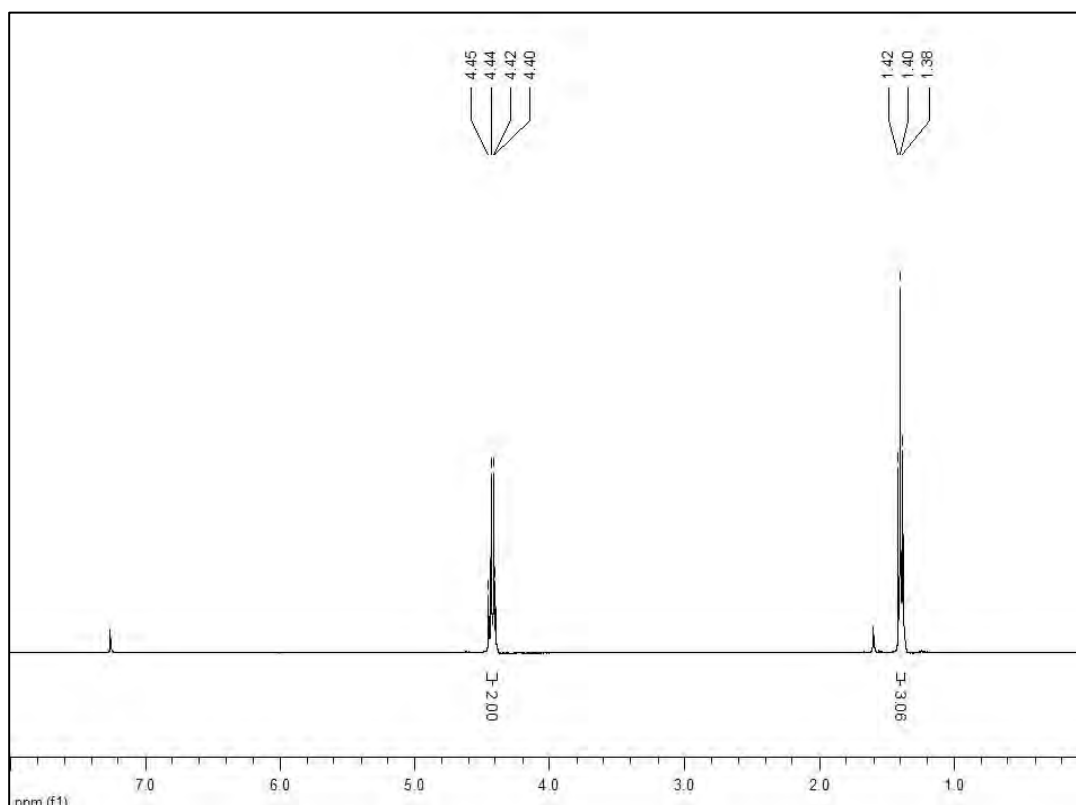
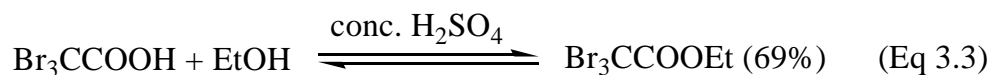
#### Part I Synthesis of Bromosilane Using Pd(II) Catalyst

##### 3.1 The Synthesis of Brominating Agents

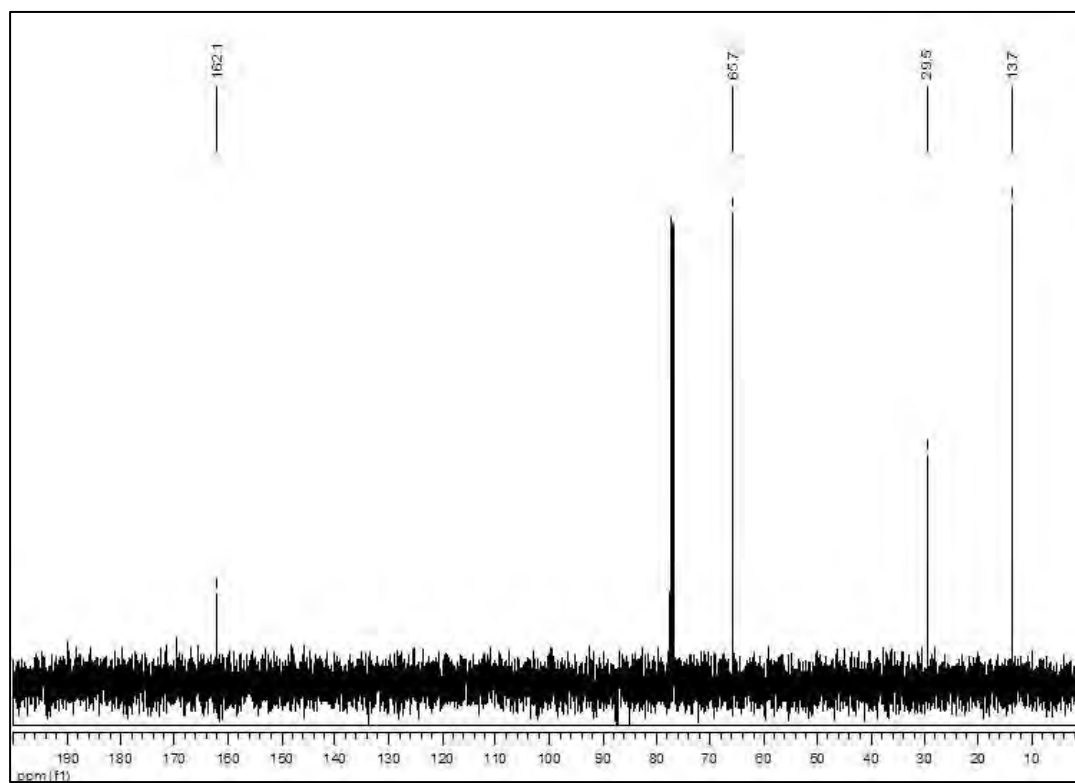
In this research, two new brominating agents, *i.e.*  $\text{Br}_3\text{CCOOEt}$  and  $\text{Br}_3\text{CCOCBr}_3$  are introduced for bromination of hydrosilanes.

The esterification of  $\text{Br}_3\text{CCOOH}$  with  $\text{EtOH}$  and concentrated  $\text{H}_2\text{SO}_4$  as a catalyst could afford  $\text{Br}_3\text{CCOOEt}$  in 69% (Equation 3.3).

The desired reagent was fully characterized by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR techniques.  $^1\text{H}$ -NMR (Figure 3.1) reveals the peak belonging to a methylene group resonating at  $\delta_{\text{H}}$  4.46 (q,  $J = 8.0$  Hz) while a methyl group appears at  $\delta_{\text{H}}$  1.40 (t,  $J = 8.0$  Hz). The  $^{13}\text{C}$ -NMR spectrum of  $\text{Br}_3\text{CCOOEt}$  (Figure 3.2) exhibits a carbonyl signal at  $\delta_{\text{C}}$  162.1, the carbon atom bearing three bromine atoms at  $\delta_{\text{C}}$  65.7 and two peaks at 29.5 and 13.7 belonging to methylene and methyl carbons, respectively.

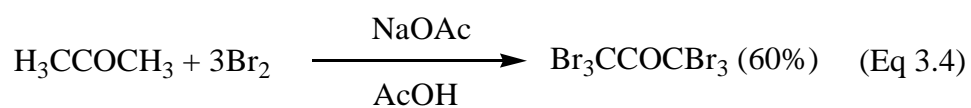


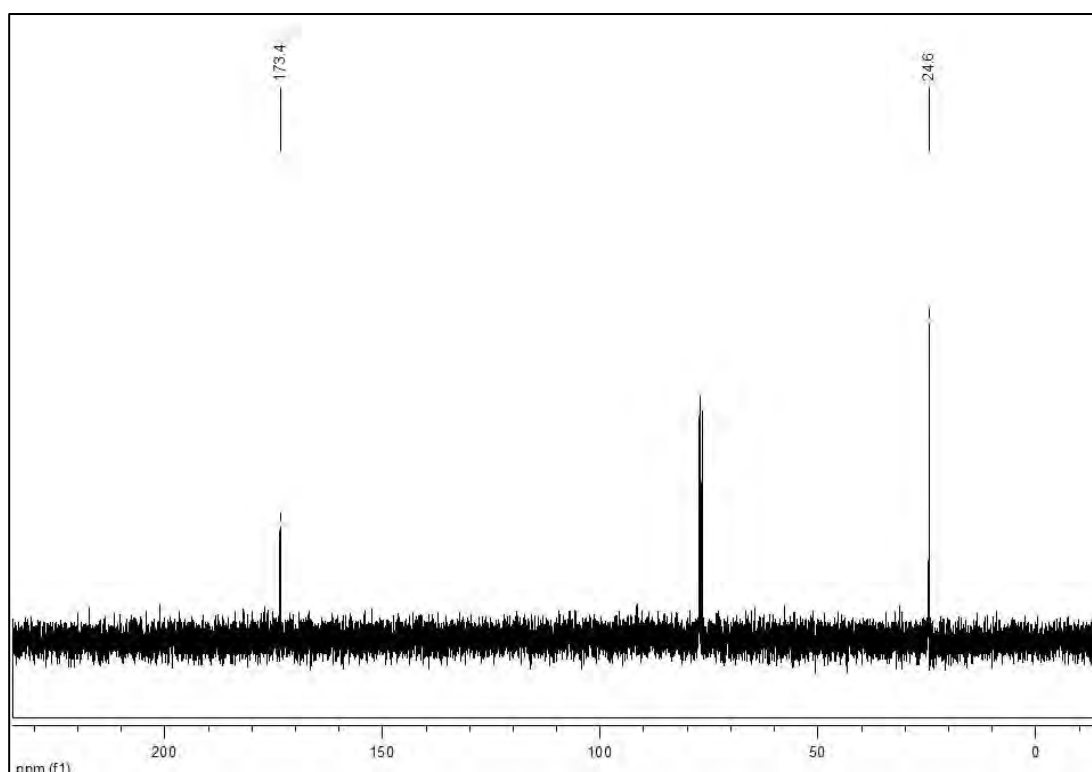
**Figure 3.1** The  $^1\text{H}$ -NMR spectrum of  $\text{Br}_3\text{CCOOEt}$



**Figure 3.2** The  $^{13}\text{C}$ -NMR spectrum of  $\text{Br}_3\text{CCOOEt}$

The reaction of acetone, bromine, sodium acetate in glacial acetic acid was used to prepare  $\text{Br}_3\text{CCOCBr}_3$  (Equation 3.4). The  $^{13}\text{C}$ -NMR spectrum of  $\text{Br}_3\text{CCOCBr}_3$  (Figure 3.3) exhibits a carbonyl carbon at  $\delta_{\text{C}}$  173.4 and the other peak of the carbon bearing bromine atoms at  $\delta_{\text{C}}$  24.6.





