CHAPTER II

EXPERIMENTAL

2.1 Instruments

2.1.1 Infrared Spectroscopy (IR)

The IR spectra were recorded on Perkin-Elmer Model IR 1430 Infrared Spectrophotometer. Solid samples were generally examined as a pressed potassium bromide disc, while liquid samples were neatly examined on sodium chloride cell.

2.2.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

The ^{1}H (PMR) and ^{13}C (CMR) spectra were taken by using Bruker Model ACF 200 Spectrometer operating at 200.13 MHz for proton and 50.32 MHz for carbon-13 nuclei. The samples were dissolved as 5% solution in $CDCl_3$ or any suitable solvents as indicated. The chemical shift (δ) were given in ppm against solvent peak.

2.2.3 Mass Spectrometry (MS)

The MS spectra of compound (3) and (4) were recorded by VG Analytical-Autospec EQ. EI+ 70 eV Resolution 10,000. The author was deeply appreciated Professor Dr.Gerard

Deleris, Universite' of Bordeux II, France for furnishing the HRMS spectras. The other MS spectras were obtained by Jeol Mass Spectrometer Model JMS-DX-300/JMA 2000 at 70 eV.

2.2.4 Elemental Analyses

The elemental analyses were examined by Perkin-Elmer CHNO Analyzer Model 240C.

2.2.5 Melting Point (m.p.)

Melting points were determined on a Fisher-John melting point apparatus and were uncorrected.

2.2.6 Rotary Evaporator

The rotary evaporator was used to evaporate a large quantity of volatile solvent from a solution of organic compounds. Evaporation was conducted under reduced pressure (a water pump was the most convenient).

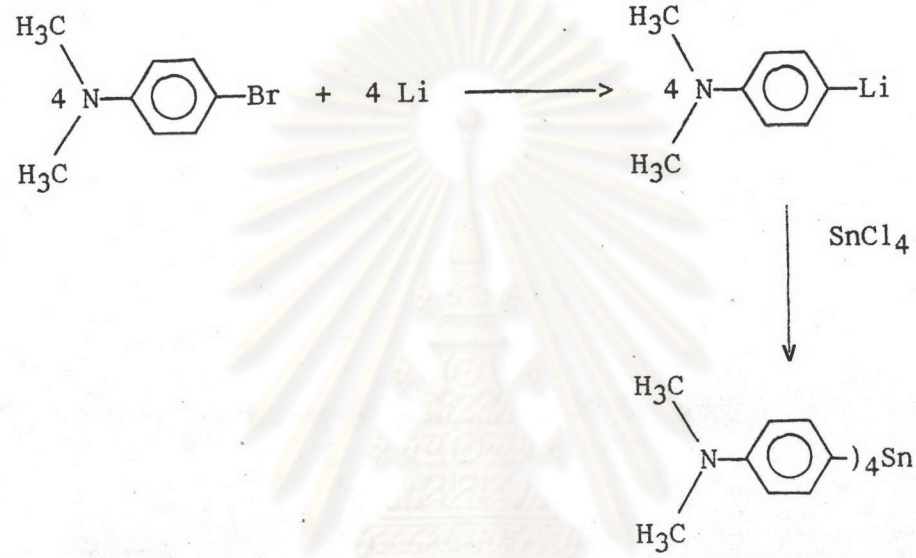
2.2 Reagents

1. Organotin compounds : butyltin trichloride, reagent grade, Aldrich, United state of America : used without further purification.
2. 4-Bromo-N,N-dimethylaniline, reagent grade, Fluka, Switzerland.

3. 1-Propanethiol, reagent grade, Fluka, Switzerland : used without further purification.
4. 2-Bromopyridine, reagent grade, Fluka , Switzerland: used without further purification.
5. Butyltin trichloride, reagent grade , Fluka , Switzerland: used without further purification.
6. Butylbromide, reagent grade, Fluka, Switzerland: used without further purification.
7. Triethylamine, reagent grade, Fluka, Switzerland : used without further purification.
8. Stannic chloride, reagent grade, Fluka, Switzerland : used without further purification.
9. Magnesium sulfate anhydrous, reagent grade, Fluka, Switzerland.
10. Anhydrous benzene : removed trace of water by refluxing with sodium metal and distilled before used.
11. Anhydrous ether, treated in the same manner as benzene.
12. Lithium metal
13. Sodium bicarbonate
14. Solvents : methanol, chloroform, dichloromethane, acetone, ethanol; commercial grade, were distilled before used.

