

CHAPTER III

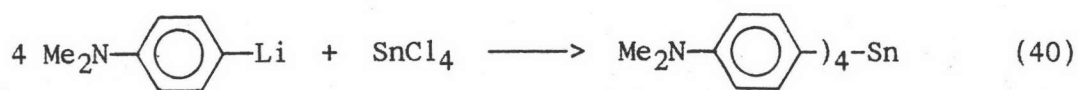
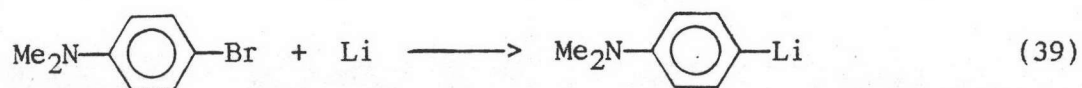
RESULTS AND DISCUSSION

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

The similarity in the reactions of the Grignard reagent and aryl lithium derivatives suggested that the latter might be useful in the synthesis of other organometallic compounds, especially since lithium derivatives of unusual types could be prepared. The lithium derivatives were all easily prepared in much the same manner as the Grignard reagents. The reactants and the solvents had to be absolutely dry and the moisture had to be totally excluded from the reaction medium. This can be achieved by using proper equipments and known procedure. This reaction, consisting of many steps, required careful operation.

The p-dimethylaminophenyl lithium was prepared from 4-bromo-N,N-dimethylaniline and lithium metal as in Eq.(39). To start the reaction a little of 4-bromo-N,N-dimethylaniline was added and the mixture was heated for a few minutes.

The synthesis of tetrakis-(4-dimethylaminophenyl)stannane was modified by replacing the solvent, diethyl ether, by benzene after the lithium derivative had been formed and allowed the lithium derivative to react with stannic chloride in benzene.



(1)

The structure of tetrakis-(4-dimethylaminophenyl)stannane was characterized by IR, NMR and MS as well as its melting point.

3.1.1 Infrared spectrum of tetrakis-(4-dimethylaminophenyl)stannane

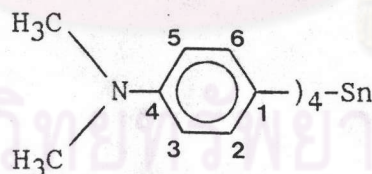
The IR spectrum of compound (1) (Fig.5) was tabulated in Table 5.

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Table 5 Characteristic group absorptions of tetrakis-(4-dimethylaminophenyl)stannane

Wavenumber (cm ⁻¹)	Functional groups	The vibration of bonds
3080	=C-H (aromatic)	stretch
2800-3000	C-H	stretch
1590, 1510	C=C	stretch
1350	C-N	stretch
1440, 1080	C-Sn	stretch
600-810	p-substituted	stretch

3.1.2 The NMR spectrum of tetrakis-(4-dimethylamino-phenyl)stannane.



The PMR data (Fig.6) showed the signals of two methyl groups of dimethylaniline group as singlet at δ 2.96 ppm. The eight aromatic protons were displayed at δ 6.77 with coupling constant of Sn¹¹⁹-H 9.27 Hz and 7.50 ppm. with coupling constant of Sn¹¹⁷-H 19.14 Hz and Sn¹¹⁹-H 26.10 Hz.

The CMR spectrum (Fig.7) indicated five carbons signals which corresponded to thirty two carbon atoms. There was one singlet at δ 40.08 ppm. which belonged to N-methyl carbons $((\text{CH}_3)_2\text{NC}_6\text{H}_4)$. The singlet at δ 112.79 ppm. with coupling constant of $^{13}\text{C}-^{119}\text{Sn}$ 26.65 Hz. was assigned to C_2 and C_6 . The singlet signal at δ 124.61 was C_1 , while the singlet at δ 138.10 ppm. with coupling constant of $^{13}\text{C}-^{119}\text{Sn}$ 20.82 Hz. was interpreted as C_3, C_5 . Another singlet at δ 150.8 ppm was assigned to C_4 .

3.1.3 Mass spectrum of tetrakis-(4-dimethylaminophenyl) stannane

The mass spectrum of tetrakis-(4-dimethylamino-phenyl)stannane (Fig.8) showed the fragmentation ion peak m/e (% relative intensity) : 600 (82.70, M^+), 480 (8.12), 240 (32.59), 120 (32.50). The possible mass fragmentation pattern of this compound (1) was shown in scheme 1.

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

The products from redistribution reaction between tetrakis-(4-dimethylaminophenyl)stannane and stannic chloride were characterized by NMR and MS. The products gave the similarity patterns because they were in the same series, but the

intensity of each peak was different. IR spectra were not available at this time. This problem could be overcome by the characterization with high resolution mass spectrometry which gave exact molecular ions.

3.2.1 PMR and CMR of the products from redistribution reaction of tetrakis-(4-dimethylaminophenyl)stannane and stannic chloride

The PMR and CMR data of the products in this reaction could be used to confirm the molecular structures. The molecular structures of bis-(4-dimethylaminophenyl)stannane dipropylsulfide (2), tris-(4-dimethylaminophenyl)stannane propyl sulfide (3), (4-dimethylaminophenyl)stannane tripropylsulfide (4) were shown in Fig 4.

The PMR data displayed the signal of the methyl group of propanethiol groups at δ 0.87-0.96 ppm. ($\text{SCH}_2\text{CH}_2\text{CH}_3$). The multiplet at δ 1.57-1.59 ppm. was assigned to protons in methylene group ($\text{SCH}_2\text{CH}_2\text{CH}_3$). The triplet at δ 2.67-2.83 ppm. was the methylene group which adjoined to sulfur atom ($\text{SCH}_2\text{CH}_2\text{CH}_3$). Another singlet at δ 2.96-3.10 ppm. was the protons of two methyl groups in dimethylaniline group ($(\text{CH}_3)_2\text{NC}_6\text{H}_4$). The doublet at 6.80 ppm. with coupling constant of $\text{Sn}^{119}\text{-H}$ in range 11.15-12.18 Hz. and another doublet at δ 7.50 ppm. with coupling constant of $\text{Sn}^{117}\text{-H}$ in range 21.88-24.01 Hz. and $\text{Sn}^{119}\text{-H}$ in range 21.10-34.40

H_z. were interpreted as aromatic proton in para-substitution.