**Figure 3.3** The <sup>13</sup>C-NMR spectrum of Br<sub>3</sub>CCOBr<sub>3</sub>

### 3.2 Conditions Optimization Study for the Synthesis of Bromosilane Using Pd(II) Catalyst

Various parameters including type of brominating agents, ratio of brominating agents : amounts of PdCl<sub>2</sub>: halosilane, reaction time, reaction media and temperature were investigated to search for a suitable system for the preparation of bromosilanes from hydrosilanes using Pd(II) catalyst.

#### 3.2.1 The Effect of Brominating Agents

Eight commercially available brominating agents: CBr<sub>4</sub>, Br<sub>3</sub>CCOOH, Br<sub>3</sub>CCOOEt, Br<sub>2</sub>HCCOOH, Br<sub>2</sub>HCCOOEt, CHBr<sub>3</sub>, CH<sub>2</sub>=CHCH<sub>2</sub>Br and CH<sub>3</sub>CH<sub>2</sub>Br are used in this research. The other brominating agent employed, Br<sub>3</sub>CCOOEt was synthesized as described in 2.3. The results of the effect of type of brominating agents on the conversion of triisopropylsilane (TIPS-H) to triisopropylsilyl bromide (TIPS-Br) are reported in Table 3.1.



**Table 3.1** The effect of brominating agents on the conversion of TIPS-H to TIPS-Br
$$(i\text{-Pr})_3\text{SiH} + \text{brominating agent} \xrightarrow[\text{RT, 15 min}]{\substack{1\% \text{ PdCl}_2 \\ \text{THF}}} (i\text{-Pr})_3\text{SiBr}$$

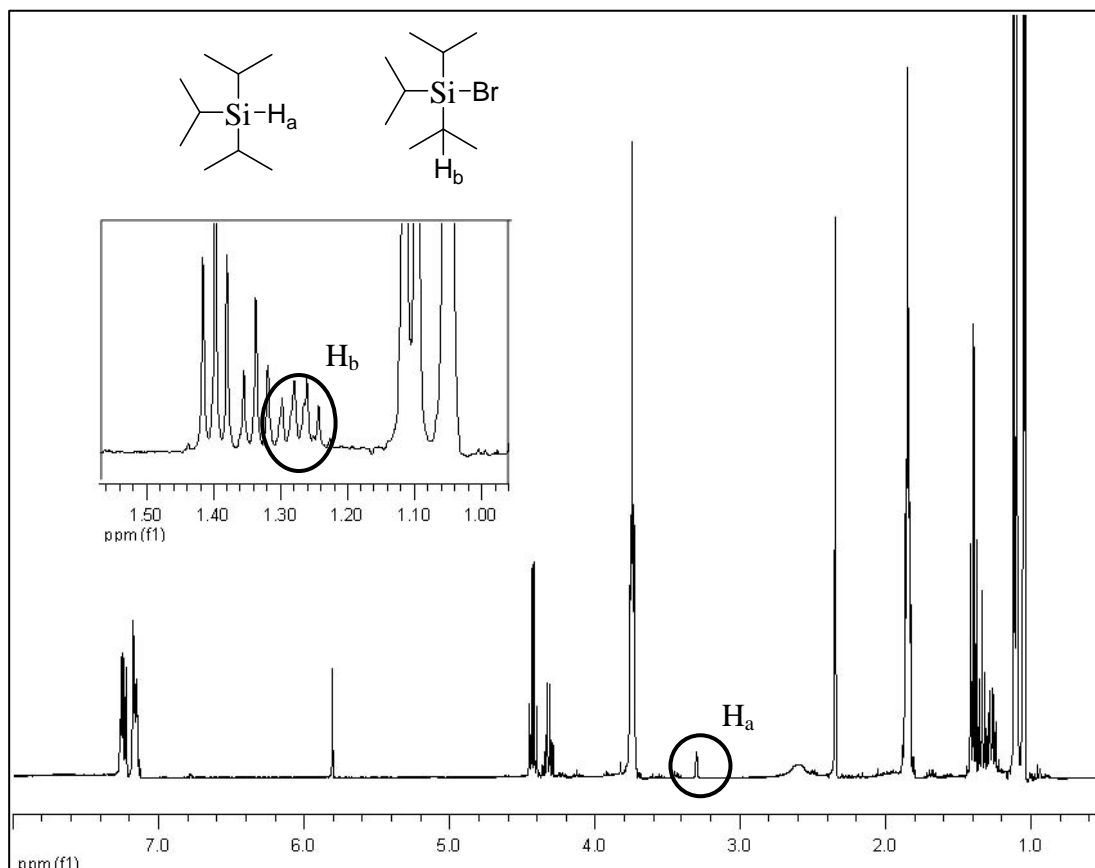
Entry	Brominating agent	Equivalent (mmol)	% Yield <sup>a</sup> TIPS-Br	% Recovery <sup>a</sup> TIPS-H	MB (%)
1	none	-	0	100	100
2	CBr <sub>4</sub>	0.75	39	53	92
3	Br <sub>3</sub> CCOOH	1.00	36	64	100
4	Br <sub>3</sub> CCOOEt	1.00	44	55	99
5		1.25	60	39	99
6		1.50	67	29	96
7	CHBr <sub>3</sub>	1.00	9	91	100
8	Br <sub>2</sub> CHCOOH	1.50	7	91	98
9	Br <sub>2</sub> CHCOOEt	1.50	6	92	98
10	CH <sub>2</sub> =CHCH <sub>2</sub> Br	3.00	5	93	98
11	CH <sub>3</sub> CH <sub>2</sub> Br	3.00	9	90	99

<sup>a</sup> determined by <sup>1</sup>H-NMR

The percentage yield of TIPS-Br was quantified by <sup>1</sup>H-NMR technique. For calculation, toluene is used as an internal standard. Following the Equation 3.5, the percentage yield of desired product (A) was determined by the comparison of the integration of the peak belonging to the desired product (A) and that of methyl group of toluene.

$$\% \text{ Yield A} = \frac{\text{Integration of A}}{\text{Integration of internal std}} \times \frac{\#H \text{ of internal std}}{\#H \text{ of A}} \times 100 \quad (\text{Eq 3.5})$$

An example of the <sup>1</sup>H-NMR spectrum of the crude reaction mixture of TIPS-H with Br<sub>3</sub>CCOOEt and toluene is presented in Figure 3.4.



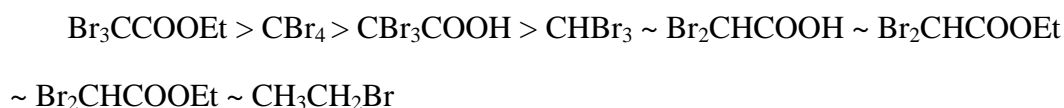
**Figure 3.4** The  $^1\text{H}$ -NMR spectrum of the crude reaction mixture of TIPS-H with  $\text{Br}_3\text{CCOOEt}$  and toluene

From Figure 3.4, %yield of product and %recovery of substrate were calculated by using the integration of peak  $\text{H}_a$  ( $\delta_{\text{H}} = 3.28$ ) and  $\text{H}_b$  ( $\delta_{\text{H}} = 1.27$ ), respectively.

Considering the effect of brominating agents on the conversion of TIPS-H to TIPS-Br in the presence of 1%  $\text{PdCl}_2$  as a catalyst for 15 min at RT, it was observed that when the reaction was carried out in the absence of brominating agent (entry 1), no desired product formed. The brominating agent bearing electron-withdrawing group such as  $\text{Br}_3\text{CCOOH}$  (entry 3) produced the desired product in 36% yield. Using  $\text{CBr}_4$  and  $\text{Br}_3\text{CCOOEt}$ , TIPS-Br was also attained in moderate yield (entries 2 and 4). However, due to the toxicity of  $\text{CBr}_4$  and the fact that  $\text{Br}_3\text{CCOOH}$  being quite difficult to be homogeneous in this reaction mixture,  $\text{Br}_3\text{CCOOEt}$  was found to be the best choice for the preparation of TIPS-Br. In addition, the yield of TIPS-Br could be

increased to 60 and 67% when the amount of Br<sub>3</sub>CCOOEt was increased to 1.25 and 1.50 mmol, respectively (entries 5-6). Other brominating agents selected including CHBr<sub>3</sub>, Br<sub>2</sub>CHCOOH, Br<sub>2</sub>CHCOOEt produced the desired product only in trace amount.

The order of the efficiency of brominating agents explored could be arranged as:

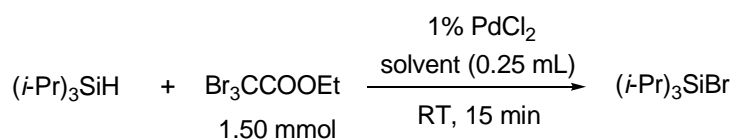


From the above study, Br<sub>3</sub>CCOOEt, CBr<sub>4</sub> and Br<sub>3</sub>CCOOH are uncovered to be efficient brominating agents. Br<sub>3</sub>CCOOEt is the most appropriate brominating agent for bromination of TIPS-H with the main reason as less toxicity, high reactivity and as a new brominating agent which has never been reported.

### 3.2.2 The Effect of Solvent

The reaction media was required to rescue the reaction become homogeneous with Br<sub>3</sub>CCOOEt. Different reaction media were investigated to observe the effect of solvent and the results are accumulated in Table 3.2.

**Table 3.2** The effect of solvent on the conversion of TIPS-H to TIPS-Br



Entry	Solvent	% Yield <sup>a</sup> TIPS-Br	% Recovery <sup>a</sup> TIPS-H	MB (%)
1	none	7	95	102
2	THF	67	29	96
3	1,4-dioxane	36	65	101
4	CH <sub>3</sub> CN	71	27	98
5 <sup>b</sup>	CH <sub>2</sub> Cl <sub>2</sub>	10	88	98

<sup>a</sup> determined by <sup>1</sup>H-NMR

<sup>b</sup> not completely soluble

The yield of TIPS-Br was detected in trace amount when the reaction was carried out without any extra solvent (entry 1). 1,4-Dioxane is less polar solvent while  $\text{CH}_2\text{Cl}_2$  is non-polar solvent. These gave the desired product in low yield. THF and  $\text{CH}_3\text{CN}$  provided good yield of TIPS-Br (entries 2 and 4).  $\text{CH}_3\text{CN}$  is more toxic than THF [38]. Thus, THF is the proper solvent for the preparation of TIPS-Br.

### 3.2.3 The Effect of Amount and Type of Catalyst

No reaction occurred when Pd catalyst was not present. Thus, the amount and type of catalyst was investigated to explore for optimum conditions of the synthesis of bromosilane. The results are presented in Table 3.3.