2.3 Redistribution reaction of tetrakis-(4-dimethylaminophenyl) stannane and stannic chloride

2.3.1 Preparation of tetrakis-(4-dimethylaminophenyl) stannane (1)



(1)

A 250-ml three necked round-bottomed flask was fitted with a reflux condenser, a dropping funnel, an efficient stirrer, and inlet and outlet tube for dry nitrogen. A calcium chloride tube was attached to the dropping funnel to protect the apparatus from moisture. To the flask was added 50 ml of dry ether and lithium chips or shavings (0.76 g., 0.11 mol) and vigorous stirring was carried out. A solution of 4-Bromo-N,N-dimethylaniline (10 g , 0.05 mol) in dry ether (50 ml) was added

dropwise in a small portion and the mixture was heated for a few minutes to start the reaction. When the reaction started, the remaining solution was added dropwise with such a rate that the reaction mixture was under spontaneous refluxing. The reaction was then refluxed for two hours. Ether was distilled off from the reaction mixture using Dean-Stark apparatus. Dry benzene (50 ml) was added and then stannic chloride (1.37 ml, 0.01 mol) in dry benzene (25 ml) was added dropwise with vigorous stirring. The reaction was stirred at room temperature for one hour. Water (25 ml) was slowly added and then the resulting suspension was filtered and chloroform (20 ml) was added in order to dissolve product into organic layer. The aqeous phase was extracted with chloroform (3x25 ml). The combine organic phase and chloroform extracts was washed with water (3x25 ml), dried with magnesium sulfate anhydrous, filtered and the organic layer was evaporated at reduced pressure. The residue was then recrystallized from a mixture of chloroform and methanol to obtain white needle crystals (2.2 g, 64.8 %), m.p. 202 ^{o}C (m.p. of literature : 203 ^{o}C).

IR (KBr pellet, max cm^{-1}) : 3200 (aromatic =C-H), 2800-3100 (C-H), 1590 (C=C), 1350 (C-N), 1080 (Ph-Sn), 810 (p-substituted). (Fig. 5)

PMR(200 MHz, $CDCl_3$, ppm.) : 2.96 (s, $2NCH_3$), 6.77 (d, H_3 and H_5, J_{32} (Sn^{119}-H)= 9.27 Hz.) and 7.50 (d, H_2 and H_6, J_{23} (Sn^{117}-H)= 19.14 Hz. and J_{23} (Sn^{119}-H)= 26.10 Hz.) (Fig. 6)

CMR ($CDCl_3$, ppm.) : 40.08 (s, $2CH_3$), 112.79 (s, C_2 and C_6, J (^{13}C-^{119}Sn)= 26.65 Hz.), 124.61 (s, C_1), 138.10 (s, C_3 and C_5, J (^{13}C-^{119}Sn) 20.82 Hz.), 150.8 (s, C_4). (Fig. 7)