The CMR spectrum showed just eight peaks. Singlet at δ 13.00-13.34 ppm. was assigned to methyl carbon (SCH₂CH₂CH₃).

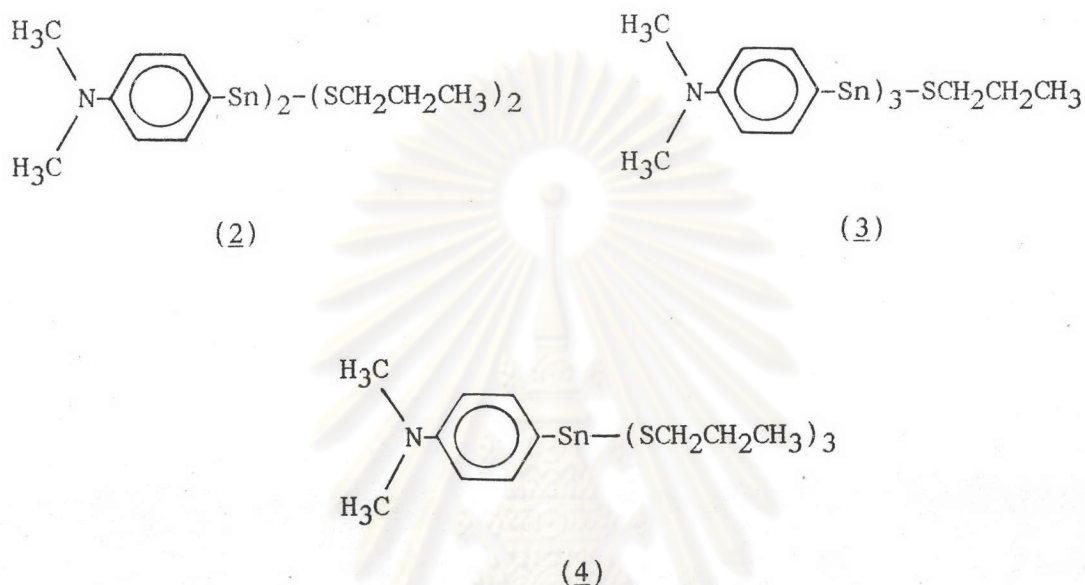


Figure 4 (2) Bis-(4-dimethylaminophenyl)stannane dipropylsulfide
 (3) Tris-(4-dimethylaminophenyl)stannane propylsulfide
 (4) (4-dimethylaminophenyl)stannane tripropylsulfide

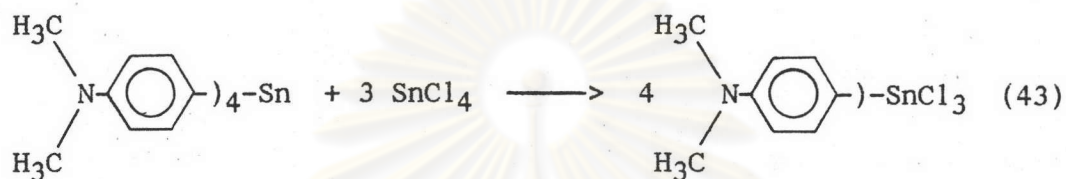
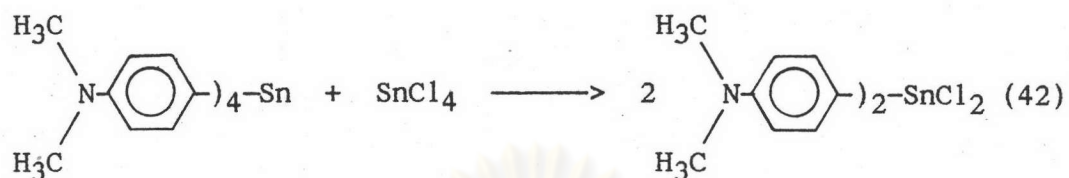
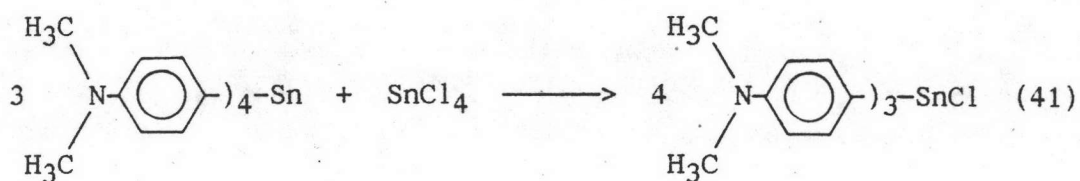
The other singlet at δ 27.46-27.76 ppm. was methylene carbon (SCH₂CH₂CH₃). A singlet at δ 29.37-30.76 ppm. was the S-CH₂ group. The singlet at 40.07-40.16 ppm. was assigned to N-methyl carbons. The singlet signals of aromatic carbons were exhibited at δ 112.56-112.70 ppm. (C₂ and C₆) with coupling constant of ¹³C-¹¹⁹Sn in 25.43-51.45 Hz., 122.58-123.30 ppm. (C₁), 136.87-137.50 ppm. (C₃ and C₅) with coupling constant of ¹³C-¹¹⁹Sn in 25.16-39.87 Hz. and 151.30-151.47 ppm. (C₄).

3.2.3 Mass spectrum of the products from redistribution reaction of tetrakis-(4-dimethylaminophenyl) stannane and stannic chloride.

