3.DISCUSSION AND CONCLUSION

The preparation of bis(tributyltin) oxide ,$(Bu_3Sn)_2O$,or T.B.T.O in this research was carried out by using commercial stannic chloride, $SnCl_4$, and attempt to purpose for cassiterite, SnO_2, as starting material. First, bis(tributyltin) oxide was prepared by two methods, Grignard method and Wurtz method, then select the best methods to prepare T.B.T.O. by using cassiterite, SnO_2, as a starting material by changing SnO_2 form to solution of $SnCl_4$.

3.1 The preparation of bis(tributyltin) oxide by Grignard method

There are three steps in the preparation of bis(tributyltin) oxide ,$(Bu_3Sn)_2O$.

(1) Preparation of tetrabutyltin, Bu_4Sn, from BuMgCl (Grignard reagent)

(2) Preparation of tributyltin chloride, Bu_3SnCl from Bu_4Sn by disproportionation reaction.

(3) Preparation of bis(tributyltin) oxide, $(Bu_3Sn)_2O$ from Bu_3SnCl by alkaline hydrolysis.

And alternative method in preparation of bis(tributyltin) oxide, $(Bu_3Sn)_2O$ from Bu_3SnCl by Grignard method was

(1) Preparation of tributyltin chloride, Bu_3SnCl , from BuMgCl (Grignard reagent)

(2) Preparation of bis(tributyltin) oxide, $(Bu_3Sn)_2O$ from Bu_3SnCl by alkaline hydrolysis.

3.1.1 Preparation of tetrabutyltin, Bu_4Sn, by Grignard method

There are two steps to prepare tetrabutyltin, Bu_4Sn, by Grignard method. First, the butylmagnesium chloride was prepared which was showed in equation 2-2. Second, The Bu_4Sn was prepared from $SnCl_4$ which was shown in equation 2-3.

From the result it was found that product was colourless liquid, which was obtained from reduced pressure distillation at 106-118 °C/0.7 mmHg (Table 2.5) compare with standard tetrabutyltin from reference.[38,40] The tetrabutyltin was colourless or slightly yellow oily liquid, boiling point was 127°C/1.7 mmHg (342°C at atmosphere pressure) , and dissolve in organic solvent. The tetrabutyltin from this experiment was colourless liquid, boiling point 106-118°C/0.7 mmHg (317-335°C at atmosphere pressure). Consideration of standard tributyltin chloride from reference it was colorless liquid, boiling point was 152-156°C/14 mmHg (320-330°C at atmosphere pressure). The boiling point of product from this experiment was nearly to tributyltin chloride than tetrabutyltin. So the product may be tributyltin chloride.

The study of IR spectra [2,38,39] of this product, Figure 2.5, it was shown vibration spectra of aliphatic hydrocarbon near the frequency of 3000 cm^{-1} and 2850 cm^{-1}, the methyl group show asymmetric stretching ($\nu_{as}CH_3$-) at 2872 cm^{-1} and C-H asymmetric bending

($\sigma_{as}CH_3$-) at 1450 cm^{-1}, C-H symmetric bending ($\sigma_{s}CH_3$-) at 1375 $cm^{-1}$and C-H scissoring vibration of methylene (σ_s-CH_2-) at 1465 cm^{-1}. If the compounds have several group of –CH_2- in the same molecule the two strong bands of asymmetric stretching of methylene group were shown at 2926 cm^{-1}(ν_{as} -CH_2-) and 2853 cm^{-1} (ν_s-CH_2-). All bands show characteristic of straight chain hydrocarbon compounds.

In the finger print region which was shown characteristic of compounds. It was found their medium bands at 513 cm^{-1} of symmetric stretching Sn – C bond (ν_s-Sn-C), and 601 cm^{-1} of asymmetric stretching Sn – C bond (ν_{as}-Sn-C).(Table3.1). The two bands were characteristic band of tributyltin compound. When consider the two bands near 1200 cm^{-1} and 1300 cm^{-1}, it was found that the intensity of two bands are equal to each other like IR spectra standard tributyltin compound (Figure 2.10).