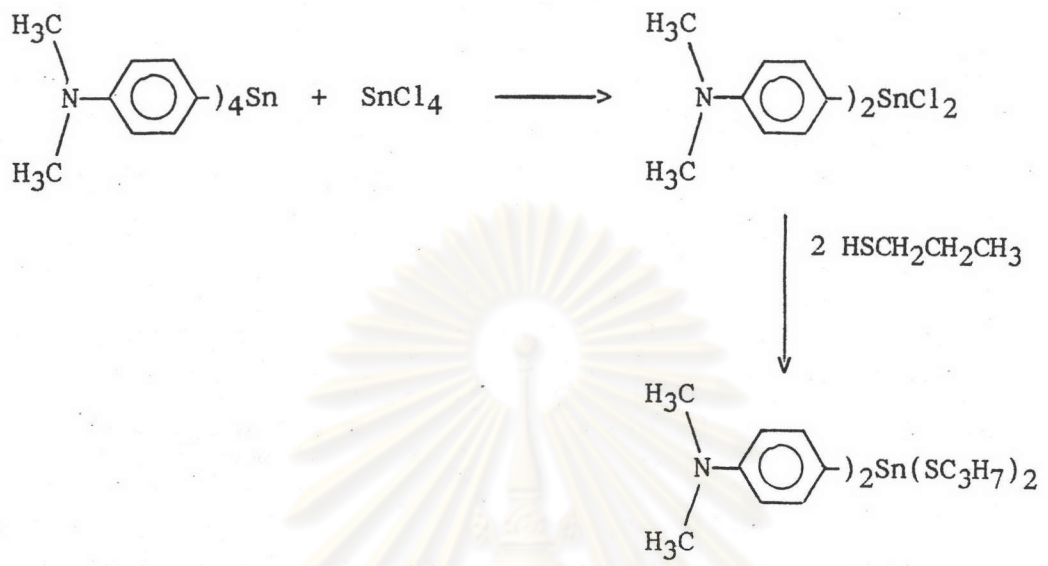
MS m/e (% rel.int.) : 600 (M^+,82.7), 480 (8.12), 240 (32.59), 120 (32.50). (Fig. 8, scheme 1)

Elemental analysis calculated for $C_{32}H_{40}NSn$ (556.69) :

Calculated C 68.98% : H 7.19% : N 2.51% : Sn 21.32%

Found C 68.35% : H 6.98% : N 2.34% : Sn 21.21%

2.3.2 Preparation of bis-(4-dimethylaminophenyl)stannane dipropylsulfide (2)



(2)

In a 250 ml-flask was placed a solution of tetrakis-(4-dimethylaminophenyl)stannane (100 mg., 0.167 mmol) in dry benzene (30 ml). To this was added dropwise with stirring a solution of stannic chloride (0.02 ml, 0.167 mmol) in dry benzene (40 ml) at room temperature under dry nitrogen atmosphere. The reaction mixture was stirred for 20 minutes. White precipitate formed and the color of the solution changed from colorless to green. To this mixture a solution of 1-propanethiol (0.06 ml, 0.668 mmol) and triethylamine (0.09 ml, 0.66 mmol) in dry benzene (10 ml) was added dropwise. The stirring was continued for one hour, then filtered out the precipitate. The filtrate was washed

with water (20 ml), dilute solution of sodium bicarbonate (20 ml) and water (3 x 20 ml). The organic phase was dried over magnesium sulfate anhydrous, filtered and evaporated on a rotary evaporator to obtain a pale yellow viscous liquid (0.28 g., 56%).