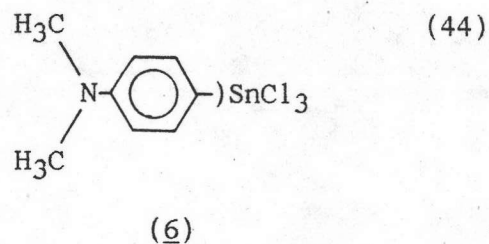
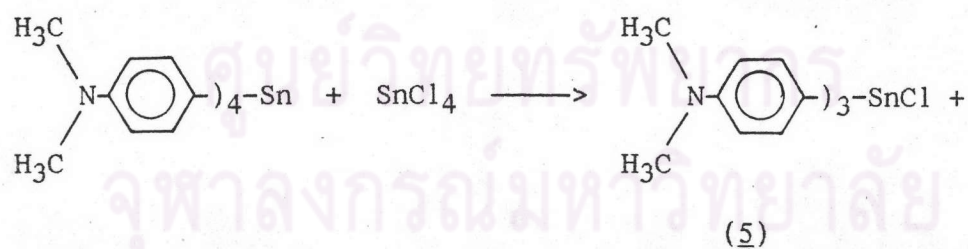
The mass spectrum of compound (3) (Fig.13) from 3:1 mole ratio of the reactants exhibited the fragmentation ion peak m/e (%rel. int.) : 554.9665 (13), 479.9556 (65), 239.9977 (100), 121.0784 (83). The possible mass fragmentation pattern of this compound was displayed in scheme 2.

The mass spectrum of compound (4) (Fig.16) from 1:3 mole ratio of the reactants showed the molecular ion peak at m/e (%rel. int.) : 464.9820 (23), 389.9783 (33), 271.9763 (19), 195.1704 (22), 121.0877 (100). The possible mass fragmentation pattern of this compound was shown in scheme 3.

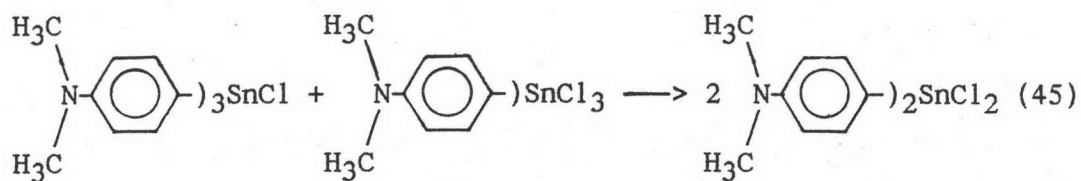
After preparation of tetrakis-(4-dimethylaminophenyl) stannane (1), according to the method described above, the redistribution reaction with stannic chloride was carried out, to yield either mono-, di- or tri-organotin chlorides containing dimethyl amino groups. Depending on the mole ratio of the reactants one of the three following reactions seemed to proceed :



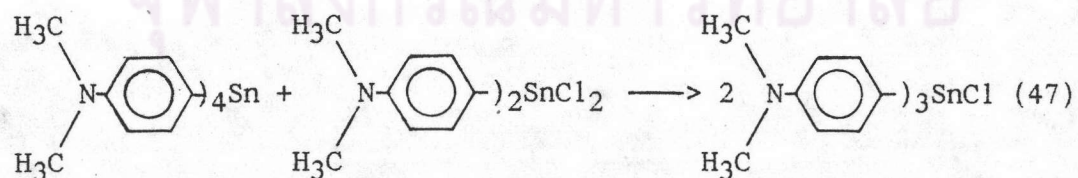
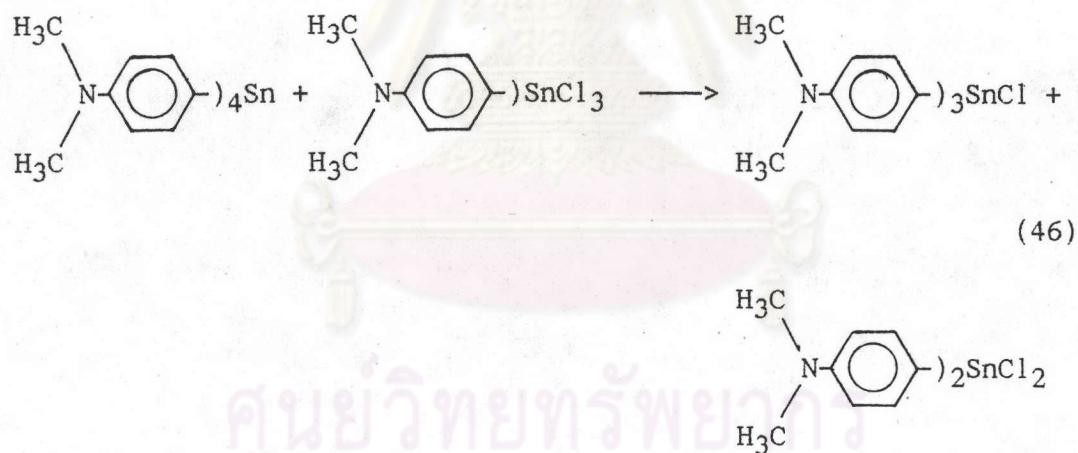
The first step in the consecutive reaction occurring in the Kocheskov redistribution reaction should be as Eq.(44). When the redistribution of the reactants was carried out at room temperature an equimolar mixture of tris-(4-dimethylaminophenyl) stannane chloride (5) and (4-di-methylaminophenyl)stannane trichloride (6) was obtained.



For the equimolar amounts of the reactants, the subsequently occurring reaction was shown below :