The study of the percentage of carbon and hydrogen, found that C = 45.20, H = 8.67 compare with the calculated, C =55.36, H= 10.45 for tetrabutyltin and the calculated C= 44.24, H= 8.36 for tributyltin chloride. It was nearly to tributyltin than tetrabutyltin.

So the product must be tributyltin chloride than tetrabutyltin. From the reaction of the preparation of tetrabutyltin consider step by step as seen in equations 2-6 – 2-9.. It was found that the main product might be Bu_3SnCl if the reaction was not completely.

From equations 2-9 if the reaction was not completely, the Bu_3SnCl can not change to Bu_4Sn, main product must be Bu_3SnCl. So Bu_3SnCl could be prepared directly by Grignard method.

Table 3.1 Infrared spectra: some Sn-C (aliphatic) stretching frequencies [2]

Compounds	State	ν(Sn-C) (cm^{-1})			Reference
(a) Compounds with 4 Sn-C bonds					
Me_4Sn	Liquid		528s		224
Et_4Sn	Liquid		508s		224
Pr_4Sn	Liquid	509s		500s	224
Bu_4Sn	Liquid	592s		503s	41
(b) Compounds with 3 Sn-C bonds					
Bu_3SnCl	Liquid	601s		513m	41
Bu_3SnBr	Soln. in cyclohexane	599s		503m	34
Bu_3SnI	Soln. in cyclohexane	598s		501s	34
$(Bu_3Sn)_2O$	Soln.	648,595		509	154

3.1.2 The preparation of tributyltin chloride by Grignard reaction

Tributyltin chloride could be prepared directly by Grignard method as shown in equation 2-2 and 2-10

From the result it was found that product was colourless liquid, which obtained from reduced pressure distillation at 108-115 °C/0.7 mmHg (Table 2.5) compare with standard tributyltin chloride from reference [38,40] The tributyltin chloride was colourless liquid, boiling point was 152-156°C/14 mmHg (320-330°C at atmosphere pressure) , and dissolve in organic solvent. The tributyltin chloride from this experiment was colourless liquid, boiling point 108-115°C/0.7 mmHg (320-331°C at atmosphere pressure). It was found that, the boiling point of product from this experiment was nearly to standard tributyltin chloride.

The study of IR spectra [6,38-40] of this product, Figure 2.8, it showed vibration spectra of aliphatic hydrocarbon near the frequency of 3000 cm^{-1} and 2850 cm^{-1}, the methyl group show asymmetric stretching ($\nu_{as}CH_3$-) at 2870 cm^{-1} and C-H asymmetric bending

($\sigma_{as}CH_3$-) at 1450 cm^{-1}, C-H symmetric bending ($\sigma_{s}CH_3$-) at 1375 cm^{-1}. If the compounds have several group of $-CH_2$- in the same molecule the two strong bands of asymmetric stretching of methylene group were shown at 2926 cm^{-1}(ν_{as}-CH_2-) and 2853 cm^{-1} (ν_{s}-CH_2-). All bands show characteristic of straight chain hydrocarbon compounds.

In the finger print region which was shown characteristic of compounds, Table 3.1. It was found medium bands at 513 cm^{-1} of symmetric stretching Sn – C bond (ν_{s}-Sn-C), and 601 cm^{-1} of asymmetric stretching Sn – C bond (ν_{as}-Sn-C). The two bands were characteristic band of tributyltin chloride compound. When consider the two bands near 1200 cm^{-1} and 1300 cm^{-1}, it was found that the intensity of two bands are equal to each other like IR spectra standard tributyltin compound (Figure 2.10).

The study of the percentage of carbon and hydrogen , found that C = 43.20, H = 7.89 compare with the calculated C= 44.24, H= 8.36 for tributyltin chloride. So it can conclude that the product of this step was tributyltin chloride as expected.