**Table 3.3** The effect of the amount and type of catalyst to convert TIPS-H to TIPS-Br

$$\begin{array}{c}
 (i\text{-Pr})_3\text{Si-H} + \text{Br}_3\text{CCOOEt} \xrightarrow[\text{RT, 15 min}]{\text{catalyst, THF}} (i\text{-Pr})_3\text{Si-Br} \\
 \text{1.50 mmol}
 \end{array}$$

Entry	Catalyst (%mol)	%Yield <sup>a</sup> TIPS-Br	% Recovery <sup>a</sup> TIPS-H	MB (%)
1	none	0	100	100
2	1.0% PdCl <sub>2</sub>	67	29	96
3	1.0% PdBr <sub>2</sub>	42	60	102
4	1.0% Pd(0) on charcoal	70	28	98
5	0.5% PdCl <sub>2</sub>	50	49	99

<sup>a</sup> determined by <sup>1</sup>H-NMR

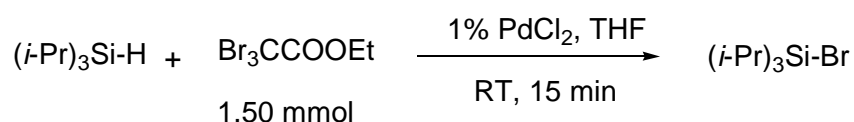
As the results presented in Table 3.3, it was observed that the reaction could not occur in the absence of Pd catalyst (entry 1). Comparing the efficiency of palladium catalyst: PdCl<sub>2</sub>, PdBr<sub>2</sub> and Pd(0) on charcoal (entries 2- 4), it was found that Pd(0) on charcoal could assist the bromination of TIPS-H with Br<sub>3</sub>CCOOEt rapidly. Nonetheless, a larger amount of the catalyst Pd(0) on charcoal (10 mg) than PdCl<sub>2</sub> (1.8 mg) was required. Thus, PdCl<sub>2</sub> was selected as a catalyst for conversion of TIPS-H to TIPS-Br. In addition, the amount of catalyst was explored. Using 1.0% PdCl<sub>2</sub>, TIPS-Br was achieved in 67% yield. Decreasing the amount of PdCl<sub>2</sub> to 0.5%

mol rendered the amount of the target product to 50%. Thus, 1.0% PdCl<sub>2</sub> is the proper catalyst for preparation of TIPS-Br.

### 3.2.4 Reaction Conditions Optimization

The standard condition was proceeded by using TIPS-H with Br<sub>3</sub>CCOOEt in THF at RT; however, the reaction could not reach the complete conversion. Therefore, the optimization of reaction conditions was investigated to find out more proper conditions. The results are shown in Table 3.4.

**Table 3.4** The effect of reaction conditions on the conversion of TIPS-H to TIPS-Br



Entry	Reaction condition	%Yield <sup>a</sup> TIPS-Br	% Recovery <sup>a</sup> TIPS-H	MB (%)
1	Room temp (~ 25°C)	67	29	96
2	Reflux temp (~ 63°C)	101	0	101
3	Sonication	80	21	101

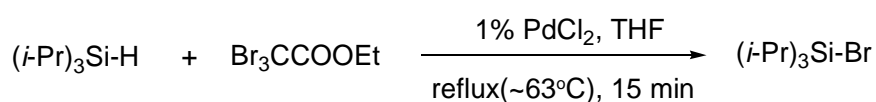
<sup>a</sup> determined by <sup>1</sup>H-NMR

Table 3.4 reveals that the standard reaction carried out at RT provided the desired product only 67%. The quantitative yield of TIPS-Br could be achieved when the reaction was performed at refluxing THF (~ 63°C). With the aids of sonication, the reaction could possibly be performed to attain TIPS-Br in 80% yield. This observation is surely still called for further investigation since this process could be simply carried out without using high energy. The optimized conditions for the synthesis of TIPS-Br were the reaction of TIPS-H with Br<sub>3</sub>CCOOEt in THF at reflux temperature for 15 min.

### 3.2.5 The Effect of the Amount of Br<sub>3</sub>CCOOEt

For optimizing reaction conditions, the effect of the amount of Br<sub>3</sub>CCOOEt was explored with the aim to obtain the most appropriate amount of Br<sub>3</sub>CCOOEt for the synthesis of TIPS-Br. The results are displayed in Table 3.5.

**Table 3.5** The effect of the amount of Br<sub>3</sub>CCOOEt on the conversion of TIPS-H to TIPS-Br



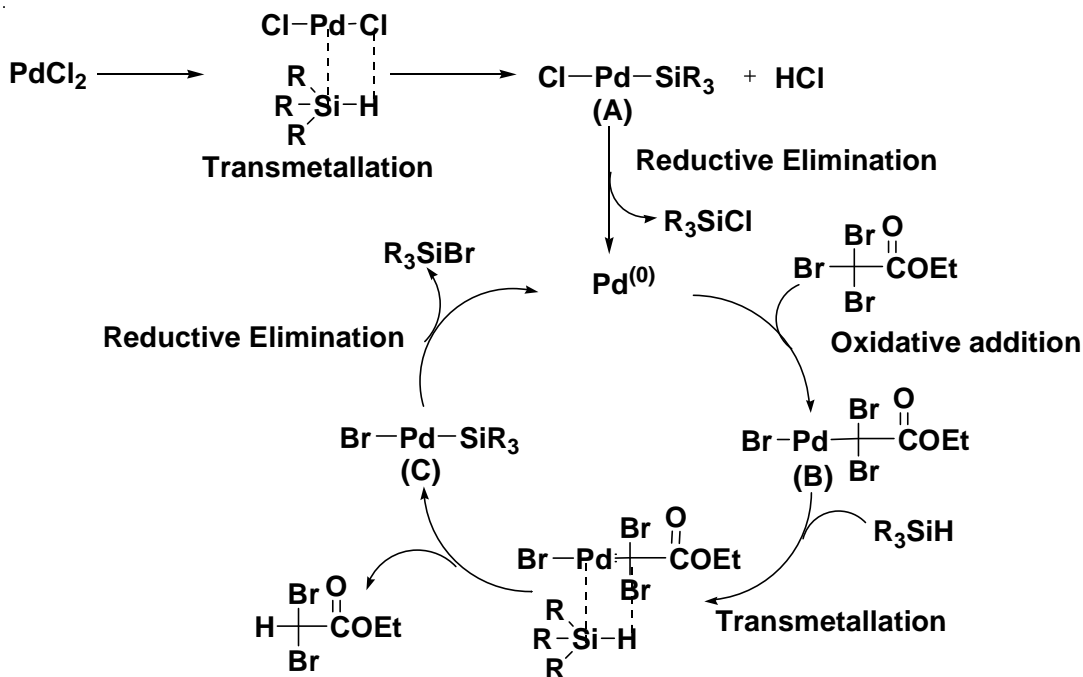
Entry	Br <sub>3</sub> CCOOEt (mmol)	%Yield <sup>a</sup> TIPS-Br	% Recovery <sup>a</sup> TIPS-H	MB (%)
1	1.00	80	23	103
2	1.25	100	0	100
3	1.50	100	0	100

<sup>a</sup> determined by <sup>1</sup>H-NMR

Table 3.5 exhibits the effect of the amount of Br<sub>3</sub>CCOOEt. The use of either 1.50 or 1.25 mmol of the reagent still provided the desired product quantitatively. Nevertheless, using 1.00 mmol of Br<sub>3</sub>CCOOEt, only 80% of TIPS-Br was achieved. Thus 1.25 mmol of Br<sub>3</sub>CCOOEt was found to be appropriate for the production of TIPS-Br in quantitative yield.

### 3.2.6 Proposed Mechanistic Pathway for the Synthesis of Bromosilane Using Pd(II) Catalyst and Br<sub>3</sub>CCOOEt

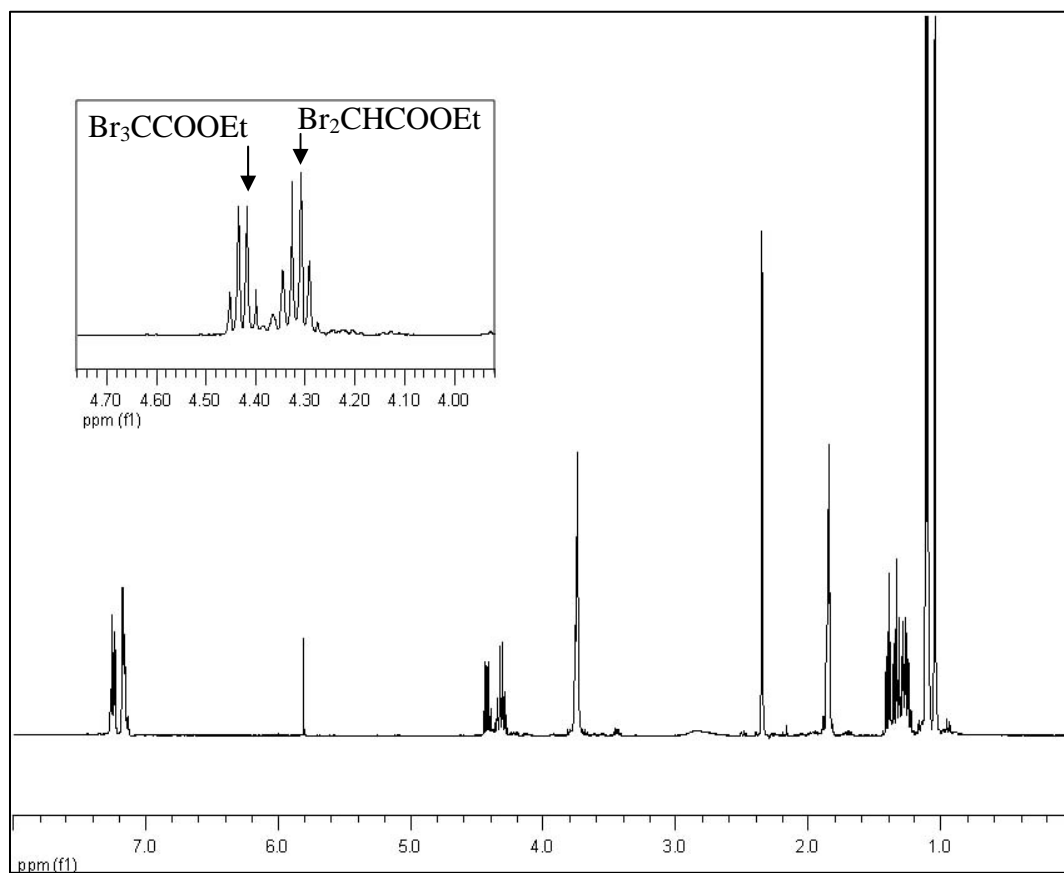
The proposed mechanistic pathway was believed to take place similar to that reported by Ferreri [39] as outlined in Scheme 3.1.