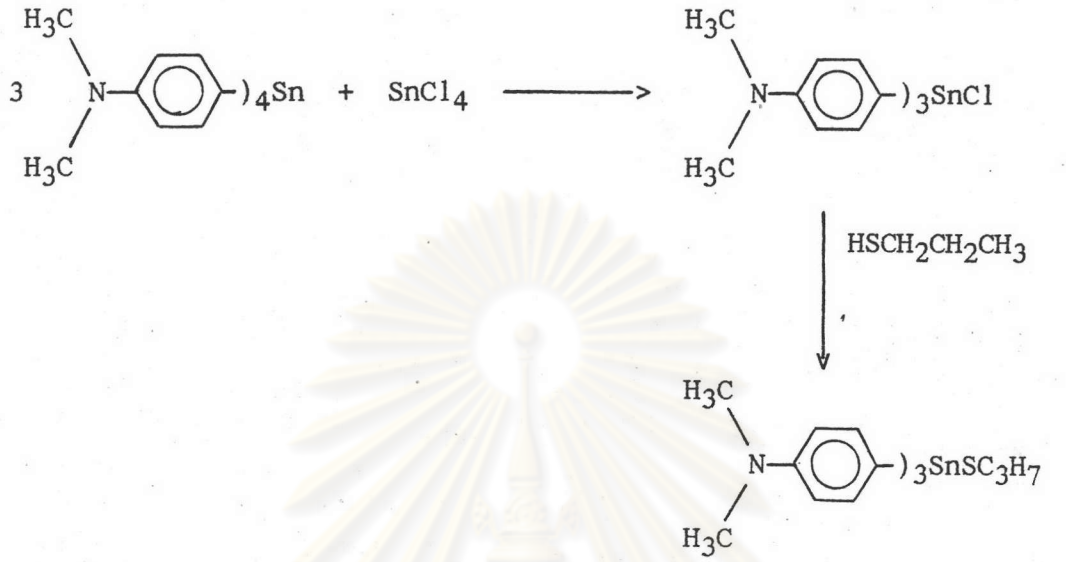
PMR (200 MHz, $CDCl_3$, ppm.) : 0.92 (t, 6H, $2SCH_2CH_2CH_3$), 1.59 (m, 4H, $2SCH_2CH_2CH_3$), 2.70 (t, 4H, $2SCH_2CH_2CH_3$), 3.10 (s, 12H, $2(CH_3)_2NC_6H_4$), 6.80 (d, 4H aromatic protons, J_{32} (Sn^{119}-H)= 12.18 Hz.) and 7.50 (d, 4H aromatic protons, J_{23} (Sn^{117}-H)= 24.01 Hz. and J_{23} (Sn^{119}-H)= 32.02 Hz.)

(Fig. 9)

CMR ($CDCl_3$, ppm.) : 13.30 (s, $SCH_2CH_2CH_3$), 27.57 (s, $SCH_2CH_2CH_3$), 29.50, 30.08 (s, $SCH_2CH_2CH_3$), 40.08 (s, $(CH_3)_2NC_6H_4$), 112.56 (s, C_2 and C_6, J (^{13}C-^{119}Sn)= 40.25 Hz), 122.58 (s, C_1), 136.88 (s, C_3 and C_5, J (^{13}C-^{119}Sn)= 35.22 Hz.), 151.45 (s, C_4).

(Fig. 10)

2.3.3 Preparation of tris-(4-dimethylaminophenyl)stannane propylsulfide (3).



(3)

In a 250 ml. flask was placed a solution of tetrakis-(4-dimethylaminophenyl)stannane (500 mg., 0.835 mmol) in dry benzene (30 ml). To this solution was added dropwise with stirring a solution of stannic chloride (0.03 ml, 0.278 mmol) in dry benzene (40 ml) at room temperature under dry nitrogen atmosphere. The reaction mixture was stirred for 45 minutes. White precipitate formed and the color of the solution changed from colorless to green. To this mixture a solution of 1-propanethiol (0.1 ml, 1.112 mmol) and triethylamine (0.1 ml, 1.2 mmol) in dry benzene (10 ml) was added dropwise. The stirring was continued for one hour, then filtered out of the

precipitate. The filtrate was washed with water (30 ml), dilute solution of sodium bicarbonate (30 ml) and water (3 x 30 ml). The organic phase was dried over magnesium sulfate anhydrous, filtered and evaporated under reduced pressure to give a pale yellow viscous liquid (0.23 g., 37.27%).

PMR (200 MHz, $CDCl_3$, ppm.) : 0.87 (t, 3H, $SCH_2CH_2CH_3$), 1.57 (m, 2H, $SCH_2CH_2CH_3$), 2.67 (t, 2H, $SCH_2CH_2CH_3$), 2.96 (s, 9H, $3(CH_3)_2NC_6H_4$), 6.79 (4H aromatic protons, J_{32} (Sn^{119}-H)= 11.25 Hz.) and 7.50 (d, 4H aromatic protons, J_{23} (Sn^{117}-H)= 21.88 Hz. and J_{23} (Sn^{119}-H)= 34.40 Hz.).