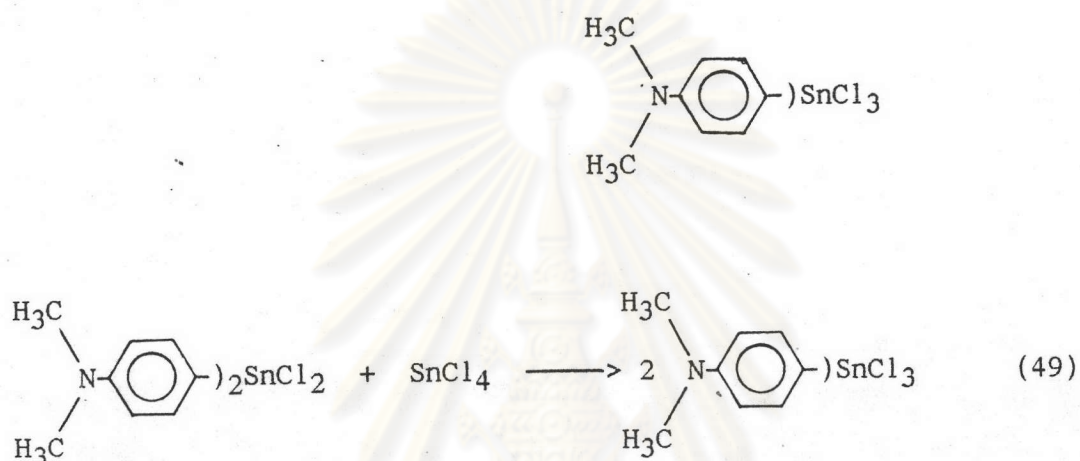
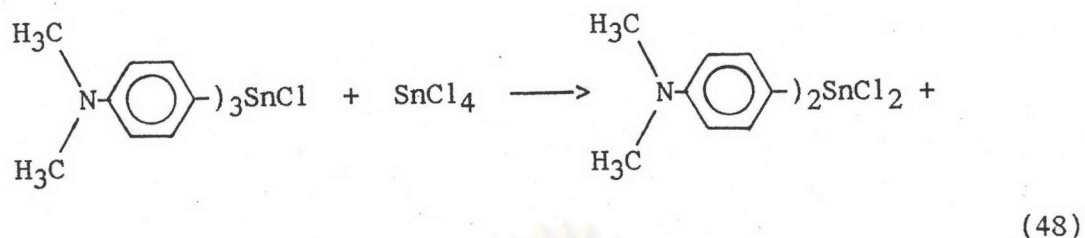


If there was an excess of tetrakis-(4-dimethylamino-phenyl)stannane, the resulting mixture after completion of reaction (44) and consisting of compound (1), (5) and (6) underwent further reaction to give compound (5) and some of compound (7). This was expressed in the following reactions. :



If there was an excess of stannic chloride in mixture of

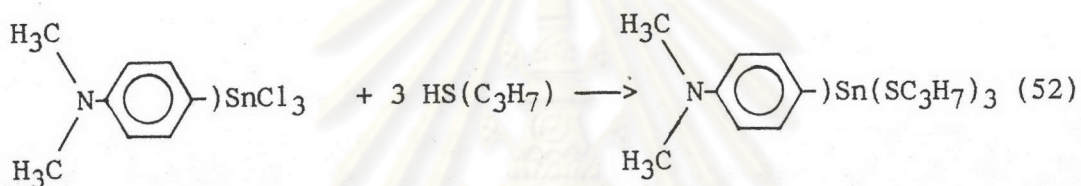
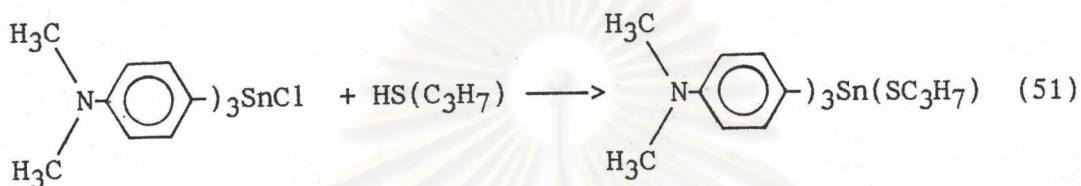
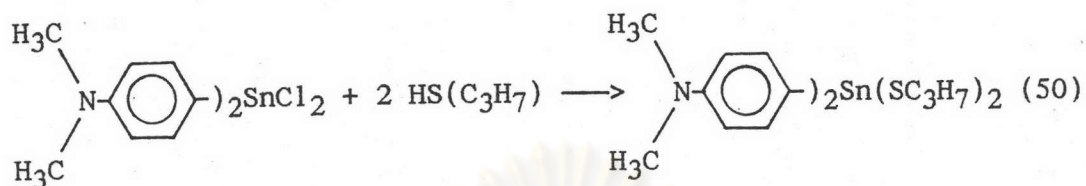
reactants after completion of reaction (44), the following reactions became important :



The products also contained traces of impurity which was formed from the acid hydrolysis of compound (1) with HCl generated during the reaction by residual water.

During the addition of stannic chloride in benzene to compound (1), white precipitate was formed. It was, presumably, an intermolecular complex of compound (5), (6) and (7). It was found that the reactions were the same either at room temperature or heating the mixture for one hour. Because compound (5)-(7) were sensitive to moisture, therefore they have not been isolated but rather quenched the reaction mixture with stoichiometric

amounts of propanethiol and a base. Triethylamine was used as a base and triethylamine hydrochloride was filtered off and the products were worked up as usually.



Because of unpleasant smell of the products containing propanethiol group, 2-mercaptobenzothiazol was used instead of propanethiol. The experiment underwent in the same manner as explained above, however, the expected product was not obtained, instead the starting materials were recovered. Thus, 2-mercapto benzothiazol was not suitable for this reaction presumably it was too bulky.

3.3 Redistribution reaction of tetrakis-(4-dimethylaminophenyl) stannane and butyltin trichloride

Mixed dimethylaminophenylstannane compounds were prepared

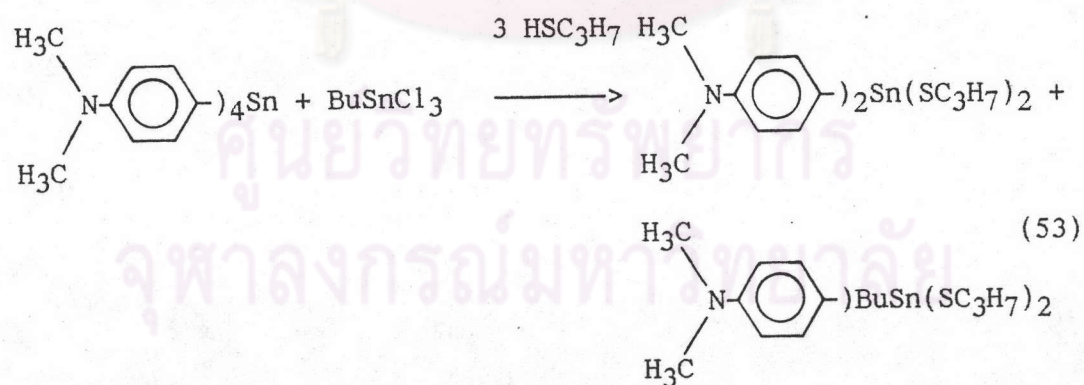
by redistribution reaction in the same manner as compound (2)-(4), but the reaction had to proceed at low temperature around 0-5 °C because the alkylation of butyltin trichloride with tetraaryltin was exothermic. When a solution of butyltin trichloride in dry benzene was added to a solution of tetrakis-(4-dimethylaminophenyl)stannane, some white precipitate formed. Then the reaction mixture was quenched with 1-propanethiol.

