

# Synthesis of Mixed Aliphatic, Aromatic and Halogen Substituted Tin Compounds and Their Analysis for Conformation

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**Summary:** Organotin compounds are very useful in all walks of life. These compounds have an advantage over other metallic compounds, since the inorganic tin species formed upon degradation are non toxic, no environmental pollution. Organotin compounds were synthesized and analysed. The identity of products were confirmed by classic and modern techniques.

## Introduction

The use of organotin compounds as antifungal agents has shown marked growth during the last two decades [1] following the classic studies in the 1950's by Vander Kark and Liujten [2,3]. Later reports [4] claimed that organotin compounds appeared to be very phytotoxic for general use specially at high concentration, but mixed aliphatic aromatic organotin compounds are safe for use in all walks of life [4]. Importance of organotin compounds can be realized by having a look on the tremendous increase in the production of these compounds. The major organotin compound producing countries, USA, U.K. Germany, Japan and Netherland have doubled their production in the last decade [5]. Rees and Webb [6] found that di-n-butyltin diphenoxide can be conveniently prepared by direct interaction of di-n-butyl tinoxide with phenols in tetralin. The mixed organo-tin compounds were prepared similarly by

direct interaction of di-n-butyl tinoxide with corresponding para, meta, and orthochlorophenols in tetralin under specially mild experimental condition. The water produced in reaction was trapped in Dean and Stark apparatus with xylene.

## Results and Discussion

Table-1 below shows the results obtained along with theoretically calculated yield and actual yield.

Table 1: %age of Tin and Chlorine.

Organotin compounds	Elements	calculated%	Found	Yield %
A	Sn	24.33	23.84	98
	Cl	14.5	14.3	98
B	Sn	24.33	23.53	97
	Cl	14.5	14.4	99
C	Sn	24.33	23.94	98
	Cl	14.5	14.4	99

The %age yield of tin and chlorine obtained by above methods is excellent i.e. 99 - 98%. Therefore, these methods are recommended for this type of work.

#### Interpretation of Infra-red Spectrum (I.R.)

I.R. Spectrum was recorded by 2000 spectrophotometer double beam in which the sample and reference light was compensated as liquid film of samples as neujol mulls.

Absorption frequency associated with Sn - O group. Interpretation of the spectra is a complex and difficult. The imperial calculation [9] indicates that Sn - O stretching frequency should occur at 571 wave number of shoulder at 556 wave number. The observed values of three compounds (p.m.o) going from para to ortho, there is decrease in wave number that mean interaction at ortho position is more than meta and para which were expected theoretically. The bands at 1010, 992 and 606 wave number are for unsubstituted benzene ring from in plane C. - C. deformation modes in which carbon atoms move radically for substituted benzene these "Radical Modes" can interact with the single bound stretching vibration of the substituent. Therefore, these can be used to characterize the halogen-substituent. These are found in the 1300, wave number region.

Table 2: C - H in plane deformation and benzene ring substitution.

Compounds	Literature values (cm <sup>-1</sup> )	Observed values (cm <sup>-1</sup> )
A	1300 - 1265	1297 - V
	1190 - 1155	1172 - M
	1130 - 1100	1102 - V
	1025 - 1000	1018 - M
B	1300 - 1260	1270 - W
	1165 - 1150	1160 - W
	1120 - 1085	1090 - W
	1090 - 1060	1070 - W
C	1290 - 1250	1260 - M
	1180 - 1150	1160 - M
	1650 - 1100	1130 - M
	1055 - 1010	1040 - M

C - H out of plane deformation and benzene ring substitution:

A	860 - 800	835 vs 2 adj H
B	960 - 900	910 s 3 adj H
	820 - 790	790 m
C	960 - 850	855 m 3 adj H
	760 - 745	752 s

Abbreviation are used:-

W = weak intensity,

S = Strong,

I.P = In plane.

Str = Stretching.

M = medium,

V = Very strong intensity.

O.P = Out of plane.

Def = deformation or bending.

A = Di-*n*-butyl-tin-bis (*para*, chlorophenoxide).

B = Di-*n*-butyl-tin-bis (*meta*, chlorophenoxide).

C = Di-*n*-butyl-tin-bis (*ortho*, chlorophenoxide).

In all compounds, butyl does not absorb in sodium chloride region but they show benzene ring absorptions.