(Fig. 11)

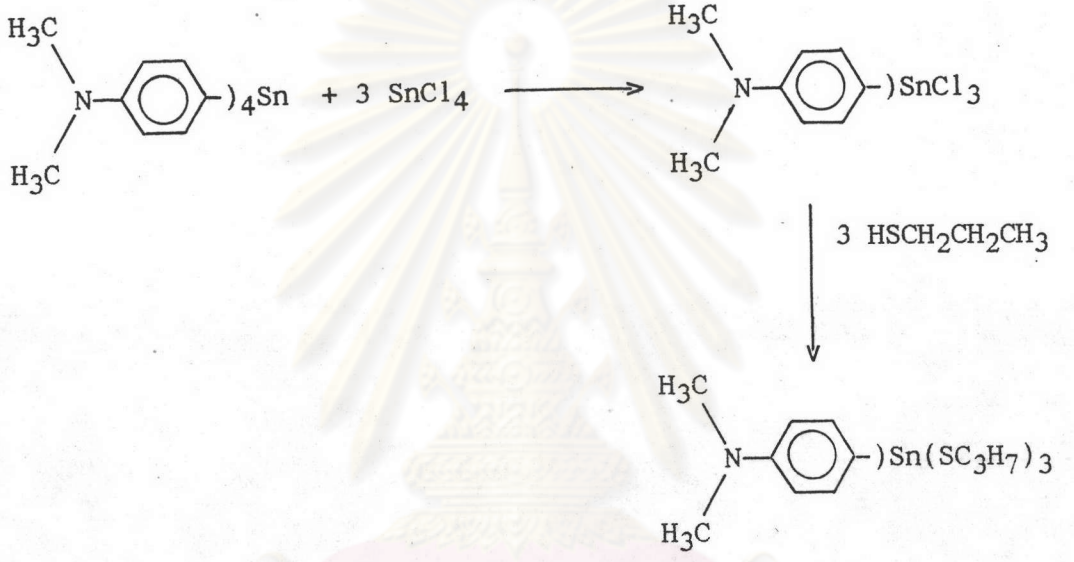
CMR ($CDCl_3$, ppm.) : 13.34 (s, $SCH_2CH_2CH_3$), 27.76 (s, $SCH_2CH_2CH_3$), 29.37 (s, $SCH_2CH_2CH_3$), 40.16 (s, $(CH_3)_2NC_6H_4$), 112.70 (s, C_2 and C_6, J (^{13}C-^{119}Sn)= 25.43 Hz.), 123.30 (s, C_1), 137.50 (s, C_3 and C_5, J (^{13}C-^{119}Sn)= 25.16 Hz.), 151.30 (s, C_4)

(Fig. 12)

HRMS m/e (%rel.int.) : 554.3594 (M^+) calculated for $C_{27}H_{37}N_3SnS$

554.9665 (M^+,13), 479.9556 (65), 239.9977 (100), 121.0784 (83). (Fig. 13, scheme 2)

2.3.4 Preparation of 4-dimethylaminophenylstannane tripropylsulfide (4).



(4)

In a 250 ml flask was placed a solution of tetrakis-(4-dimethylaminophenyl)stannane (200 mg, 0.334 mmol) in dry benzene (30 ml). To this was added dropwise with stirring a solution of stannic chloride (0.17 ml, 0.02 mmol) in dry benzene (40 ml) at room temperature under nitrogen atmosphere. The reaction mixture was stirred for 45 minutes. White precipitate formed and the color of the solution changed form

colorless to green. To this mixture a solution of 1-propanethiol (0.36 ml, 4.008 mmol) and triethylamine (0.59 ml, 4.21 mmol) in dry benzene (10 ml) was added dropwise. The stirring was continued for one hour and then filtered out the precipitate. The filtrate was washed with water (30 ml), dilute solution of sodium bicarbonate (30 ml) and water (3 x 30 ml). The organic phase was dried over magnesium sulfate anhydrous, filtered and evaporated under reduced pressure to obtain a pale yellow viscous liquid (0.12 g, 20 %).