**Scheme 3.1** The proposed mechanistic pathway towards the conversion of hydrosilanes to bromosilanes using  $\text{Br}_3\text{CCOOEt}$  and  $\text{Pd(II)}$  catalyst

$\text{PdCl}_2$  and hydrosilane are reacted *via* transmetallation generating  $\text{HCl}$  and  $\text{Pd(II)}$  complex (A) and continuous reductive elimination to give chlorosilane and  $\text{Pd(0)}$  as active species which is the first species in the catalytic cycle. In the first cycle,  $\text{Br}_3\text{CCOOEt}$  undergoes oxidative addition with  $\text{Pd(0)}$  to produce the corresponding  $\text{Pd(II)}$  complex (B). Then, it proceeds with hydrosilane by transmetallation to generate  $\text{Br}_2\text{CHCOOEt}$  as by-product and  $\text{Pd(II)}$  complex (C). Ultimately, the main product is bromosilane.  $\text{Pd(0)}$  is back to the catalytic cycle.

To prove this assumption, the crude mixture derived from the reaction of TIPS-H with  $\text{Br}_3\text{CCOOEt}$  was examined by  $^1\text{H-NMR}$ . Figure 3.5 clearly reveals the detection of  $\text{Br}_2\text{CHCOOEt}$  as by-product at  $\delta_{\text{H}}$  4.32 (2H, q,  $\text{Br}_2\text{CHCOOCH}_2\text{CH}_3$ ,  $J=7.2$ ) and TIPS-Br as a desired product at  $\delta_{\text{H}}$  1.27 (3H, m,  $\text{Si}(\text{CH}(\text{CH}_3)_2)_3$ ).



**Figure 3.5** The  $^1\text{H}$ -NMR spectrum of the reaction mixture using  $\text{Br}_3\text{CCOOEt}$  for 15 min at refluxing THF

## Part II Synthesis of Bromosilane Using $\text{Br}_3\text{CCOCBr}_3$ and UV Irridiation

An alternative approach has been successfully developed by utilizing  $\text{Br}_3\text{CCOCBr}_3$  with the aids of UV irradiation for the synthesis of bromosilanes. Under this circumstance, there is no need to use Pd(II) catalyst. It should be mentioned at this point that this methodology has not been reported in chemical literature before. Therefore, this is a new protocol to prepare bromosilane from hydrosilane.



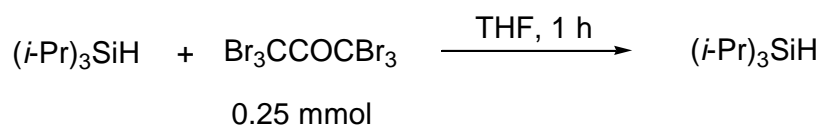
### 3.3 Conditions Optimization for the Synthesis Bromosilane Using UV Irradiation

Several parameters such as reaction condition, solvent, reaction time, ratio of silane: brominating agent were examined to search for an appropriate system for the synthesis of bromosilane.

#### 3.3.1 Reaction Conditions

Various conditions for the synthesis of bromosilane were studied using  $\text{Br}_3\text{CCOCBr}_3$  as a brominating agent. The outcome is collected as presented in Table 3.6.

**Table 3.6** The effect of the reaction condition on the conversion of TIPS-H to TIPS-Br



Entry	Condition	% Yield <sup>a</sup> TIPS-Br	% Recovery <sup>a</sup> TIPS-H	MB (%)
1	RT	49	56	105
2	reflux	66	35	101
3 <sup>b</sup>	UV	89	10	99
4	sonication	80	15	95

<sup>a</sup> determined by <sup>1</sup>H-NMR

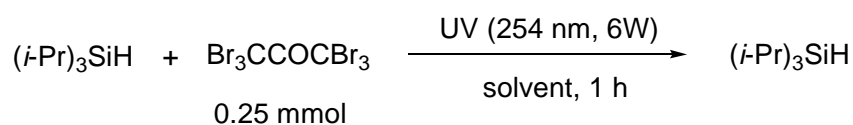
<sup>b</sup> 254 nm, 6W

According to the results displayed in Table 3.6, only 49% yield of the desired product was achieved within 1 h at RT. When UV light (254 nm, 6 W) was applied to the reaction mixture, 89% yield of TIPS-Br was obviously achieved. Two reaction conditions including that performing at refluxing THF and that with sonication gave TIPS-Br in better yield (entries 2-3); however, slightly lower than using UV. This implies that the mechanistic pathway for the bromination aided by UV irradiation may operate through a different pathway, possibly a radical process.

### 3.3.2 Effect of Solvent

Since  $\text{Br}_3\text{CCOCBr}_3$  is a solid reagent, the suitable solvent that can solubilize the reagent and make the reaction become homogeneous is essential. Thus, various solvents were explored to find out appropriate solvents for the preparation of TIPS-Br. The results are collected in Table 3.7.

**Table 3.7** The effect of solvent on the conversion of TIPS-H to TIPS-Br



Entry	solvent (0.25 mL)	%Yield <sup>a</sup> TIPS-Br	% Recovery <sup>a</sup> TIPS-H	MB (%)
1	None	30	70	100
2	THF	96	5	101
3	1,4-dioxane	80	17	97
4 <sup>b</sup>	CH <sub>3</sub> CN	94	7	101
5 <sup>c</sup>	CH <sub>2</sub> Cl <sub>2</sub>	15	83	98

<sup>a</sup> determined by <sup>1</sup>H-NMR

<sup>b</sup> The reaction took a long time to be completely soluble.

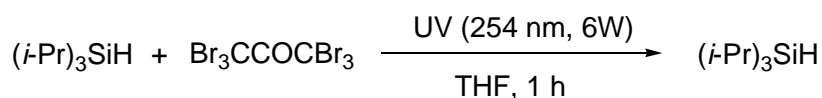
<sup>c</sup> not completely soluble

Based on the data shown in Table 3.7, no reaction occurred when CH<sub>2</sub>Cl<sub>2</sub> was used as a reaction medium (entry 5). Without any extra solvent, the reaction produced the desired product in only 30% yield (entry 1), whereas using THF gave the target product in high yield (entry 2). The same trend was observed for CH<sub>3</sub>CN and 1,4-dioxane (entries 3-4).

### 3.3.3 The Effect of the Amount of $\text{Br}_3\text{CCOCBr}_3$

The amount of  $\text{Br}_3\text{CCOCBr}_3$  may affect the production of TIPS-Br. The results are accumulated in Table 3.8.

**Table 3.8** The effect of the amount of Br<sub>3</sub>CCOBr<sub>3</sub> on the conversion of TIPS-H to TIPS-Br



Entry	Br <sub>3</sub> CCOBr <sub>3</sub> (mmol)	%Yield <sup>a</sup>		MB (%)
		TIPS-Br	TIPS-H	
1	0.25	96	5	101
2	0.30	100	0	100
3	0.35	100	0	100

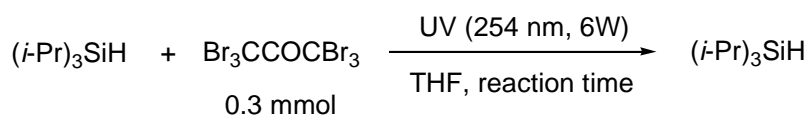
<sup>a</sup> determined by <sup>1</sup>H-NMR

It was clearly revealed that when the amount of Br<sub>3</sub>CCOBr<sub>3</sub> was increased from 0.25 to 0.30 mmol (entries 1-2), TIPS-Br was obtained in quantitative yield. The quantitative yield of the desired product could be obtained utilizing Br<sub>3</sub>CCOBr<sub>3</sub> equal or more than 0.30 mmol. Thus, using 0.30 mmol Br<sub>3</sub>CCOBr<sub>3</sub> was selected for further examination.

### 3.3.4 Effect of Reaction Time

From the optimal conditions as previously described, TIPS-H could be transformed to TIPS-Br in quantitative yield. Reaction time is another crucial factor to examine in order to reach the appropriate reaction time for the preparation of TIPS-Br. The outcome is collected in Table 3.9.

**Table 3.9** The effect of reaction time on the conversion of TIPS-H to TIPS-Br



Entry	Reaction time (min)	%Yield <sup>a</sup>		MB (%)
		TIPS-Br	TIPS-H	
1	30	94	8	102
2	45	100	0	100
3	60	100	0	100

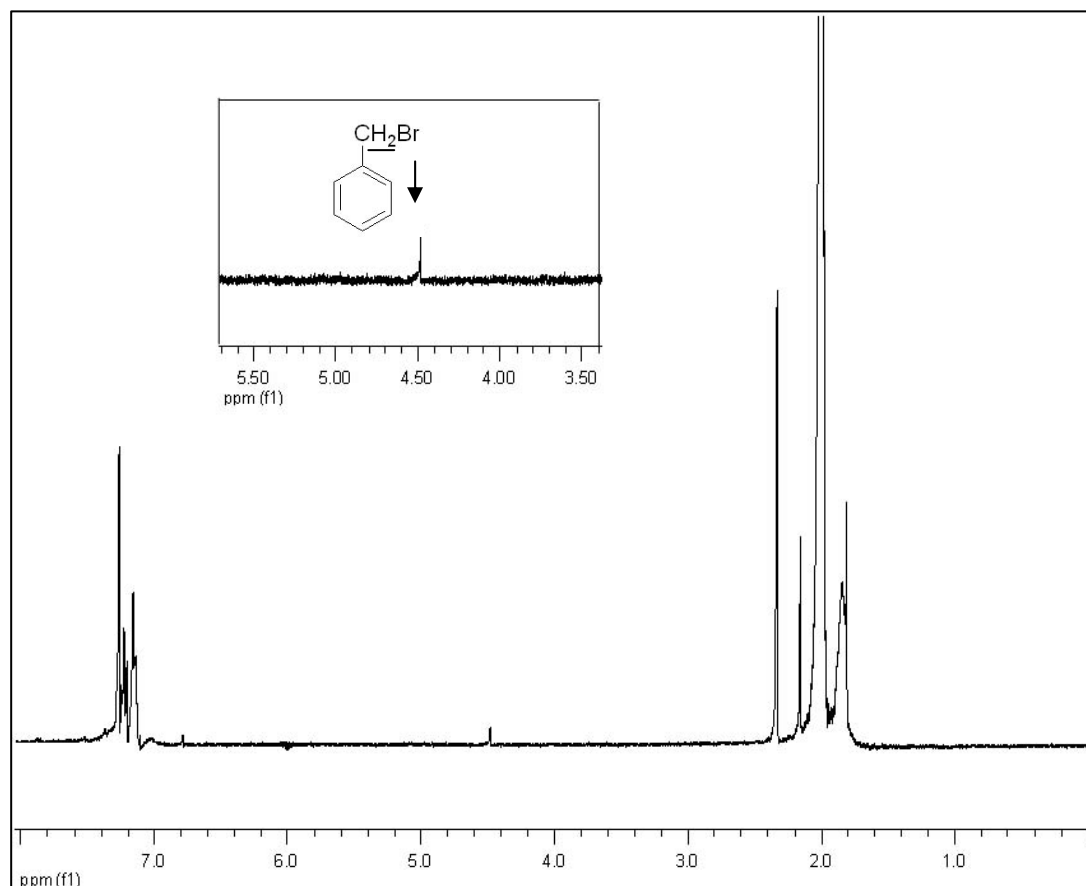
<sup>a</sup> determined by <sup>1</sup>H-NMR

Table 3.9 shows the effect of reaction time for the generation of TIPS-Br. When the reaction time from 60 was decreased to 45 min, the target product was still achieved in quantitative yield. 94% yield of TIPS-Br was obtained when the reaction time was reduced to 30 min. Therefore, the reaction time could be minimized to 45 min while the quantitative yield of the desired product was still remained.