3.1.3 The preparation of bis(tributyltin) oxide.

The bis(tributyltin) oxide was prepared by alkaline hydrolysis as seen in equation 2-11

From the result it was found that product was colourless liquid, which obtained from reduced pressure distillation at 115-119 °C/0.1 mmHg (Table 2.5) compare with standard bis(tributyltin) oxide from reference.[40] The bis(tributyltin) oxide was colorless liquid, boiling point was 180°C/2mmHg (394°C at atmosphere pressure) , and dissolve in organic solvent. The bis(tributyltin) oxide from this experiment was colourless liquid, boiling point 115-119°C/0.1 mmHg (391-398°C at atmosphere pressure). It was found that, the boiling point of product from this experiment was nearly to standard bis(tributyltin) oxide.

The study of IR spectra [2,6] of this product, Figure 2.11, it showed vibration spectra of aliphatic hydrocarbon near the frequency of 3000 cm^{-1} and 2850 cm^{-1}, the methyl group show asymmetric stretching ($\nu_{as}CH_3$-) at 2870 cm^{-1} and C-H asymmetric bending ($\sigma_{as}CH_3$-) at 1450 cm^{-1}, C-H symmetric bending ($\sigma_{s}CH_3$-) at 1375 cm^{-1}. If the compounds have several group of $-CH_2$- in the same molecule the two strong bands of asymmetric stretching of methylene group were shown at 2926 cm^{-1}(ν_{as}-CH_2-) and 2853 cm^{-1} (ν_{s}-CH_2-). All bands show characteristic of straight chain hydrocarbon compounds.

In the finger print region which was shown characteristic of compounds (Table 3.1). It showed medium bands at 509 cm^{-1} of symmetric stretching Sn – C bond (ν_{s}-Sn-C), two bands near to 648 cm^{-1} and 595 of asymmetric stretching Sn – C bond (ν_{as}Sn-C). The three bands were characteristic band of tributyltin compound. When consider the two bands near 1200 cm^{-1} and 1300 cm^{-1}, it was found that the intensity of two bands are similar to IR spectra of standard bis(tributyltin) oxide compound (Figure 2.13). And the most important band was strong asymmetric stretching Sn - O – Sn bond (ν_{as}Sn-O-Sn) at 784-769 cm^{-1}(Table 3.2) compare to the band at 780 cm^{-1}(Figure 2.11).

Table 3.2 Infrared spectra: Absorption bands associated with Sn-O group [2]

Compounds	State	Absorbtion band (cm^{-1}) And assignments	Reference
Me_3SnOH	Solid	917m σ(Sn-OH)	123
Et_3SnOH	Solid	885s σ(Sn-OH)	136
Ph_3SnOSn_3Ph	Soln. or solid	777-770sν_{as} (Sn-O-Sn)	40,66,122,131, 175
R_3SnOSn_3R	Liquid	784-769sν_{as} (Sn-O-Sn)	40,136,154,245
Bu_3SnOR	Soln.	1100-946sw-m ν_{as} (Sn-O-C) 525-514 ν_{as} (Sn-O-C)	42,150,54,195
$Ph_3SnOP(O)Ph_3$	Soln.	394m ν_s (Sn-O-C)	195
R_2SnO	Solid	576-561 ν_s (Sn-O-C)	40,136
Ph_2SnO	Solid	575-571 ν_s (Sn-O-C)	40,175
$R_2Sn(OR')_2$	Soln.	$\approx$ 600wν_s (O-Sn-O) 478-466 ν_s (O-Sn-O)	149,150,154

From the mass spectrum in Figure 2.15 , the important peaks of mass-to-charge ratio (m/z) appear at 177,255,314,370,428,484 and 540. The base peak appear at 41 m/z. When it was compared with mass spectrum of standard T.B.T.O[42] (Figure 2.17), it was found that the peaks of sample were nearly to standard spectrum. And the peaks appear at high m/z, because T.B.T.O. has high molecular weight (598). Since tin has many isotopes as shown in Table 1.4, the highest % abundance is ^{120}Sn, so the mass spectrum of sample appear many peaks at the same m/z. In consideration of fragmentation of compound, it was found that the fragmentation was simple fission of butyl groups (C_4H_9- or Bu-), which was shown in Figure 3.1. Because the bond length of Sn-C bond longer than C-C bond (Sn-C = 2.17 A^{O}, C-C =1.54 A^{O}), so the dissociation energy of Sn-C bond (45-55 kcal/mol) lower than C-C bond (80-90 kcal/mol)[2]. Then the first fragmentation was butyl group and the last fragment was Sn-O-Sn.