#### Proton Magnetic Resonance Studies

The spectra were recorded at 60 Mc/s on a Perkin-Elmer R-12 spectrometer, using deuteriochloroform with TMS as solvent. There are ten naturally occurring tin isotopes only three (<sup>115</sup>Sn, <sup>117</sup>Sn, <sup>119</sup>Sn) of them have nuclear spin I = 1/2. Due to their higher abundance, <sup>117</sup>Sn, <sup>119</sup>Sn [6] are important ones (<sup>115</sup>Sn, 0.35%, <sup>117</sup>Sn, 7.67%, <sup>119</sup>Sn 8.68%) <sup>117</sup>Sn and <sup>119</sup>Sn isotopes not only coupled with α-CH, β-CH and γ-CH etc. but also with directly bonded oxygen. This is giving rise to satellite signal which is seen in all NMR spectra of compounds A, B and C. Aliphatic and aromatic groups are observed in their respective regions, butyl group 0.9 - 1.7 PPM and aromatic benzene disubstituted 6.5 - 7.3 PPM. The ratio of aliphatic aromatic protons was calculated by NMR and found 2.24, 2.25 and 2.24 (theoretical 2.25).

The organotin compounds are useful and fungistats in paper, textile and in polyvinyl paints manufacture, as wood preservative as biostats in hospital maintenance and especially fungicides in the field of agriculture. The tin in its inorganic form is generally non-toxic, the attachment of aliphatic, aromatic groups, makes tin compounds biological active [9].

PVC become discolored and suffered a rapid deterioration in physical properties during the calendering process. These problems were over come by using organic compounds as stabilizers. At least millions tons of organotin compounds are consumed per year in PVC industry in U.K. Organotin compounds has been approved by USA Food and drugs administration for use in PVC for use in PVC packing of food stuff and many European countries have followed this lead.

The main objective of the work reported was to prepare di-*n*-butyltin bis (*p*-chlorophenoxide), di-*n*-butyltin bis (*m*-chlorophenoxide), and di-*n*-butyltin

bis (*O* - chlorophenoxide). These compounds have been prepared by the direct interaction of di-*n*-butyltin oxide and respective chlorophenols, using tetralin as solvent. The yield is good but can be improved by using inert atmosphere during reaction, since these compounds are very hygroscopic. Di-*n*-butyltin bis (*p* and *O* - chlorophenoxides) are solid, m. p 78 - 80°C and 60 - 65°C, respectively. Di-*n*-butyltin bis (*m*-chlorophenoxide) is pale yellowish very viscous liquid.

Amount of water produced is greater than expected, specially for *para* and *ortho* chlorophenols; it was due to the sensitivity of chlorophenols. An expected amount of water was produced when anhydrous meta chlorophenol was used.

Organotin compounds are very useful in all walks of life for example for agriculture an anti-fungal, industry, preservation of materials and in marine anti-fouling paints. The Sn- O bounds are weak, they can easily converted into other organic compounds. These compounds can act as the precursor for the preparation of other compounds.

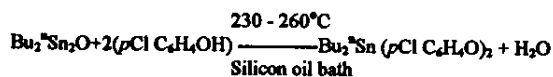
Recent studies with triphenyltin acetate have indicated that this compound may be a potential tumour growth inhibitor [10] and opens up the interesting possibility of using organotin compounds in anti-cancer treatment. Organotin compound have an advantage over other organometallic compound. The inorganic tin species formed upon degradation are non-toxic and no environmental pollution problem.

### Experimental

A round bottom three parallel necked flask was fitted with mechanical stirrer, Dean and Stark apparatus with xylene in the side arm, reflux condenser, drying tube and stopper. Di-*n*-butyltin oxide (18.12 g 0.07 mol) was suspended in tetralin (50 cm<sup>3</sup>) and *p*-chlorophenol (46.25 g .35 mol) added in three necked round flask. The flask was placed in the silicon oil bath. The reaction mixture was heated under reflux at 230 - 260°C (bath temperature) with continuous stirring by mechanical stirrer, for four hours.