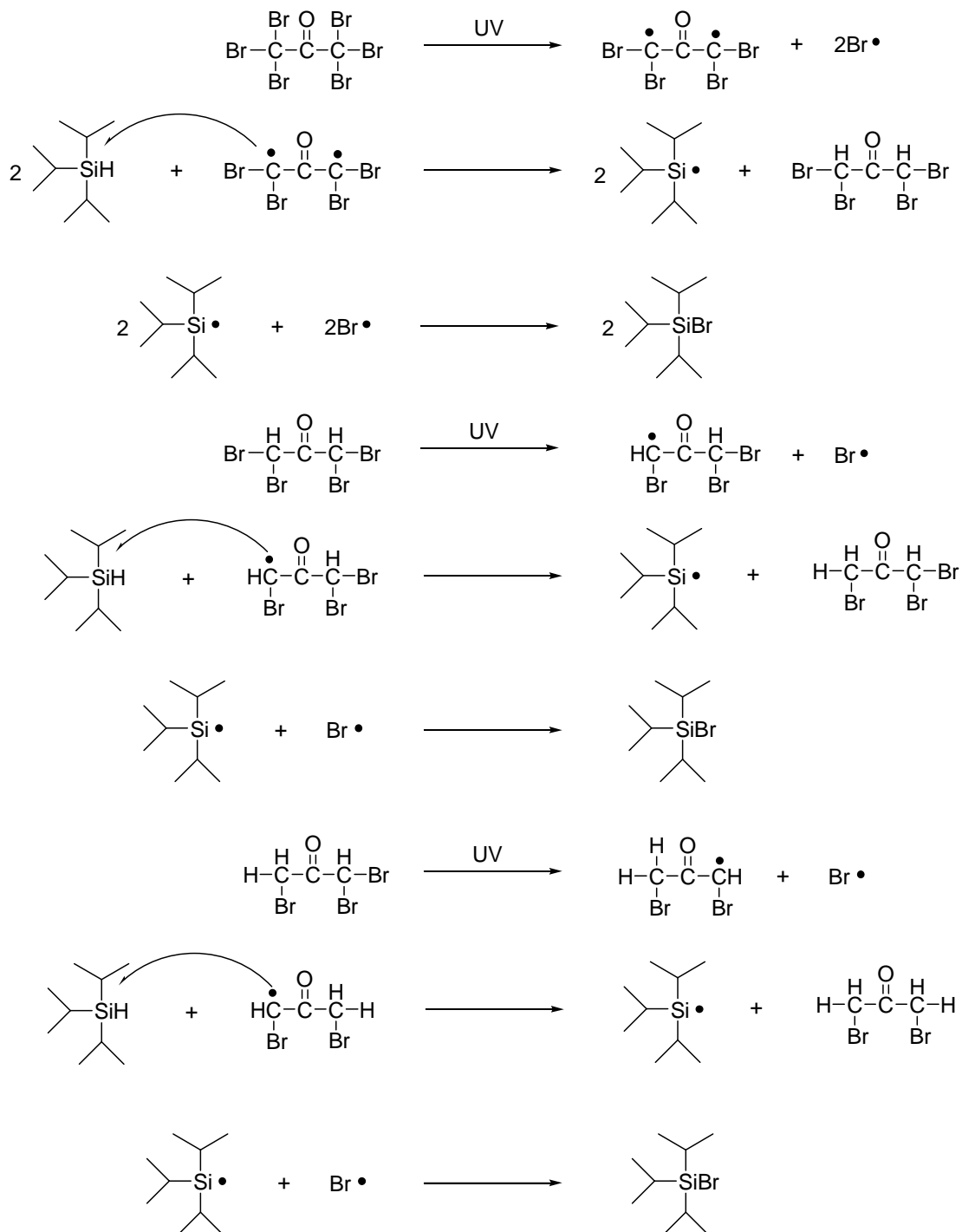
### 3.3.5 Proposed Mechanism for the Synthesis of Bromosilane Using $\text{Br}_3\text{CCOBr}_3$ and UV Irridiation

The mechanistic pathway for the synthesis of bromosilane using  $\text{Br}_3\text{CCOBr}_3$  and UV irradiation has never been reported. It was believed that the main reaction mechanism should take place *via* a radical process. To prove this hypothesis, the reaction was tested by trapping the reaction with 2,2-diphenyl-1-picrylhydrazyl (DPPH), a well-know radical scavenger.  $\text{Br}_3\text{CCOBr}_3$  was first dissolved in THF, followed by dropping of DPPH solution. The color of the solution was changed from violet to brown. Performing a blank test, TIPS-H was used instead of  $\text{Br}_3\text{CCOBr}_3$ , the purple color of DPPH solution was not decolorized. Thus, the mechanism operated should involve a radical pathway in which C-Br bond of  $\text{Br}_3\text{CCOBr}_3$  is broken.

Another set of experiment was conducted by replacing *N*-bromosuccinimide (NBS) with  $\text{Br}_3\text{CCOBr}_3$  in the reaction with toluene. NBS has been known to generate a bromine radical and could convert toluene to 1-(bromomethyl)benzene under UV irradiation in  $\text{CH}_3\text{CN}$  [39]. Figure 3.6 shows the  $^1\text{H-NMR}$  spectrum of the reaction mixture which was attained from the reaction of  $\text{Br}_3\text{CCOBr}_3$  and toluene for 4 h under UV irradiation at 254 nm, 6 W. 1-(Bromomethyl)benzene exhibits the peak belonging to a methylene group resonating at  $\delta_{\text{H}}$  4.50 (2H, s,  $\text{Ph-CH}_2\text{Br}$ ). The result from this experiment clearly demonstrated that  $\text{Br}_3\text{CCOBr}_3$  should behave the same as NBS *via* a radical pathway. Thus, the proposed mechanism for the synthesis of bromosilane using  $\text{Br}_3\text{CCOBr}_3$  under UV irradiation is believed to occur through a radical process by C-Br bond of  $\text{Br}_3\text{CCOBr}_3$  is broken generating a bromine radical. The proposed mechanism is described below.

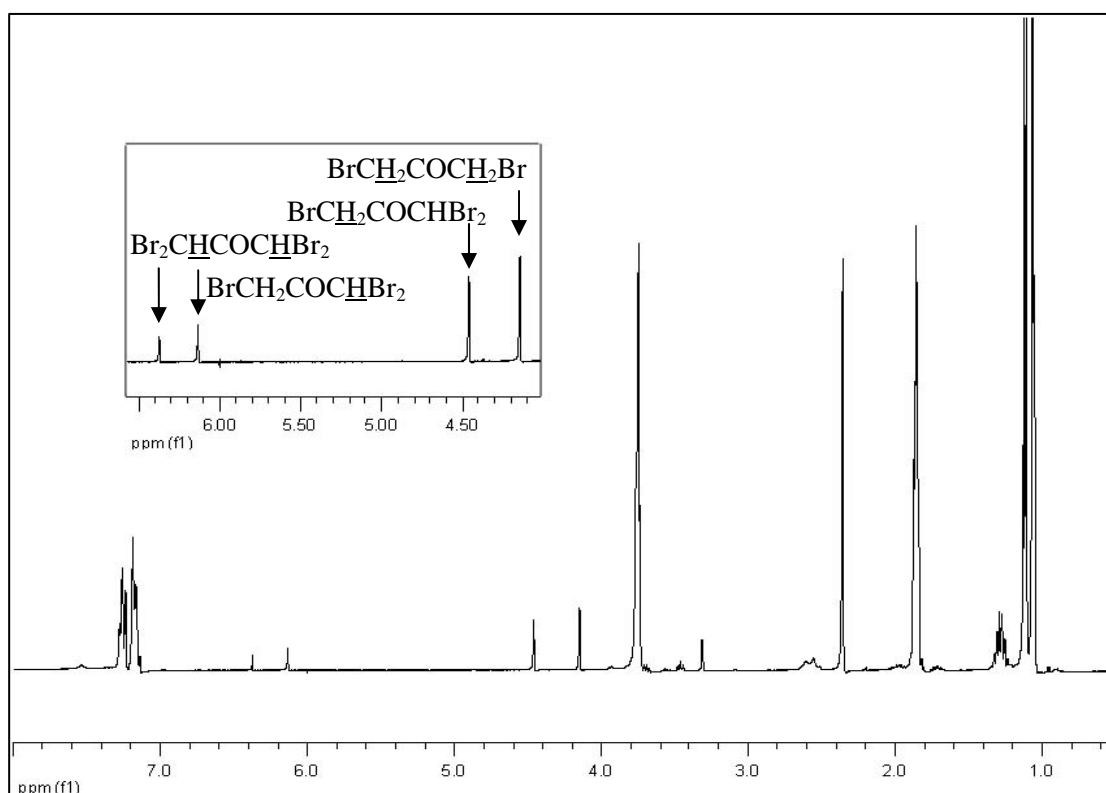


**Figure 3.6** The  $^1\text{H-NMR}$  spectrum of the reaction mixture using  $\text{Br}_3\text{CCOCBr}_3$  with toluene for 4 h under UV irradiation at 254 nm, 6 W



**Scheme 3.2** The proposed mechanistic pathway towards the conversion of hydrosilanes to bromosilanes using  $\text{Br}_3\text{CCOCBr}_3$  under UV irradiation

With the ratio of TIPSH :  $\text{Br}_3\text{CCOCBr}_3$  (1:0.25), TIPS-Br was produced in almost quantitative yield. This implies that  $\text{Br}_3\text{CCOCBr}_3$  could release more than one bromine radical. From  $^1\text{H-NMR}$  spectrum (Figure 3.7), the signals belonging to  $\text{Br}_2\text{CHCOCHBr}_2$  at  $\delta_{\text{H}}$  6.38 (1H, s),  $\text{BrCH}_2\text{COCHBr}_2$  at  $\delta_{\text{H}}$  4.48 (2H, s),  $\text{BrCH}_2\text{COCHBr}_2$  at  $\delta_{\text{H}}$  6.23 (1H, s) and  $\text{BrCH}_2\text{COCH}_2\text{Br}$  at  $\delta_{\text{H}}$  4.13 (2H, s) could be clearly detected. C-Br bond of  $\text{Br}_3\text{CCOCBr}_3$  was believed to homolytically cleave by UV irradiation giving a bromine radical and produced  $\text{Br}_2\text{CHCOCHBr}_2$ . A bromine radical abstracted Si-H bond of hydrosilane to generate a silicon radical which then reacted with another bromine radical to furnish bromosilane. With longer reaction time, a bromine radical from  $\text{Br}_2\text{CHCOCHBr}_2$  could be released and converted to  $\text{BrCH}_2\text{COCHBr}_2$ . The generated bromine radical was continuously proceeded with hydrosilane to yield bromosilane. With the same fashion, the C-Br bond of  $\text{BrCH}_2\text{COCHBr}_2$  could be cleaved to generate  $\text{Br}^\cdot$  and finally the signal of  $\text{BrCH}_2\text{COCH}_2\text{Br}$  was detected.