PMR (200 MHz, $CDCl_3$, ppm.) : 0.96 (t, 9H, $3SCH_2CH_2CH_3$), 1.59 (m, 6H, $3SCH_2CH_2CH_3$), 2.83 (m, 6H, $3SCH_2CH_2CH_3$), 2.96 (s, 6H, $(CH_3)_2NC_6H_4$), 6.77 (d, 2H aromatic protons, J_{32} (Sn^{119}-H)= 11.15 Hz.) and 7.44 (d, 2H aromatic protons, J_{23} (Sn^{117}-H)= 23.52 Hz. and J_{23} (Sn^{119}-H)= 33.52 Hz.)

(Fig. 14)

CMR ($CDCl_3$, ppm.) : 13.25 (s, $SCH_2CH_2CH_3$), 27.46 (s, $SCH_2CH_2CH_3$), 30.14, 30.31, 30.76 (s, $SCH_2CH_2CH_3$), 40.07 (s, $(CH_3)_2NC_6H_4$), 112.67 (s, C_2 and C_6, J (^{13}C-^{119}Sn)= 51.45 Hz.),

CMR ($CDCl_3$, ppm.) : 122.76 (s, C_1), 136.87 (s, C_3 and C_5, J (^{13}C-^{119}Sn)= 39.87 Hz.), 151.47 (s, C_4). (Fig. 15)

HRMS m/e (%rel.int.) : 464.3086 (M^+) calculated for $C_{17}H_{31}NSnS_3$ 464.9820 (M^+,23), 389.9783 (33), 271.9763 (19), 195.1704 (22), 121.0877 (100). (Fig. 16, scheme 3)

2.4 Redistribution reaction between tetrakis-(4-dimethylamino-phenyl)stannane with butyltin trichloride.

Add a solution of butyltin trichloride in dry benzene 25 ml dropwise to a well-stirred solution of tetrakis-(4-dimethylaminophenyl)stannane in dry benzene 30 ml in a 250 ml flask fitted with a condenser, dropping funnel and inlet and outlet tubes for dry nitrogen. Stirring was allowed for one hour at 0-5 °C. White precipitate formed. Then, a solution of 1-propanethiol and triethylamine in dry benzene 25 ml was added dropwise into the mixture and the mixture was stirring for one hour and then filtered. The filtrate was washed with water 30 ml, dilute solution of sodium bicarbonate (30 ml) and water (3 x 30 ml). The organic layer was dried over magnesium sulfate, filtered and evaporated to dryness under reduced

pressure to give a pale yellow viscous liquid mixed with white solid. The reaction mixture was isolated by gas chromatography. The mole ratio and the amounts of tetrakis-(4-dimethylamino phenyl)stannane, butyltin trichloride and 1-propanethiol were tabulated in Table 4.

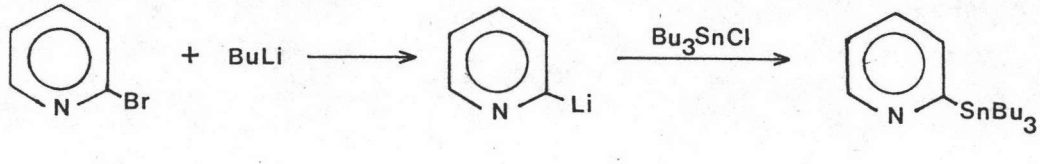
Gas chromatographic (conditions : packed column SE 30 ; column temperature 150 ^{o}C, injection temperature 220 ^{o}C, nitrogen carrier gas flow rate 40 ml/min and using FID detector)

Table 4 The mole ratios of the reactants and 1-propanethiol used in the reaction between tetrakis-(4-dimethylaminophenyl) stannane and butyltin trichloride

mole ratio	tetrakis-(4-dimethyl-aminophenyl)stannane	butyltin trichloride	1-propanethiol
1:1	1.2 g, 2.004 mmol	0.33 ml, 2.004 mmol	0.54 ml, 6.012 mmol
2:1	0.8 g, 1.336 mmol	0.11 ml, 0.668 mmol	0.54 ml, 6.012 mmol
1:2	1.8 g, 3.006 mmol	1 ml 6.012 mmol	1.62 ml 18.036 mmol

2.5 Redistribution reaction between tributyl-2-pyridylstannane with stannic chloride

2.5.1 Preparation of tributyl-2-pyridylstannane (11)



(11)