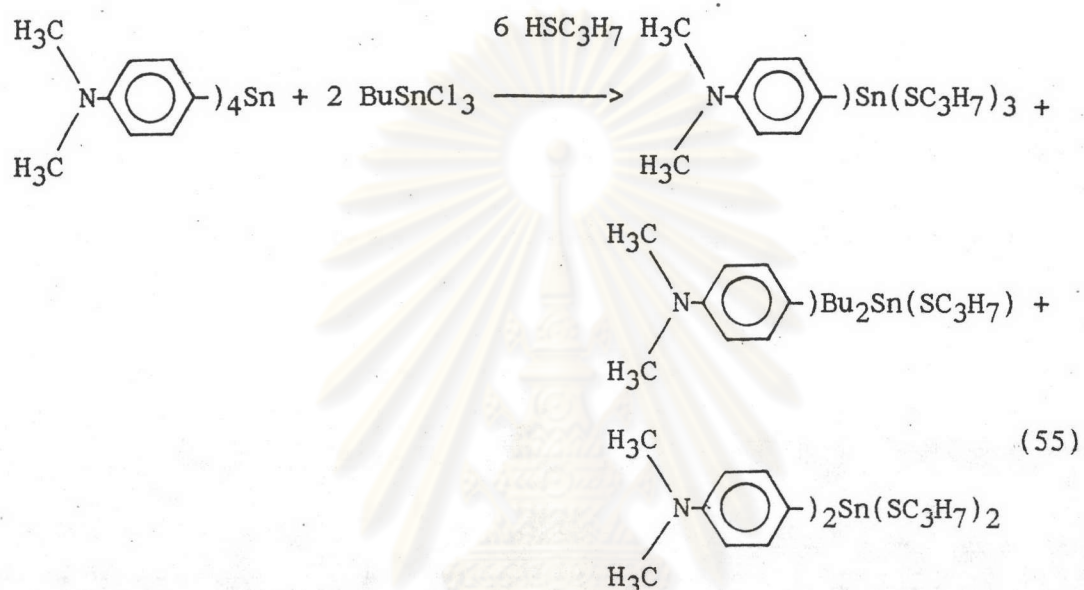
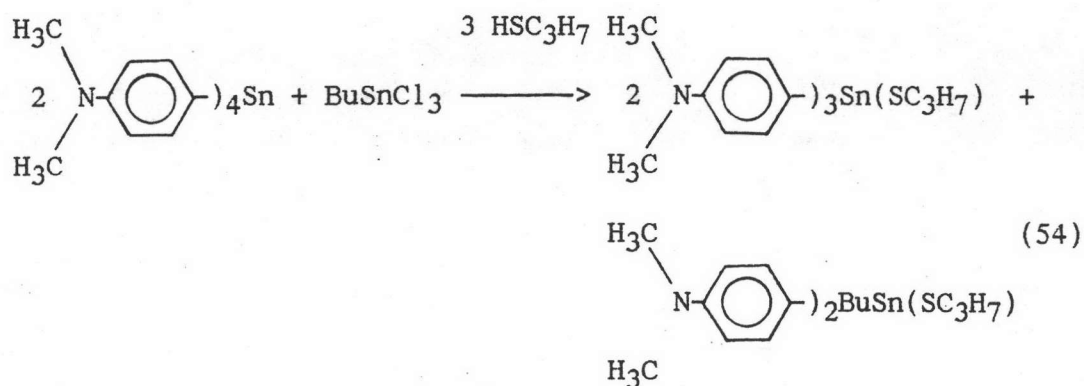
The reaction mixtures in 1:1 (8), 2:1 (9) and 1:2 (10) mole ratios were determined by NMR which were shown in Fig. 17-22. The reaction mixtures were passed through silica gel, however, silica gel was too acidic and it broke Ph-Sn bond to give dimethylaniline. Moreover, paper chromatography technique was tried without success. Thus, all mixtures were monitored by GC, which proved to be quite valuable. Gas chromatograms of the reaction mixture (8), (9) and (10) were shown in Fig. 23, 24 and 25, respectively.

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Table 6 Retention time of the reaction mixtures and compounds
(2)-(4)

compounds	R _t (min)
The reaction mixture of 1:1 mole ratio (8)	8.89, 13.09
The reaction mixture of 2:1 mole ratio (9)	1.04, 11.80
The reaction mixture of 1:2 mole ratio (10)	7.53, 12.10
compound (2)	8.92
compound (3)	1.09
compound (4)	7.49