The analysis of the percentage of carbon and hydrogen found that C = 48.92, H = 9.02 compare with the calculated C= 49.86, H= 9.62 for bis(tributyltin) oxide.
The determination of percentage of tin (%Sn) in organotin compounds was 38.27 as shown in Table 2.3, compare to the calculated %Sn = 39.82 for bis(tributyltin) oxide.

It can be concluded that the product of this step was the expected bis(tributyltin) oxide.

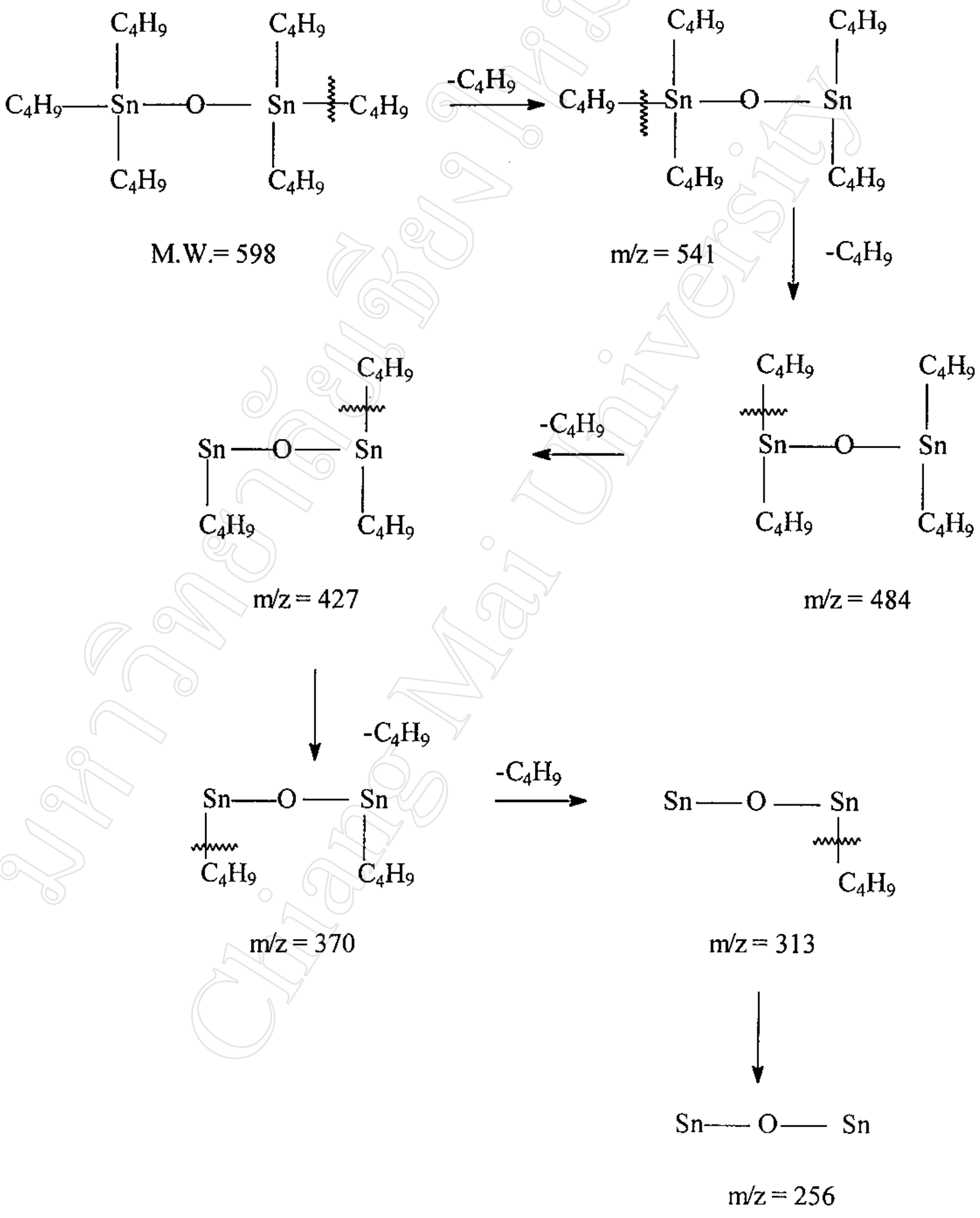

Figure 3.1 Fragmentation of bis(tributyltin) oxide[17]

3.2 The preparation of bis(tributyltin) oxide by Wurtz method

There are three steps in the preparation of bis(tributyltin) oxide by Wurtz method as seen in equation 2-12 – 2-14.

3.2.1 The preparation of tetrabutyltin, Bu_4Sn by wurtz method

From the result it was found that product was colourless liquid, which obtained from the reduced pressure distillation at 116-120 °C/0.6 mmHg (Table 2.5) compare with standard tetrabutyltin from reference.[38,40] The tetrabutyltin was colourless or slightly yellow oily liquid, boiling point was 127°C/1.7 mmHg (342°C at atmosphere pressure) . The tetrabutyltin from this study was colorless liquid, boiling point was 116-120°C/0.6 mmHg (337-343°C at atmosphere pressure). Consideration of tributyltin chloride from literature is a colorless liquid, boiling point is 152-156°C/14 mmHg (320-330°C at atmosphere pressure). The boiling point of product from this experiment was nearly to tetrabutyltin than tributyltin chloride. So the product may be tetrabutyltin.

The study of IR spectra [2,3] of this product, Figure 2.6, showed vibration spectra of aliphatic hydrocarbon near the frequency of 3000 cm^{-1} and 2850 cm^{-1}, the methyl group show asymmetric stretching ($\nu_{as}CH_3$-) at 2872 cm^{-1} and C-H asymmetric bending