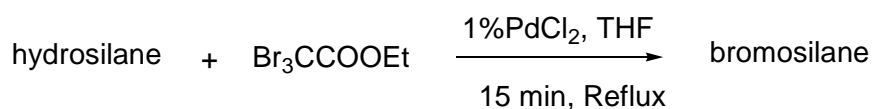
**Figure 3.7** The  $^1\text{H-NMR}$  spectrum of the reaction mixture using  $\text{Br}_3\text{CCOCBr}_3$  (0.25 mmol) for 1 h under UV irradiation at 254 nm, 6 W

### 3.4 The Synthesis of Other Bromosilanes

#### 3.4.1 The Synthesis of Bromosilanes from Hydrosilane Using Pd(II) Catalyst and Br<sub>3</sub>CCOOEt

The condition for the synthesis of bromosilane using Pd(II) catalyst and Br<sub>3</sub>CCOOEt was optimized as previously addressed. Employing this optimized conditions, the synthesis of other bromosilanes from diverse hydrosilanes such as triethylsilane (Et<sub>3</sub>SiH), triphenylsilane (Ph<sub>3</sub>SiH), *tert*-butyldimethylsilane (*tert*-BuMe<sub>2</sub>SiH), chlorodiphenylsilane (Ph<sub>2</sub>ClSiH) and phenyldimethylsilane (PhMe<sub>2</sub>SiH) was explored. The results are collected in Table 3.10.

**Table 3.10** The conversion of hydrosilanes to bromosilanes using Pd(II) catalyst and Br<sub>3</sub>CCOOEt



Entry	Hydrosilane	Equivalent (mmol)	% Yield <sup>a</sup> Si-Br	% Recovery <sup>a</sup> Si-H	MB (%)
1	Ph <sub>3</sub> SiH	1.25	65	36	101
2		1.50	75	24	99
3		1.75	90	9	99
4 <sup>b</sup>		1.75	91	7	98
5	Ph <sub>2</sub> ClSiH	1.25	82	21	103
6		1.50	82	17	99
7 <sup>b</sup>		1.50	75	25	100
8	PhMe <sub>2</sub> SiH	1.25	51	47	98
9		1.50	46	53	99
10 <sup>b</sup>		1.50	45	52	97
11		1.25	60	37	97
12	Et <sub>3</sub> SiH	1.50	70	28	98
13		1.75	65	44	94
14 <sup>b</sup>		1.75	64	42	97



**Table 3.10** (continued)

Entry	Hydrosilane	Equivalent (mmol)	% Yield <sup>a</sup> Si-Br	% Recovery <sup>a</sup> Si-H	MB (%)
15		1.25	61	35	96
16	<i>tert</i> -BuMe <sub>2</sub> SiH	1.50	53	45	98
17 <sup>b</sup>		1.50	50	49	99

<sup>a</sup> determined by <sup>1</sup>H-NMR

<sup>b</sup> The reaction was carried out for 30 min.

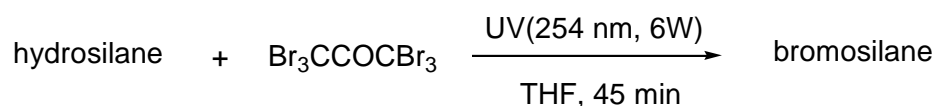
Under optimal conditions, with Br<sub>3</sub>CCOOEt 1.25 mmol and 1% PdCl<sub>2</sub> in refluxing THF (~63°C), 65% of the desired bromosilane was obtained (entry 1). When the amount of Br<sub>3</sub>CCOOEt was increased to 1.75 mmol (entry 3), 90% yield of Ph<sub>3</sub>SiBr was achieved. Even though the reaction time was prolonged to 30 min, the comparable yield of the corresponding bromosilane (91%, entry 4) was attained. Thus, the suitable condition for the synthesis of Ph<sub>3</sub>SiBr is using 1.75 mmol of Br<sub>3</sub>CCOOEt for 15 min.

The bromination of Ph<sub>2</sub>ClSiH and PhMe<sub>2</sub>SiH could also be accomplished to gain 82% Ph<sub>2</sub>ClSiBr and 51% PhMe<sub>2</sub>SiBr under optimized conditions (entries 5 and 8). The extra amount of Br<sub>3</sub>CCOOEt and reaction time could not lift up the yield of the target bromosilanes (entries 6-7, 9-10). In the case of Et<sub>3</sub>SiH, the standard condition was carried out to accomplish 60% Et<sub>3</sub>SiBr (entry 11). 70% yield of Et<sub>3</sub>SiBr was obtained using 1.50 mmol Br<sub>3</sub>CCOOEt (entry 12). Increasing the amount of Br<sub>3</sub>CCOOEt to 1.75 mmol, the target product was decreased to 65% yield (entry 13). When the reaction was conducted for 30 min, the constant yield of the desired product was determined (entry 14). For *tert*-BuMe<sub>2</sub>SiH, the best condition for the preparation of *tert*-BuMe<sub>2</sub>SiBr was the same as that performed at standard condition (entry 15).

### 3.4.2 The Synthesis of Bromosilanes from Hydrosilane Using Br<sub>3</sub>CCOCBr<sub>3</sub> and UV Irradiation

Another approach for the synthesis of bromosilane using Br<sub>3</sub>CCOCBr<sub>3</sub> coupled with UV irradiation was applied for other hydrosilanes. The results are displayed in Table 3.11.

**Table 3.11** The conversion of hydrosilanes to bromosilanes using Br<sub>3</sub>CCOCBr<sub>3</sub> and UV irradiation



Entry	Hydrosilane	Equivalent (mmol)	%Yield <sup>a</sup> Si-Br	% Recovery <sup>a</sup> Si-H	MB (%)
1	Ph <sub>3</sub> SiH	0.3	101	0	101
2	Ph <sub>2</sub> ClSiH	0.3	79	18	97
3		0.6	75	25	100
4		0.3	45	56	101
5	PhMe <sub>2</sub> SiH	0.6	43	55	98
6 <sup>b</sup>		0.6	42	58	100
7 <sup>b</sup>		0.9	46	50	96
8	Et <sub>3</sub> SiH	0.3	64	33	97
9 <sup>b</sup>		0.6	72	26	98
10	<i>tert</i> -BuMe <sub>2</sub> SiH	0.3	50	51	101
11		0.6	67	30	97
12 <sup>b</sup>		0.6	57	42	99

<sup>a</sup> determined by <sup>1</sup>H-NMR

<sup>b</sup> The reaction was carried out for 1.30 h.

Ph<sub>3</sub>SiH could be transformed to Ph<sub>3</sub>SiBr in quantitative yield under this optimal condition (entry 1). For the bromination of Ph<sub>2</sub>ClSiH, PhMe<sub>2</sub>SiH, Et<sub>3</sub>SiH and *tert*-BuMe<sub>2</sub>SiH, this optimized condition gave moderate yield of the desired products (entries 2, 4, 9, 11).

Both methodologies developed: the systems consisted of  $\text{Br}_3\text{CCOOEt}$  and  $\text{Pd(II)}$  catalyst, and that comprised of  $\text{Br}_3\text{CCOCBr}_3$  and UV irradiation have been successfully exploited for the preparation of bromosilanes from hydrosilanes. TIPS-Br could be achieved in quantitative yield. The benefit of these methods could be manifestly noticed from short reaction time compared with other previous methods reported [5]. The mechanism of the reaction using  $\text{Br}_3\text{CCOOEt}$  and  $\text{Pd(II)}$  catalyst is believed to differ from that employing  $\text{Br}_3\text{CCOCBr}_3$  and UV irradiation. The latter procedure has a certain advantage in some cases. For example, the quantitative yield of  $\text{Ph}_3\text{SiBr}$  could be accomplished using  $\text{Br}_3\text{CCOCBr}_3$  and UV irradiation while the other method using  $\text{Br}_3\text{CCOOEt}$  and  $\text{Pd(II)}$  catalyst yielding the target product only 90% yield. This is probably due to the reaction of the former method occurred through a radical process.

### **3.5 Application of the Developed Methodologies for the Synthesis of Silyl Ethers and Silyl Esters**

From the success of developing the new methodology for the preparation of TIPS-Br from TIPS-H, this optimized condition was further applied for the one-pot conversion of alcohol and carboxylic acid into silyl ether and silyl ester, respectively.

#### **3.5.1 The One-Pot Synthesis of Silyl Ethers**

Utilizing the developed methodology for the synthesis of bromosilane as previously described, two methods including using  $\text{Br}_3\text{CCOOEt}$  and  $\text{Pd(II)}$  catalyst, using  $\text{Br}_3\text{CCOCBr}_3$  and UV irradiation were performed (Step I).

Method I using  $\text{Br}_3\text{CCOOEt}$  and  $\text{Pd(II)}$  catalyst:

$\text{Br}_3\text{CCOOEt}$  was mixed with TIPS-H in the presence of a catalytic amount of  $\text{PdCl}_2$  in refluxing THF for 15 min.

Method II using  $\text{Br}_3\text{CCOCBr}_3$  and UV irradiation:

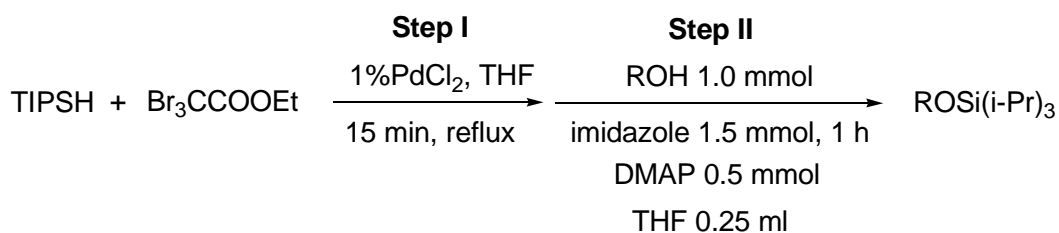
$\text{Br}_3\text{CCOCBr}_3$  was combined with TIPS-H in THF at UV light (254 nm, 6 W) for 45 min.

Both methods were applied for the synthesis of silyl ethers. The generation of bromosilane could be accomplished in step 1 which continuously adding alcohols in step II.

Step II: Alcohol 1 mmol, DMAP 0.5 mmol and imidazole 1.5 mmol were added to the mixture in step I.

Purification of the crude mixture could be performed by column chromatograph using hexane as an eluent. The effects of the optimized conditions including type of alcohols, reaction temperature and amount of TIPS-H are collected in Table 3.12 for the protocol using  $\text{Br}_3\text{CCOOEt}$  and Pd(II) catalyst and Table 3.13 for that using  $\text{Br}_3\text{CCOCBr}_3$  and UV irradiation.