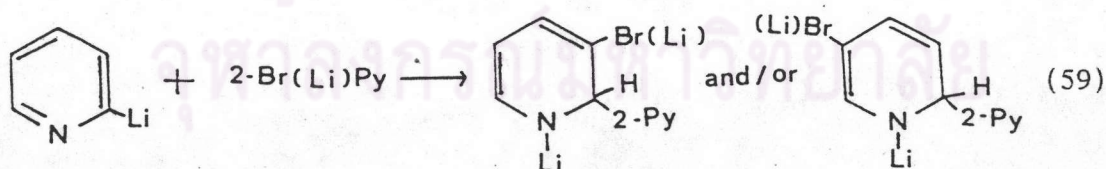
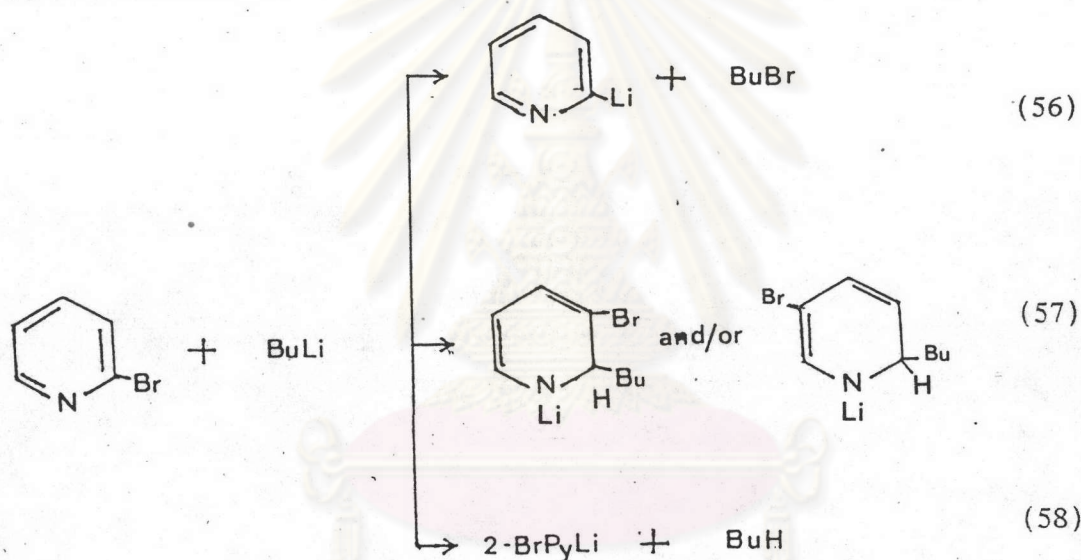


From Table 6, it showed that there were compound (2), (3) and (4) in the reaction mixture 1:1, 2:1 and 1:2, respectively. The others could be the expected products. Thus the reaction could proceed as Eq. (53)-(55).

3.4 Preparation of tributyl-2-pyridylstannane (11)

Tributyl-2-pyridylstannane was synthesized by metal-halogen exchange between butyllithium and 2-bromopyridine to obtain 2-bromopyridyllithium which was an intermediate, and

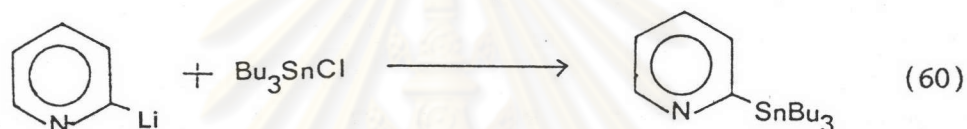
then reacted with tributyltin chloride. Compounds such as pyridyllithium derivatives are unobtained by direct reaction of lithium with the halides, and are only rarely accessible by metallation, because of the ease with which the pyridine is alkylated. In contrast, such derivatives are readily prepared by this method, since very mild conditions may be employed. Preparation of pyridyllithium is not achieved at 30–35 °C for twenty hours due to the $-N=C$ linkage has ample opportunity to add not only the interconverting agent (Eq.56) but also the pyridyllithium product as it is formed (Eq.59).



Failure to curb the activity of the azomethine function accounts in considerable. Subsequently, the application of the

interconversion technique at low temperature ($-35\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$) and short reaction time (5 to 15 minutes) was established as the most suitable means for suppressing the $-N=C$ activity.

The red solution of 2-pyridyllithium was quenched with tributyltin chloride in a slightly excess amount to be sured that the reaction was complete. The reaction in this part was undergone at room temperature. Quenching reaction was shown as Eq.(60).



Furthermore, there were some impurities in the reaction mixture and tributyl-2-pyridylstannane as a yellow green liquid which had a high boiling point. The compound (11) was purified by fractional vacuum distillation at 4 mm in good yield. The elemental analysis was consistent well with the formula tributyl-2-pyridylstannane.

3.4.1 IR spectrum of tributyl-2-pyridylstannane

The IR spectrum (Fig.26) tributyl-2-pyridylstannane was displayed in Table 6.

Table 7 Characteristic group absorptions of tributyl-2-pyridyl stannane

Wavenumber (cm ⁻¹)	Functional group	The vibration of bonds
3080 cm ⁻¹	=C-H (aromatic)	stretch
2600-2800 cm ⁻¹	C-H	stretch
1590 cm ⁻¹	C=N	stretch
1450 cm ⁻¹	C-H	bend
1130 cm ⁻¹	C-Sn	stretch
750 cm ⁻¹	o-substituted	

3.4.2 NMR spectrum of tributyl-2-pyridylstannane

The PMR spectrum (Fig.27) indicated the signal of methyl carbons at δ 0.87 ppm. (H_a). The singlet at δ 1.15 ppm., 1.36 ppm. and 1.65 ppm. were assigned as H_b, H_c, H_d of methylene groups, respectively. The four protons of pyridyl group were shown at δ 7.05 ppm., 7.40 ppm. and 8.65 ppm. as multiplet signals.

The CMR data (Fig.28) showed eleven signals which corresponded to seventeen carbon atoms in this spectrum. A singlet at δ 13.50 ppm. was assigned to methyl carbons (C_a).

The singlet at δ 17.20 ppm. was the methylene group (C_b). Two singlet signals at δ 26.81 and 27.23 ppm. were shown to be methylene carbons as labeled to C_d and C_c , respectively. Two singlet carbons at δ 28.04 ppm. and 29.03 ppm. also exhibited the methylene carbons as indicated to C_f and C_e , respectively. Five singlet signals at δ 121.70–150.00 ppm. with coupling constant of $^{13}C-^{119}Sn$ in range 10.06–60.38 Hz. displayed four carbons in pyridyl group as labeled to C_2 , C_3 , C_4 , and C_5 , respectively. The final singlet at δ 173.80 ppm. was C_1 , attached to the withdrawing N and Sn atom, showed the signal at downfield.

