



## CHAPTER IV

### RESULTS AND DISCUSSION

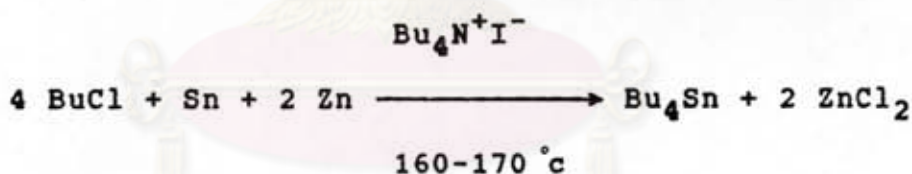
#### 4.1 Synthesis of Tetraalkyltin Compounds

The experimental results from various processes for the synthesis of organotin compounds indicated that the direct synthesis of tetraorganotins from tin metal and alkyl halides, although looked very attractive from its simplicity point of view, gave rather poor yields and required quite high temperature and pressure. This process needed an expensive catalyst, i.e. a quaternary ammonium salt, that must be recovered in the industrial application. The process also gave a mixture of products that were difficult to separate. However, this process has to be improved further before it can be used industrially.

Many factors influenced the yield of tetraalkyltins in the direct synthesis, and several attempts were made to improve it : (1) type of alkyl halides, previous investigators suggested the use of alkyl bromides to increase the rate of reactions, but it is more expensive than alkyl chlorides , (2)

reaction media, solvents were used to reduce the viscosity of the reaction mixture and must be inert, (3) auxilliary metal, zinc was used in the reaction, because zinc is more electropositive than tin but zinc chloride thus formed increase the viscosity of the reaction mixture and it is difficult to recover the product, (4) catalyst, the effective catalysts were organic bases or quaternary salts, the preferred catalysts were tetraalkylammonium iodide and trialkylamines.

Tetrabutyltin could be synthesized directly from tin powder and n-butyl chloride by using tetrabutylammonium iodide as a catalyst and solvent and zinc as an auxiliary metal at 160-170 °c.



The direct synthesis of tetrabutyltin was carried out at 160 °c, under atmospheric pressure and gave tetrabutyltin in about 40% yield. The procedure was repeated, but a pressure reactor was used in place of ordinary glassware. The later attempt gave a mixture of several organotin compounds, having dibutyltin dichloride as the main product, with a total yield of 54% . The production of dibutyltin dichloride as a major product might be due to the single charge of the

reactants to the reactor, which was necessary in a pressure reactor, and the viscosity of the mixture which increased very rapidly. Further attempt was made by using mesitylene (b.p. 160 °C) as a solvent, and tributylamine as a catalyst, instead of a quaternary ammonium salt. This modification gave tributyltin chloride as the major product and the yield of tetrabutyltin also increased but the total quantity of all organotin products was decreased, which might be due to the dilution of the reactants.

#### 4.2 Organotin Synthesis by Grignard Reaction

The synthesis of organotin compounds by Grignard reaction has been used industrially for several years. The reactants and the solvents must be absolutely dry and the humidity must be totally excluded from the reaction medium, but this can be achieved by using proper equipment and procedure. The Grignard synthesis, consisting of many steps, requires careful operation and the reactants are more expensive than the direct synthesis. However, it has good selectivity and provides higher yield.

This synthesis was modified by replacing the solvent, ether, with toluene after the Grignard reagent had been synthesized and allowed the Grignard reagent to



react with stannic chloride in toluene. This increased the yield of the product and prevent the formation of a solid stannic chloride- ether complex, which would otherwise clog the dropping funnel. It was believed that the product yield increased because stannic chloride is more soluble in toluene and toluene has much higher boiling point than ether.