**Table 3.12** The one-pot synthesis of silyl ethers by using Pd(II) catalyst and  $\text{Br}_3\text{CCOOEt}$



Entry	Alcohol	TIPS-H (mmol)	Temp	%Isolated yield
1 <sup>a</sup>		1.5	RT	55
2 <sup>a</sup>		2.0		65
3 <sup>a</sup>		2.0	Reflux	78
4 <sup>b</sup>		2.0		86
5 <sup>c</sup>		2.0	Reflux	100
6 <sup>c</sup>		2.0	Reflux	100

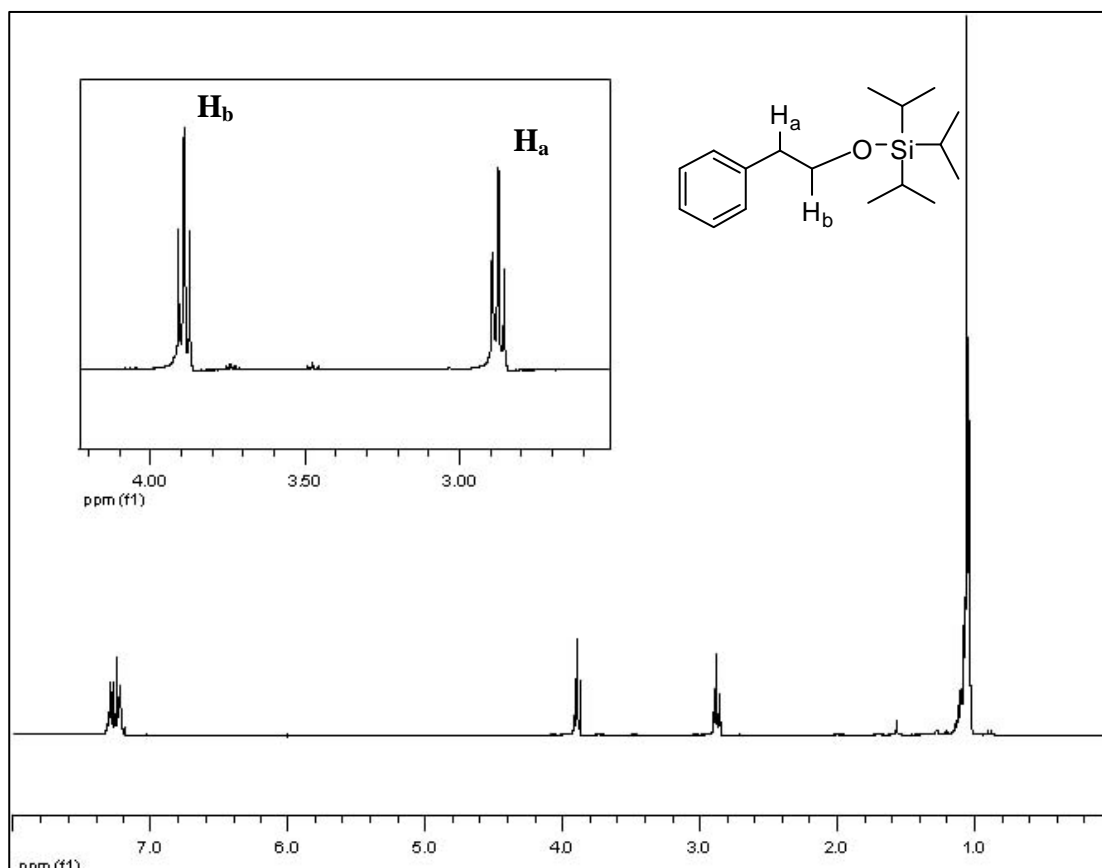
<sup>a</sup> separated by silica gel column, <sup>b</sup> separated by alumina column, <sup>c</sup> determined by <sup>1</sup>H-NMR

The search for suitable conditions, *i.e.*, the amount of TIPS-H in step I and reaction temperature in step II for the preparation of silyl ether were investigated. 2-Phenylethanol was chosen as a model. 55% of the desired product could be quantified

from the reaction using 1.5 mmol TIPS-H at RT ( $\sim 25^{\circ}\text{C}$ ). Increasing the amount of TIPS-H to 2.0 mmol, the target product was achieved in 65% yield (entry 2). Moreover, at refluxing THF ( $\sim 63^{\circ}\text{C}$ ), the yield could be lifted up to 78% (entry 3). The yield of the desired product separated by alumina column was obtained more than that conducted by silica gel column (entries 3-4).

Other selected alcohols: benzyl alcohol and geraniol (entries 5-6) were applied for the preparation of silyl ethers using optimal conditions. The desired silyl ethers could be obtained in quantitative yield (NMR yield).

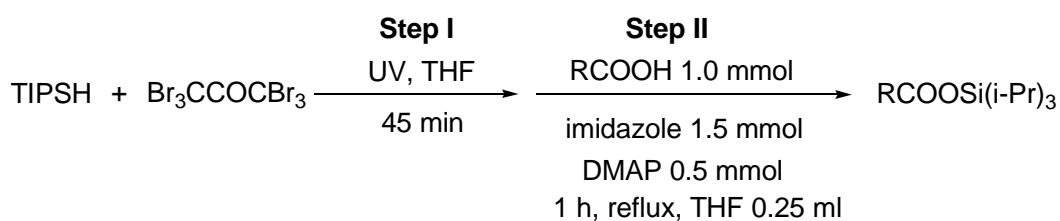
Figure 3.8 shows an example of the  $^1\text{H-NMR}$  spectrum of triisopropyl(phenethoxy)silane which was attained from the separation of the crude mixture in entry 4.



**Figure 3.8** The  $^1\text{H-NMR}$  spectrum of triisopropyl(phenethoxy)silane

The  $^1\text{H-NMR}$  spectrum of triisopropyl(phenethoxy)silane (Figure 3.8) reveals the isopropyl protons resonating at  $\delta_{\text{H}}$  1.05 (*d*,  $J = 5.1$  Hz, 21H), methylene protons at  $\delta_{\text{H}}$  2.91 (*t*,  $J = 7.2$  Hz, 2H,  $\text{H}_{\text{a}}$ ) on the carbon bearing a phenyl group, methylene protons at  $\delta_{\text{H}}$  3.92 (*t*,  $J = 7.2$  Hz, 2H,  $\text{H}_{\text{b}}$ ) connecting to a siloxyl group and aromatic protons at  $\delta_{\text{H}}$  7.25 (m, 5H).

**Table 3.13** The one-pot synthesis of silyl ethers by using  $\text{Br}_3\text{CCOCBr}_3$  and UV irradiation



Entry	Alcohol	TIPS-H (mmol)	% Yield <sup>a</sup> Silyl ether
1		1.5	65
2		2.0	100(72) <sup>b</sup>
3		2.0	100
4		2.0	101

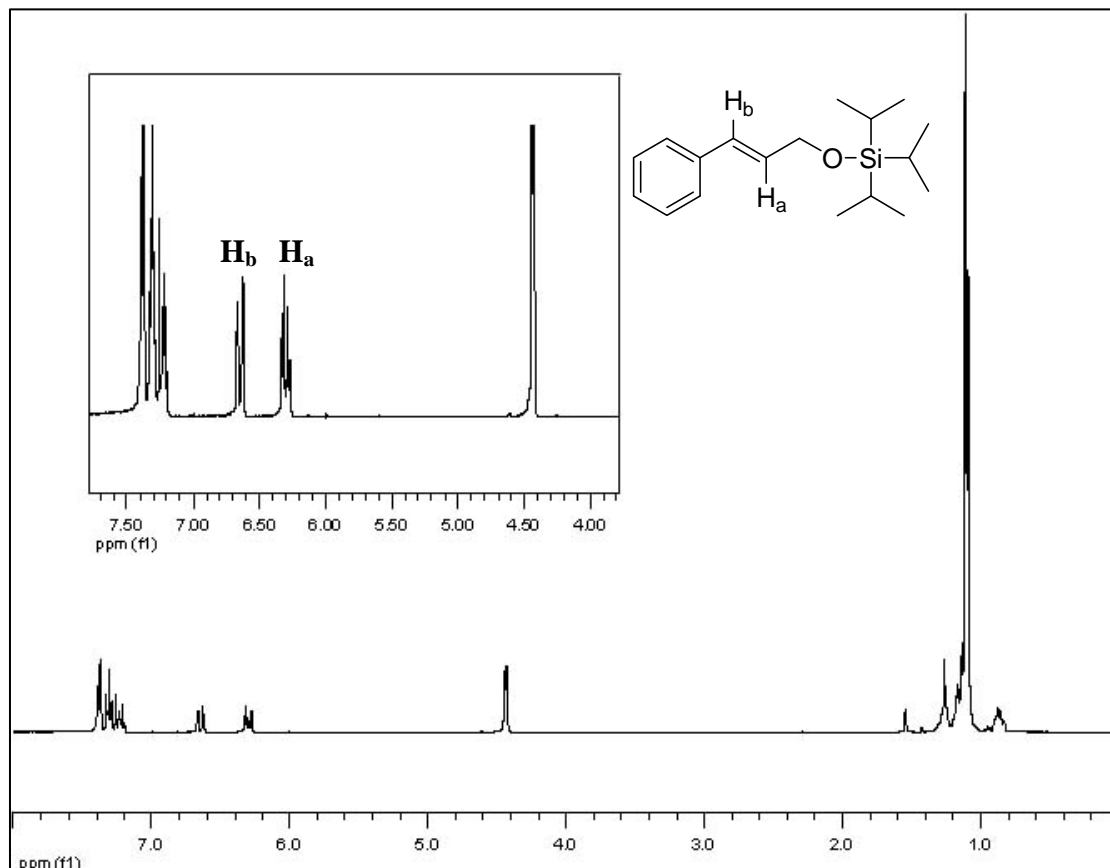
<sup>a</sup> determined by  $^1\text{H-NMR}$

<sup>b</sup> % isolated yield by alumina column

Reflux temperature ( $\sim 63^\circ\text{C}$ )

The synthesis of TIPS-Br was performed in step I using  $\text{Br}_3\text{CCOCBr}_3$  and UV irradiation. *Trans*-cinnamyl alcohol was selected as a chemical model. When the amount of TIPS-H was increased, the yield of TIPS-Br lifted. Thus, the desired silyl ether product was attained in quantitative yield (NMR yield) and 72% isolated yield (entry 2).

Figure 3.9 shows the  $^1\text{H-NMR}$  spectrum of *trans*-cinnamyloxytriisopropylsilane which was attained from the separation of the crude mixture in entry 2.