Place 50 ml of sodium-dried ether into a 250 ml three-necked round bottomed flask equipped with a dropping funnel to which was attached a calcium chloride drying tube, a reflux condenser combined with a gas inlet tube to allow the air in the apparatus assembly to be displaced by nitrogen and a thermometer. The air was displaced and maintained with a slow stream of nitrogen throughout the experiment. Fine lithium shavings was introduced (0.39 g., 0.06 mol) into the reaction flask. A solution of butylbromide (2.55 ml, 0.02 mol) in 30 ml of dried ether was placed in the dropping funnel, stirring was started and 1-2 ml of this solution was added into the reaction flask and cooled to about 0 ^{o}C. Add the remainder of butylbromide solution, then allow the reaction mixture to warm up to 15 ^{o}C during one hour.

To the cool solution of butyllithium at -20 ^{o}C in dried ice bath was added slowly, with stirring a solution of 2-bromopyridine (2.5 ml, 0.025 mol) in 20 ml of dried ether over a three-minute period and the red solution was stirred for seven minutes. To the solution of 2-pyridyllithium was added a solution of tributyltin chloride (6.9 ml, 0.02 mol), the red color suddenly disappeared and brown precipitated formed. The stirring was continued for two hours at room temperature. Then the reaction was stopped and washed with water (3x30 ml). The organic

phase was dried over magnesium sulfate, filtered and tributyl-2-pyridylstannane was isolated by fractional vaccuum distillation : 5.6 g., vapor temperature 60 ^{o}C at 4 mm., isolated yield 60 %.

IR (neat, max cm^{-1}) : 3080 (=C-H aromatic), 2900 (-C-H), 1590 (C=N), 1450 (C-H), 1130 (C-Sn), 750 (o-substitued) (Fig. 26)

PMR (200 MHz, $CDCl_3$, ppm.) : 0.87 (m, 9H, $3CH_3$), 1.15 (m, 6H, $3CH_2$), 1.36 (m, 6H, CH_2), 1.65 (m, 6H, CH_2) and 7.05, 7.40 and 8.65 (3m, 4H, pyridyl group)
(Fig. 27)

CMR ($CDCl_3$, ppm.) : 13.50 (s, CH_3), 17.20 (s, CH_2), 26.81 (s, CH_2), 27.23 (s, CH_2), 28.04 (s, CH_2), 29.03 (s, CH_2), 121.70 (s, C_2, J (^{13}C-^{119}Sn) = 30.19 Hz.), 132.30 (s, C_3, J (^{13}C-^{119}Sn)= 60.38 Hz.), 133.50 (s, J (^{13}C-^{119}Sn)= 10.06 Hz.), 150.00 (s, C_5, J (^{13}C-^{119}Sn)= 40.26 Hz.), 173.50 (s, C_1).
(Fig. 28)

MS m/e (%rel.int.) : 368.0 (M^+,28.0), 313.0 (100), 311.0 (72.9), 254.0 (36.4), 198.0 (87.9), 80.0 (8.44).

(Fig. 31, scheme 4)

Elemental analysis calculated for $C_{17}H_{31}NSn$ (368.132):

Calculated C 55.47% : H 8.48% : N 3.80% : Sn 32.24%

Found C 54.32% : H 8.42% : N 3.40% : Sn 31.19%

2.5.2 Redistribution reaction of tributyl-2-pyridyl stannane and stannic chloride in 1:1 mole ratio

The procedure was the same as in the redistribution reaction of tetrakis-(4-dimethylaminophenyl) stannane and stannic chloride except tributyl-2-pyridylstannane (0.51 g, 1.38 mmol), stannic chloride (0.16 ml, 1.38 mmol) and 1-propanethiol (5.52 mmol) were used. The reaction was carried out at room temperature and 0-5 ^oC. The product was yellow viscous liquid and white precipitate. This product was characterized by NMR in $CDCl_3$ and paper chromatography which the developing solvents was butanol-ethanol-water (3:1 and saturated with water). The compounds were detected by spraying with catechol violet after oxidation with ultra-violet irradiation.