Several organotin compounds were prepared by various modifications, which could be summarized as follows:

In the preparation of tetraallyltin and diallyldibutyltin by Grignard reaction, allyl chloride and allyl bromide were used as starting materials and was found that allyl chloride provided higher yield of the products than allyl bromide, but starting the reaction with allyl bromide was by far easier. Allyl chloride also formed insoluble chloride-Grignard reagent complex which caused difficulty in stirring. A mixture of tetraallyltin and triallyltin chloride formed could not be separated by distillation, but could be achieved by precipitating the triallyltin compound as triallyltin fluoride by addition of potassium fluoride solution. Another advantage in using toluene as a solvent, besides increasing the yield, was that, it was easy to separate the inorganic salt formed during the reaction, which were insoluble in toluene. These could be separated

together with excess magnesium by filtration. The filtrate which contained the products and excess Grignard reagent which could be readily decomposed by addition of saturated ammonium chloride solution. This modified Grignard synthesis provided selective organotin compounds with higher yield, especially for the preparation of tetraorganotin compounds, and at present has several advantages over the direct synthesis.

Characterization of the products with NMR spectroscopy showed the characteristic peaks of Sn and other nuclei (H and C) coupling. When  $\text{CH}_2$  group attached to tin atom in some compounds. The coupling constants ( $J_{\text{Sn-H}}$ ,  $J_{\text{Sn-C}}$ ) could be found in such compounds; for example, in  $^{13}\text{C}$  NMR of tetrabutyltin;  $J(^{119}\text{Sn}-^{13}\text{C}) = 156.3 \text{ Hz}$ , in  $^1\text{H}$  and  $^{13}\text{C}$  NMR of tetraallyltin;  $J(^{119}\text{Sn}-^1\text{H}) = 31.5 \text{ Hz}$  and  $J(^{119}\text{Sn}-^{13}\text{C}) = 125.7 \text{ Hz}$ .

#### 4.3 Anti-Knock Properties of Organotin Compounds

A number of organotin compounds was prepared and tested for their antiknock properties in gasoline engine. These compounds were selected on the basis of their stabilities and their solubilities in gasoline. According to accepted theory of knock suppression, we selected tin compounds with the tendency to decompose and form tin metal or tin oxide in the combustion



chamber to deactivate the free radical chain carriers. Allyl and benzyltin compounds including their complexes were selected for this purpose.

Results from octane number determinations of gasoline base mixed with organotin compounds showed that tetrabutyltin, diallyldibutyltin, and dibenzylidibutyltin have antiknock property. Tetrabutyltin increased octane number of base oil by 2-3 RON, 2-2.5 MON and diallyldibutyltin added 3-4 RON, 2-2.5 MON and dibenzylidibutyltin provided the addition of 1-2.5 RON, 1 MON to gasoline base. The increase in octane number differs due to tin susceptibility to the base oil and testing conditions (as described in the introduction). The tetraoctyltin increased the octane number by 1-2 units, while some of the compounds such as tribenzyltin chloride and its nitrogen complexes dissolved in gasoline only sparingly and did not give good results.

Benzyltin compounds enhanced octane in gasoline, but when tribenzyltin compound was used instead of dibenzyltin compound, it did not increase the octane as much as dibenzyl compound. This might be due to the high boiling point of the tribenzyl compounds. When the number of allyl groups in allyltin compounds was increased, the octane number also increased. This suggested the potential of tetraallyltin, but this compound decomposed readily in gasoline solution into a

white solid believed to be stannic oxide(25). A novel complex, triallyltindiethyldithiocarbamate was stable in air, but decomposed quickly in gasoline solution.

Blends of organotin compounds in leaded gasoline were determined in order to study the effect of tin compounds with lead antiknock compounds, whether they would be promoter or antagonist to lead. As the results shown, tetrabutyltin (which showed antiknock effect) and tribenzylbutyltin depressed the lead effectiveness. They showed antagonistic effect to lead by reducing the octane number of the leaded gasoline base by 2-3 units. The mechanism for this deactivation of alkylleads by alkyltins should be investigated further.



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A comparison of antiknock property improvement of the organotin compounds was shown in Fig. 20 and 21.