Water produced in reaction was collected in the side arm of Dean and Stark apparatus (1.65 cm<sup>3</sup>) was removed b. p. 82°C/20 mmHg. Di-*n*-butyltin bis

(*p*-chlorophenoxide) 25.14 g, 0.051 mol 71%) was obtained on distillation as very light pale yellow oil which crystallised, on cooling b. p. 214°C/125 mm Hg. There was some residue (8.97 g) and by-product (4.31 g) at b. p. 182°C/0.125 mm Hg. The mechanism of the reaction is not known but reaction is believed as follows:



Di-*n* butyltin bis (*m*, *o*-chlorophenoxide) were synthesized similarly and %age yield was determined.

### Quantitative Analysis of Tin

#### Principle

The best routine for the determination of tin in organotin compounds is based on conversion to stannic oxide which is estimated gravimetrically [8].

#### Method

Silica crucible was heated in an oven at 900°C over night, cooled in a dessicator, and its weight was recorded, 0.6004 g. The sample A was accurately weighted in the crucible the crucible was then immersed in an evaporating dish containing small amount of cold water. A solution of bromine in carbon tetrachloride about 4% concentration was added drop wise stirring continuously with glass rod.

A mixture of cooled 1:6 ratio of conc. nitric and conc. sulphuric acid about 3 cm<sup>3</sup> was added slowly and drop wise. in like manner a mixture of cooled 1:1 ratio of conc. nitric and conc. sulphuric acid was added. After a few minutes fuming nitric acid about 5 Cm<sup>3</sup> was added.

The crucible was then covered by a small watch glass in a manner to permit the escape of fumes and allowed to stand on a steam bath for half an hour.

The contents are then heated to expel the residual oxides of nitrogen and the carbon tetrachloride until a clear solution was obtained. The watch glass was now removed and the heat regulated until there was slow evolution of sulphuric acid fumes. The heating was continued until all the acid had been expelled. A grevish residue was left in the

crucible. The crucible was then heated slowly by means of a small direct flame until the evolution of white fumes had practically ceased. A more intense heat was then applied finally ending with ignition by a meker burner. The crucible with contents were ignited to constant weight and tin was estimated as Sn (iv) oxide. Similarly Tin was determined quantitatively in compounds B and C and results are tabulated.

#### *Quantitative Analysis of Chlorine*

##### *Apparatus and Methods*

The simplest apparatus consists of a flask fitted with a ground-glass stopper into sealed a length of platinum wire. To the end of wire attached an oblong of platinum gauze which acts as a hinge to clamp the sample container. The sample "A" was weighed in a gelatin capsule and placed in the sample container which had been heated to ensure complete dryness and then cooled. The flask was than charged with distilled water (a few potassium hydroxide pallets were dissolved in it) which acts as absorbent. The flask was flushed a fast flow of oxygen for a few seconds.

The sample "A" (0.01916 g) was ignited in a flame, the container and stopper were immediately inserted into the flask, combustion was complete in a few seconds. The flask was then shaken for about ten

minutes after the cloud of combustion products seem to have disappeared to ensure complete absorption. The stopper was removed and rinsed together with the gauze and wire the solution was then analysed by titration with 0.1 N AgNO<sub>3</sub> solution with the help of automatic titrometer [9]. Results for three organotin compounds A, B and C are tabulated.

##### References

1. A. Crowe, *J. Appl. Organometal Chem.* **1**, 143 (1987).
2. G.J.M. Van-der-Kark and J.G.H.Liujten, *J. Appl. Chem.* **4**, 314 (1954).
3. G.J.M. Van-der-Kark and J.G.H. Liujten, *J. Appl. Chem.* **16**, 50 (1956).
4. A. J. Pieters, Proc. of Br. insects and Fungi Conference Britghent. U.K. 6 - 9 Nov. (1961).
5. S. Chandra, *J. Chem. Tech. Biotech.* **56**, 41, (1994).
6. R. G. Rees and A.F. Webb, *J. Org. Chem.* **12**, 239 (1968).
7. W. Gerrard, J.B. Ieane, F.F. Mooney and R.G. Rees, *Spectrachim, Acta.* **19**, 1964, (1963).
8. C.J. Evans, Development in the organotin industry. "Tin Research Institute Greenford", P 491, 1966, London, U.K.
9. H. Gillman and W.B. King, *J. Am. Chem.* **51**, 1213, (1929).
10. J. Haslam, J.B. Hamilton and E.C. Squirrell, *Analyst.* **85**, 556, (1960).