($\sigma_{as}CH_3$-) at 1450 cm^{-1}, C-H symmetric bending ($\sigma_{s}CH_3$-) at 1375 $cm^{-1}$and C-H scissoring vibration of methylene (σ_s-CH_2-) at 1465 cm^{-1}. If the compounds have several group of –CH_2- in the same molecule the two strong bands of asymmetric stretching of methylene group were shown at 2926 cm^{-1}(ν_{as} -CH_2-) and 2853 cm^{-1} (ν_s-CH_2-). All bands show characteristic of straight chain hydrocarbon compounds.

In the finger print region which was shown characteristic of compounds. It found the medium bands at 503 cm^{-1} of symmetric stretching Sn – C bond (ν_s-Sn-C), and 592 cm^{-1} of asymmetric stretching Sn – C bond (ν_{as}-Sn-C). The two bands were characteristic band of tetrabutyltin compound. When consider the two bands near 1200 cm^{-1} and 1300 cm^{-1}, it was found that the intensity of two bands are similar to IR spectra standard tetrabutyltin compound (Figure 2.7)

The study of the percentage of carbon and hydrogen found that C = 55.07, H = 9.98 compare with the calculated, C =55.36, H= 10.45 for tetrabutyltin and C= 44.24, H= 8.36 for tributyltin chloride. It was nearly to tetrabutyltin than tributyltin chloride.

The product of this step must be tetrabutyltin.

3.2.2 The preparation of tributyltin chloride, Bu_3SnCl

From the result it was found that product was colorless liquid, which obtained from reduced pressure distillation at 115-120 °C/1.0 mmHg (Table 2.5) compare with standard tributyltin chloride from reference.[38,40] The tributyltin chloride was colorless liquid, boiling point was 152-156°C/14 mmHg (320-330°C at atmosphere pressure) , and dissolve in organic solvent. The tributyltin chloride from this experiment was colorless liquid, boiling point 115-120°C/1.0 mmHg (320-327°C at atmosphere pressure). It was found that, the boiling point of product from this experiment was nearly to standard tributyltin chloride.