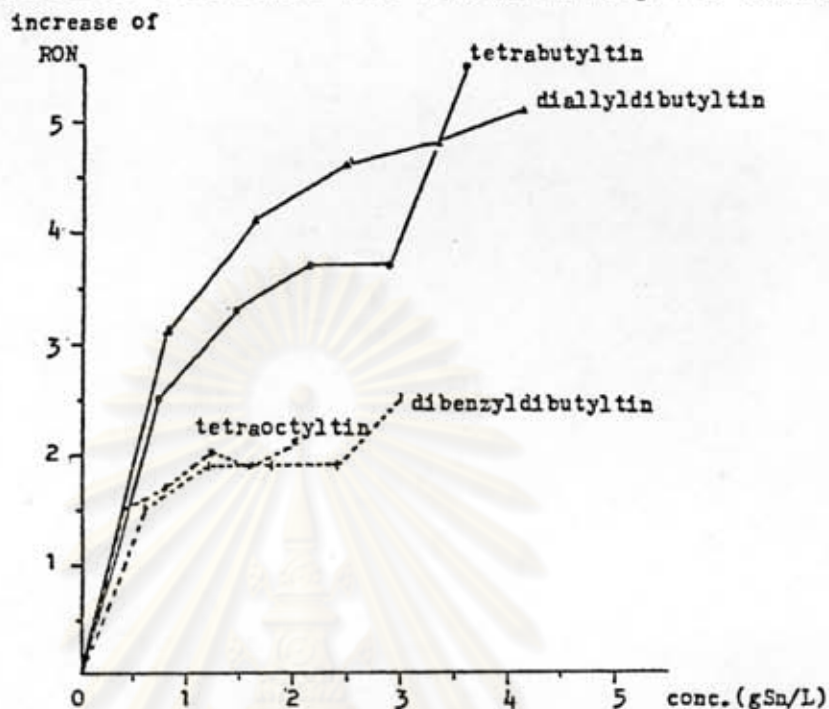


Figure 20

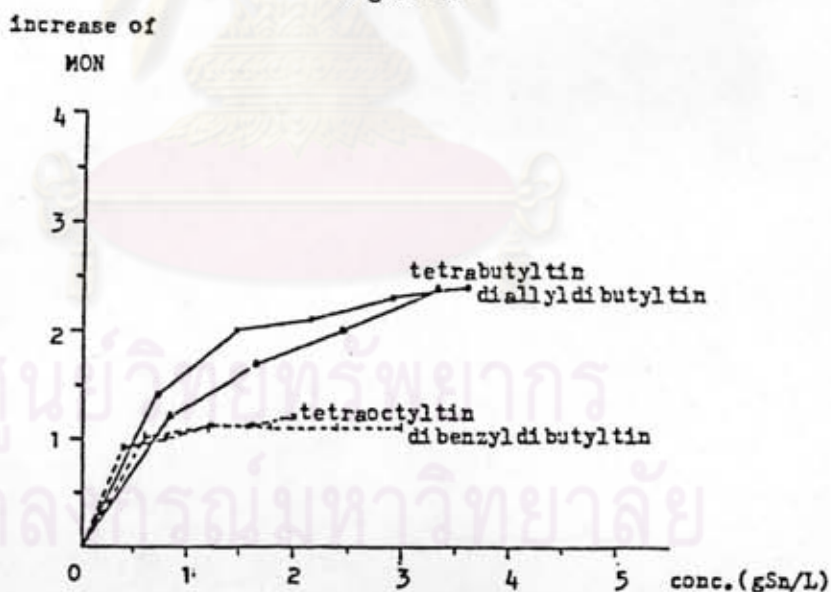


Figure 21

It could be concluded from Fig. 20 and 21 that diallyldibutyltin and tetrabutyltin were the appropriate octane improvers for both low octane base oil and high octane base oil at a concentration of approximately 1-4 g Sn/L.