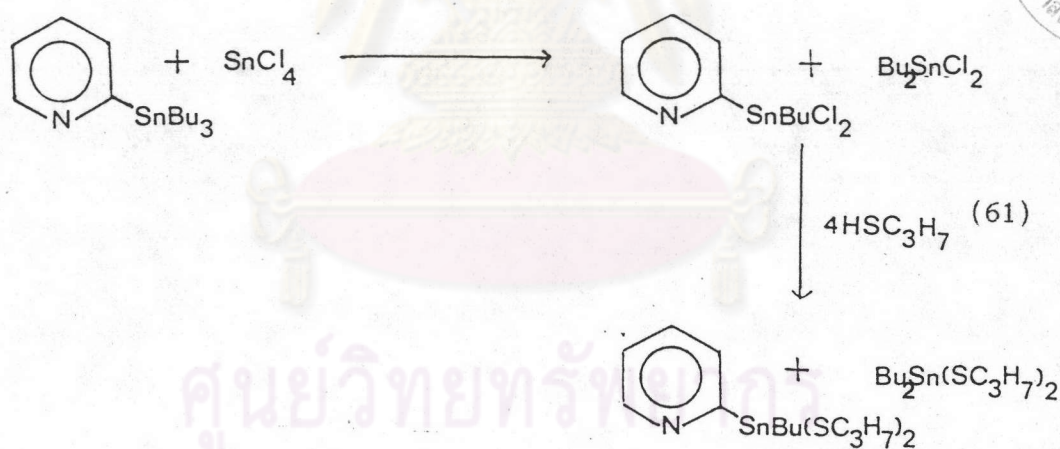
3.4.3 Mass spectrum of tributyl-2-pyridylstannane

The mass spectrum (Fig. 31) showed the molecular ion peak at m/e (%rel.int.) : 368.0 (28.0), 313.0 (100), 311.0 (72.9), 254.0 (36.4), 198.0 (87.9), 80.0 (8.44). The possible mass fragmentation pattern of this compound was exhibited in scheme 4.

3.5 Redistribution reaction of tributyl-2-pyridylstannane and stannic chloride

Redistribution reaction between tributyl-2-pyridylstannane with stannic chloride was studied in the same manner as described above. The experiment was proceeded in the

nitrogen atmosphere by using benzene as solvent. A solution of stannic chloride was added to tributyl-2-pyridylstannane solution either at room temperature and 0-5 °C, and then the color of the solution changed from yellow to colorless and some white precipitate formed. After the reaction mixture was quenched by 1-propanethiol in stoichiometric amount, The solvent was evaporated under reduced pressure. Yellow liquid and white solid were obtained and characterized by NMR in CDCl_3 . The white solid was insoluble in any organic solvent. The PMR and CMR of the mixture were shown in Fig. 32 and 33. In fact, redistribution reaction of tributyl-2-pyridylstannane and stannic chloride according to Kocheskov reaction, was shown in Eq.(61)



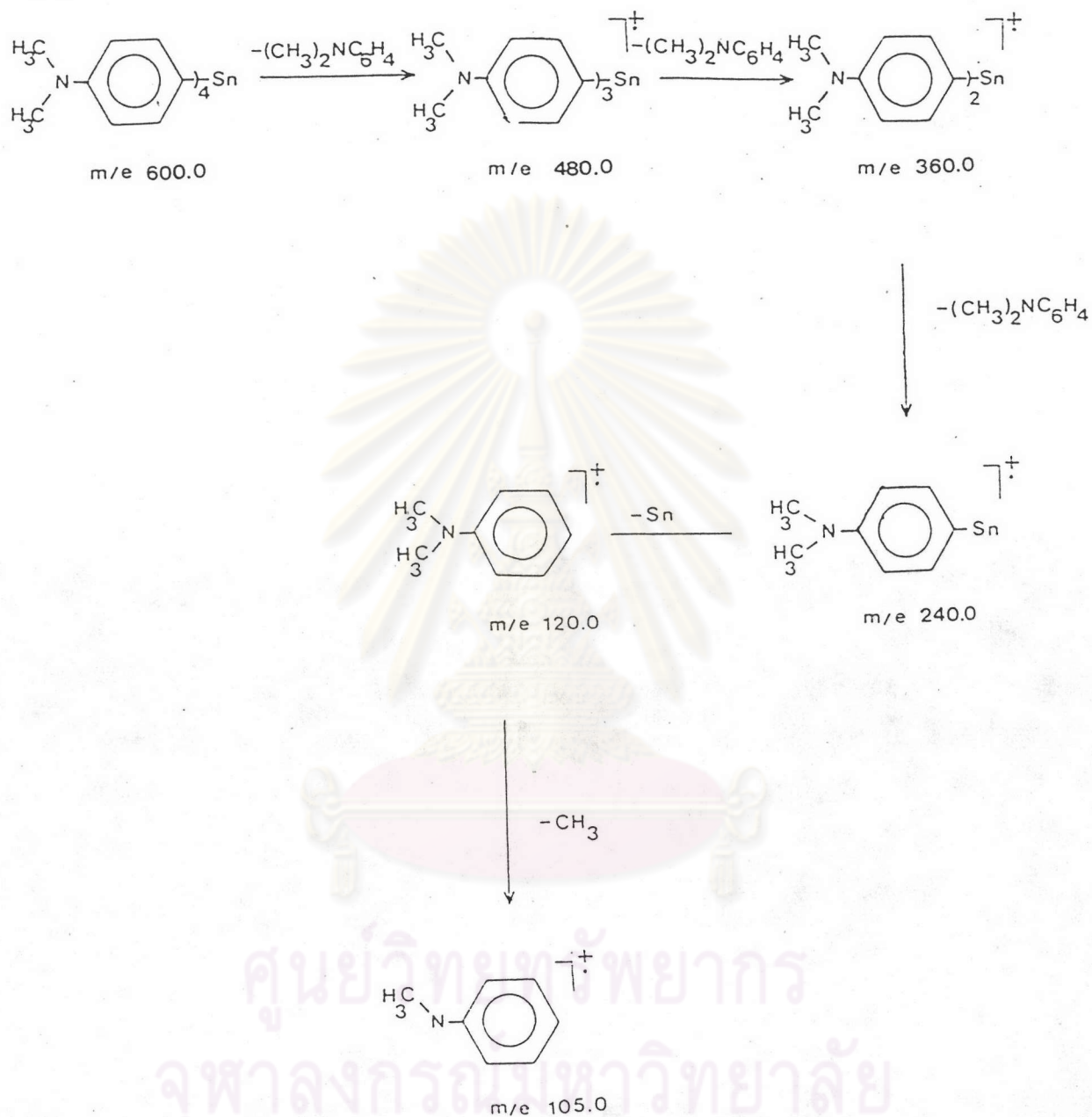
NMR examination of the mixture showed no significant formation of the expected products. In addition, paper chromatography was used to monitor the product mixture. The R_f value of the mixture was 0.00 and 0.88 while the R_f value of tributyl-2-pyridylstannane