**Figure 3.9** The <sup>1</sup>H-NMR spectrum of *trans*-cinnamyloxytriisopropylsilane

The <sup>1</sup>H-NMR spectrum of *trans*-cinnamyloxytriisopropylsilane (Figure 3.9) reveals the peaks of isopropyl protons at  $\delta_{\text{H}}$  1.08 (*d*,  $J = 6.0$  Hz, 21H), two methylene protons on the carbon bearing a siloxyl group at  $\delta_{\text{H}}$  4.46 (*d*,  $J = 3.3$  Hz, 2H),  $-\underline{\text{C}}\text{H}-$  on the carbon connecting to the methylene group at  $\delta_{\text{H}}$  6.38 (*dt*,  $J = 15.9, 4.7$  Hz, H<sub>a</sub>),  $-\underline{\text{C}}\text{H}-$  connecting to phenyl group at  $\delta_{\text{H}}$  6.68 (*d*,  $J = 15.9$  Hz, H<sub>b</sub>) and aromatic protons at  $\delta_{\text{H}}$  7.34 (*m*, 5H).

According to the outcome presented above, it could be concluded that the advantages of developed method for synthesis silyl ester are

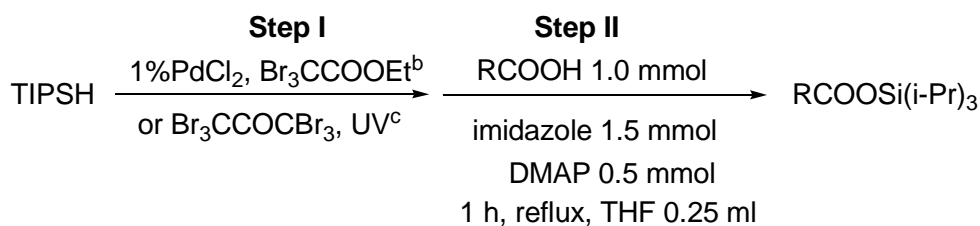
1. All primary alcohols could be completely converted to the corresponding silyl ethers in excellent yield under mild conditions by this one-pot procedure.

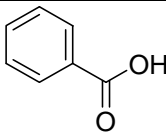
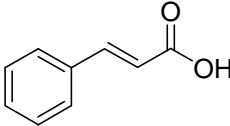
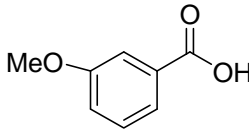
2. Low cost, in case of using Pd(II) catalyst due to its use as a catalytic amount. For the case of using UV irradiation, the reaction can be taken place in the absence of catalyst.

### 3.5.2 The One-Pot Synthesis of Silyl Esters

By the same analogy for the synthesis of silyl ether, the generated bromosilane could also be simply transformed to silyl ester by reacting with carboxylic acid. Since silyl ester is an unstable product, the purification by column chromatograph is not plausible. The yield of silyl ester produced was quantified by  $^1\text{H-NMR}$  technique. The results of the one-pot synthesis of silyl esters using Pd(II) catalyst and  $\text{Br}_3\text{CCOOEt}$  and that using  $\text{Br}_3\text{CCOCBr}_3$  and UV irradiation were collected in Table 3.14.

**Table 3.14** The one-pot synthesis of silyl esters



Entry	Carboxylic acid	% Yield <sup>a</sup> silyl ester	MB (%)
1		(100) <sup>b</sup> (101) <sup>c</sup>	(100) <sup>b</sup> (101) <sup>c</sup>
2		(102) <sup>b</sup> (100) <sup>c</sup>	(102) <sup>b</sup> (100) <sup>c</sup>
3		(101) <sup>b</sup> (101) <sup>c</sup>	(101) <sup>b</sup> (101) <sup>c</sup>

<sup>a</sup> determined by  $^1\text{H-NMR}$

<sup>b</sup> 0.5 mL THF, reflux temperature (~63°C), 15 min

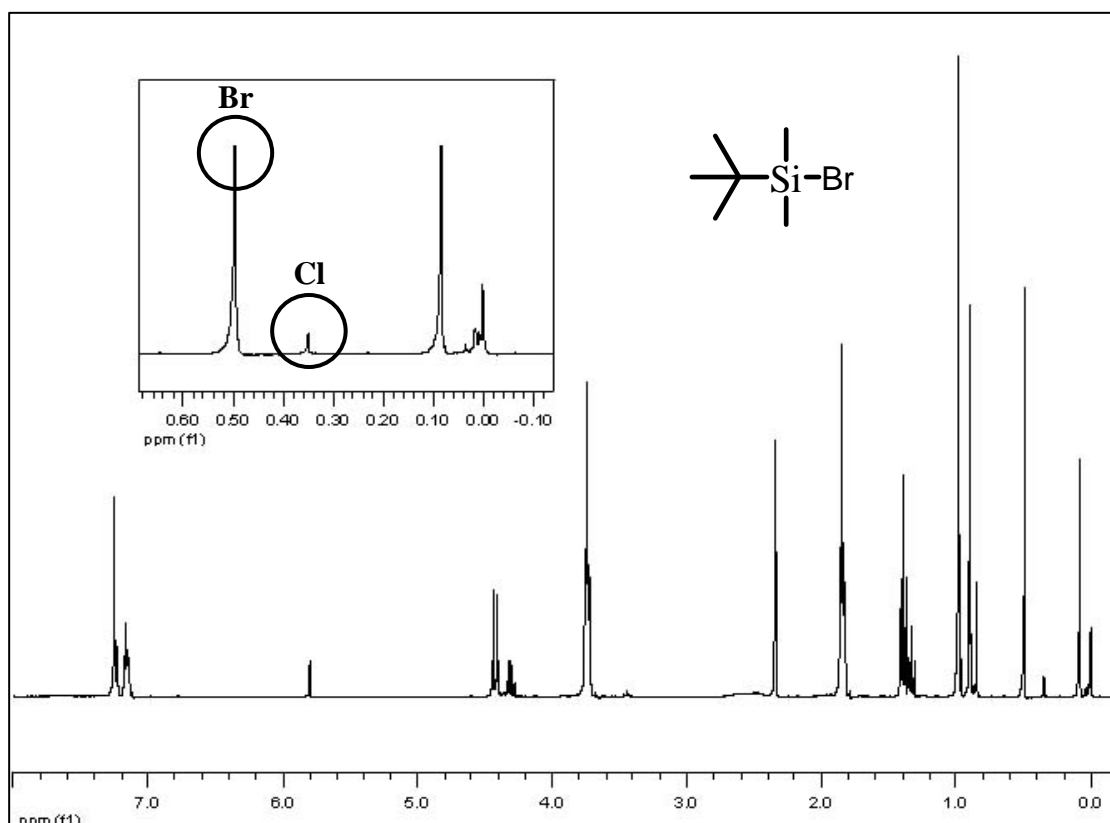
<sup>c</sup> 0.5 mL THF, 254nm, 6W, 45 min



All reactions could be performed under optimal conditions as afore-described. All selected carboxylic acids including benzoic acid, cinnamic acid and 3-methoxybenzoic could be converted to the corresponding silyl esters in quantitative yield. The benefit of this reaction is the reaction could be carried out in one-pot fashion with high yield of the desired product.

### 3.6 Relative Reactivity of Brominating Agents on the Conversion of *tert*-BuMe<sub>2</sub>Si-H to *tert*-BuMe<sub>2</sub>Si-Br

The relative reactivity of brominating agents towards hydrosilane has not been reported in literatures. The ratio of the yield of bromosilane and chlorosilane was used to determine the reactivity of selected brominating agents which based on Br<sub>3</sub>CCOOH. An example of the <sup>1</sup>H-NMR spectrum of the crude mixture using Br<sub>3</sub>CCOOEt and Cl<sub>2</sub>CHCOOEt is shown in Figure 3.10.



**Figure 3.10** The <sup>1</sup>H-NMR spectrum of *tert*-BuMe<sub>2</sub>SiH, *tert*-BuMe<sub>2</sub>SiBr and *tert*-BuMe<sub>2</sub>SiCl in the crude reaction mixture

The relative reactivity of various brominating agents to convert hydrosilane to bromosilane is described in Table 3.15.

**Table 3.15** Relative reactivity of selected brominating agents on the bromination of *tert*-BuMe<sub>2</sub>Si-H



Entry	Brominating agent	% Yield <sup>a</sup>		TIPS-Br/TIPS-Cl	Reactivity <sup>b</sup>
		TIPS-Br	TIPS-Cl		
1	Br <sub>3</sub> CCOOEt	41	6	6.83	1.71
2	Br <sub>3</sub> CCOOH	36	9	4	1
3	CBr <sub>4</sub>	17	4	4.25	1.06

<sup>a</sup> determined by <sup>1</sup>H-NMR

<sup>b</sup> based on Br<sub>3</sub>CCOOH

Considering the reactivity of brominating agents for the conversion of *tert*-BuMe<sub>2</sub>Si-H to its bromo analogues compared with Cl<sub>2</sub>CHCOOEt as a reference, it was found that the reagent bearing strong electron-withdrawing group revealed better reactivity. The order of brominating agent studied is Br<sub>3</sub>CCOOEt > Br<sub>3</sub>CCOOH ~ CBr<sub>4</sub>.

## CHAPTER IV

### CONCLUSION

With the aim to develop the new methodology for the synthesis of bromosilanes from hydrosilanes, two new and efficient protocols are uncovered. Those include the system utilizing  $\text{Br}_3\text{CCOOEt}$  and  $\text{PdCl}_2$  as a catalyst and that employing  $\text{Br}_3\text{CCOCBr}_3$  and UV irradiation. The developed methodologies could also be applied to the one-pot synthesis of silyl ethers and silyl esters accomplishedly.

To illustrate this, the first system could be performed by combination of  $\text{Br}_3\text{CCOOEt}$  with  $\text{PdCl}_2$  in refluxing THF ( $\sim 63^\circ\text{C}$ ) within 15 min while the second system could perfectly be exploited to prepare bromosilane using  $\text{Br}_3\text{CCOCBr}_3$  in THF under UV irradiation (254 nm, 6W). The mechanism of the first system was proposed to take place *via* the oxidative addition of brominating agents and Pd(0) which continuous reductive elimination to give Pd(0) and bromosilane. For the second system, the mechanistic pathway was occurred *via* a radical process. A bromine radical was released from  $\text{Br}_3\text{CCOCBr}_3$  and abstracted the proton of hydrosilane to produce a silyl radical. After that silyl radical reacted with a bromine radical to yield bromosilane. The reactivity for the conversion of hydrosilane to bromosilane was investigated to find out the most efficient brominating agent for the first system.  $\text{Br}_3\text{CCOOEt}$  displayed the highest reactivity over all brominating agents studied.

This optimal condition for the synthesis of bromosilanes could also be used for the preparation of silyl ether and silyl ester by one-pot reaction in high yield.

#### **Proposal for the Further Work**

This research concerns with the development of brominating agents and the methodology for the synthesis of bromosilane from hydrosilane. This method could be applied to prepare silyl derivatives in one-pot reaction. This outcome opened many

possibilities to deal with further exploration. For instance, it may be applied for other silicon-containing compounds such as silanol to achieve the corresponding bromosilane. The one-pot synthesis of silyl ether derivatives of complex molecules such as sugar should also be explored.

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