The study of IR spectra [2,-40] of this product, Figure 2.19, it was shown vibration spectra similar to IR spectra of tributyltin chloride, which was prepared by Grignard method (Frigure2.8). And the important bands in the finger print region present characteristic of tributyltin chloride similar to IR spectra standard tributyltin compound (Figure 2.10).

The analysis of the percentage of carbon and hydrogen found that C = 43.72, H = 8.03 compare with the calculated C= 44.24, H= 8.36 for tributyltin chloride. So it can conclude that the product of this step was tributyltin chloride.

3.2.3 The preparation of bis(tributyltin) oxide.

From the result it was found that product was colorless liquid, which receives from reduces pressure distillation at 128-133 °C/0.2 mmHg (Table 2.5) compare with standard bis(tributyltin) oxide from reference.[38,40] The bis(tributyltin) oxide was colorless liquid, boiling point was 180°C/2mmHg (394°C at atmosphere pressure) , and dissolve in organic solvent. The bis(tributyltin) oxide from this experiment was colorless liquid, boiling point 128-133°C/0.2 mmHg (391-399°C at atmosphere pressure). It was found that, the boiling point of the product from this experiment was nearly to standard bis(tributyltin) oxide.

The study of IR spectra [2,40] of this product, Figure 2.12, it showed vibration spectra similar to IR spectra of T.B.T.O., which was prepared by Grignard method (Frigure2.13). And the importance bands in finger print region present characteristic of T.B.T.O. similar to IR spectra standard T.B.T.O. (Figure 2.13).

From the mass spectrum, which was shown in Figure 2.15, the important peaks of mass-to-charge ratio (m/z) appear at 177,255,314,370,428,484 and 540. The base peak appear at 252 m/z. When it was compared with mass spectrum of standard T.B.T.O. from Figure 2.17, it was found that the peaks of sample similar to standard spectrum.

The analysis of the percentage of carbon and hydrogen found that C = 49.52, H = 9.21 compare with the calculated C= 49.86, H= 9.62 for bis(tributyltin) oxide. From the determination of tin (%Sn) in organotin compounds was 39.48 as shown in Table 2.4, compare with the calculated %Sn = 39.82 for bis(tributyltin) oxide.

It can conclude that the product of this step was bis(tributyltin) oxide.

3.3 Comparison of the two methods in preparation of bis(tributyltin) oxide.

The two methods which were used in the preparation of bis(tributyltin) oxide in these experiments were Grignard method and Wurtz method. Both methods have advantage and disadvantage. From this experiment it was found that the Grignard method gave higher yield than Wurtz method, the percentage of actual yield from Grignard method is 67 and from Wurtz method is 35. The Grignard method, although giving good yields, has some serious disadvantage, the reaction has first to be started and then must be maintained smoothly. Once the reaction stops it is difficult to start it again. The Grignard method general used for the preparation on laboratory scale, and up till now also applied in the factory but Wurtz method was appropriate to prepare in the laboratory scale. Because in large-scale the actual yield was reduced. Furthermore the sodium metal must be disperse in the large amount of hot xylene by means of special high-speed stirrer, after being cooled the xylene was replaced by the petroleum ether. So it difficult to prepare in large scale and used large amount of solvent than Grignard method.[25,28] .When its was considered in economy reason, the Wurtz method uses sodium metal, which was expensive than magnesium turning in Grignard method. So the Grignard method was chosen in preparation of bis(tributyltin) oxide from cassiterite as a starting material.