and dibutylstannane dipropylsulfide were 0.88 and 0.70, respectively. From the R_f values above, they were shown that the starting material was recovered and the redistribution reaction of tributyl-2-pyridylstannane and stannic chloride was not proceeded as expect presumably stannic chloride may be too acidic to compound (11) so that it could break pyridyl-tin bond and gave tin oxide.

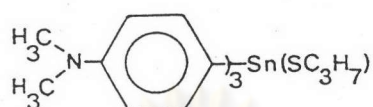


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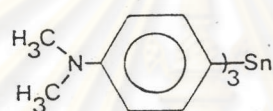
Scheme 1 The possible mass fragmentation of tetrakis-(4-dimethylaminophenyl)stannane (1)



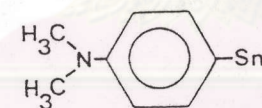
Scheme 2 The possible mass fragmentation of tris-(4-dimethylamino-phenyl)stannane propylsulfide (3)



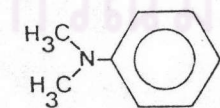
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m/e 479.9556

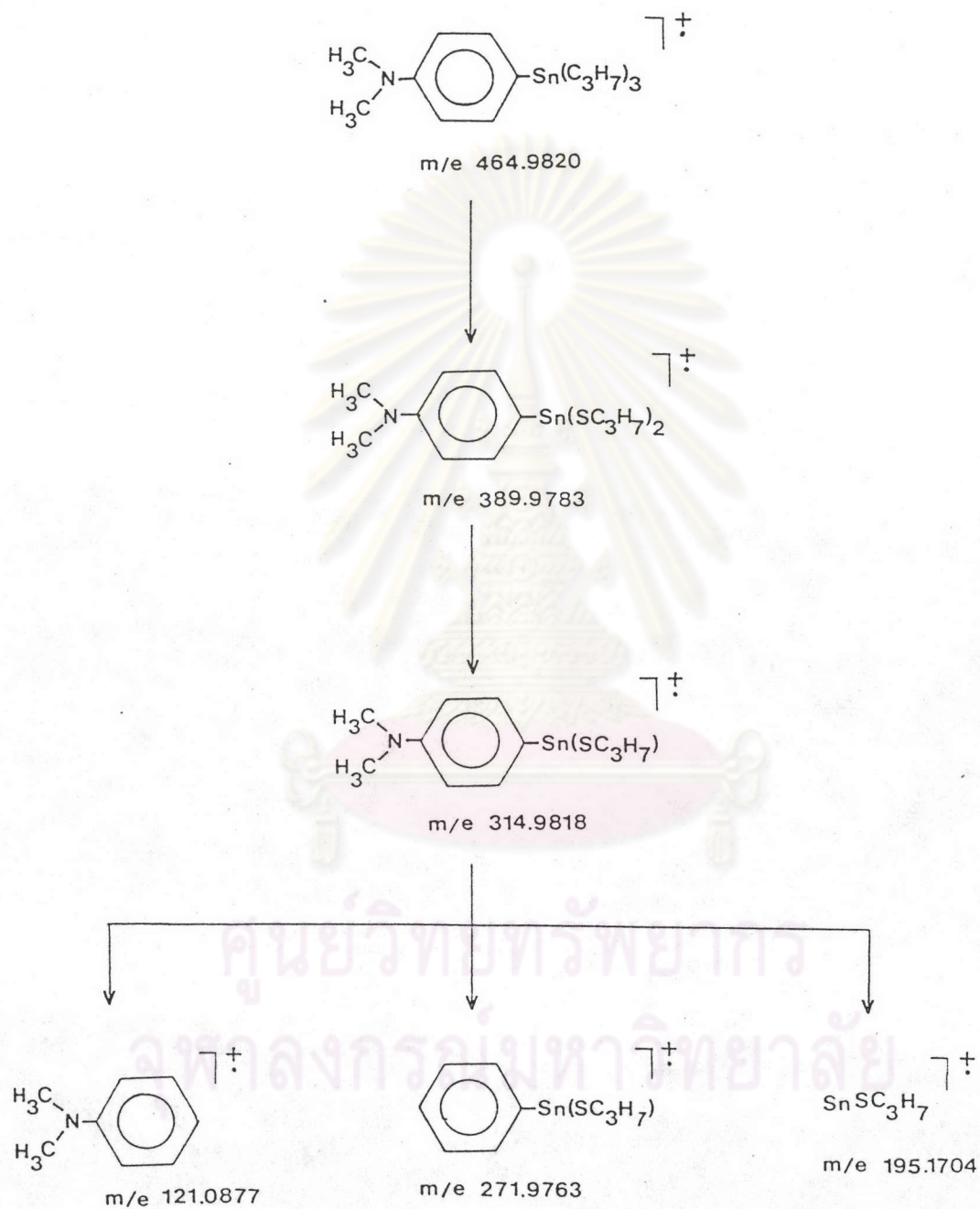


m/e 239.9977



m/e 121.0784

Scheme 3 The possible mass fragmentation of 4-dimethylaminophenyl stannane tripropylsulfide (\pm)



Scheme 4 The possible mass fragmentation of tributyl-2-pyridyl stannane (11)