3.4 The preparation of bis(tributyltin) oxide from cassiterite as starting material

3.4.1 Preparation of aqueous $SnCl_4$ from cassiterite

The determination of tin in cassiterite (SnO_2) ore by iodometry titration was 51.03 %. And in the aqueous $SnCl_4$ 800 mL have 29.84 g of $SnCl_4$.The impurity in the aqueous, tungsten (W), was eradicated by precipitation with tungstic acid (H_2WO_4) which was yellow precipitate, and the other impurities such as iron, lead , copper , arsenic, bismus were dissolve in the aqueous solution of stannic chloride.[21,17]

3.4.2 The preparation of $SnCl_4$ in toluene from aqueous stannic chloride

From the result the solution of stannic chloride was slightly yellow colour cause by iron (III) which dissolve in the solution, although ascorbic acid was added to reduces iron (III) to iron (II) but ascorbic acid was not stable in solution form. So iron (II) may be changing to iron (III) again. The appropriate condition the extraction of stannic chloride in aqueous stannic chloride to toluene phase by using 5%TOPO in toluene as extractant was in 1-6 M of hydrochloric acid. TOPO was the reagent for extraction of several metals such as Cu, As, Sb, Cd, and etc. So the solution was not pure.

3.4.3 The preparation of tributyltin chloride from stannic chloride in toluene

The preparation of tributyltin chloride from stannic chloride in toluene was carried out as the alternative Grignard method (equation 2-10).

From the result, the brown gel was formed before the distillation. So the boiling point could not be determine. From IR spectra in Figure 2.14 showed broad band in the region of 3500-3000 cm^{-1} and band in the finger print (1350-400 cm^{-1}) was not sharp because the compound was not pure. So it was difficulty to identify. By comparison with standard tributyltin chloride, the two bands near 1200 cm^{-1} and 1300 cm^{-1} were not clear, Its could be used to identify the compound. The band near 700 cm^{-1} may be toluene band from the solution of stannic chloride in toluene. So band near 700 cm^{-1} of organotin compound was shielded by toluene band. Boiling point of toluene (110^{o}C) was nearly to stannic chloride (114^{o}C). So toluene could not separate by distillation.

This experiment could not prepare tributyltin chloride by Grignard method, so the preparation of bis(tributyltin) oxide from cassiterite ore was not possible. It is also happen in the work of Noppawan Auchariyaphituk. [17] The reasons may be the effect of impurities in cassiterite ore, although some impurities was eradicated such as tungsten but the other such as Pb, Cu , As, Bi and etc was not eradicated. Otherwise the cassiterite ore which was used in this experiment was low grade, the percentage of tin less than the cassiterite in commercial grade (%Sn in this experiment = 51.03 and the low grade cassiterite ore in commercial = 65 %). And The condition in extraction of stannic chloride from aqueous phase to toluene phase was not appropriate, so the efficiency of extraction was not satisfactory.

3.2 Conclusion

This research has been intended to prepare bis(tributyltin) oxide from cassiterite directly. The two methods, Grignard method and Wurtz method, for the preparation of bis(tributyltin) oxide, T.B.T.O., from anhydrous stannic chloride, $SnCl_4$, as a starting material was investigated first. Then select the best methods to prepare T.B.T.O. by using cassiterite, SnO_2, as a starting material. It can be conclude as following:

(1) The preparation of bis(tributyltin) chloride from commercial stannic chloride by Grignard method was carried out according to the literature method.

First, the Grignard reagent, butylmagnesium chloride (BuMgCl), was prepared. Second, the tributyltin chloride was prepared by Grignard method and it was changed to bis(tributyltin) oxide by hydrolysis with strong base (NaOH).

(2) The preparation of bis(tributyltin) chloride from commercial stannic chloride by Wurtz method was carried out according to the literature method.

First, the tetrabutyltin was prepared by wurtz method. Second, the tributyltin chloride was prepared by disproportionation reaction. Third, the bis(tributyltin) oxide was prepared by alkaline hydrolysis.

(3) The attempt to prepare bis(tributyltin) chloride from cassiterite ore by Grignard method

First step is the preparation of aqueous $SnCl_4$ from cassiterite by fusion with sodium peroxide. Second extracted $SnCl_4$ to toluene from aqueous $SnCl_4$ by liquid-liquid extraction using trioctylphosphine oxide (TOPO) extractant. And then the Bu_3SnCl was prepared from $SnCl_4$ in toluene by Grignard method.

The tributyltin chloride cloud not prepared from cassiterite ore. So the preparation of bis(tributyltin) oxide from cassiterite ore was not successful.