SYNTHESIS, REACTION AND STRUCTURAL STUDIES OF TRIORGANOTIN CARBOXYLATES

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DISSERTATION SUBMITTED IN THE FULFILMENT
OF THE REQUIREMENTS
FOR THE DEGREE OF MASTER OF SCIENCE

FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR

MAC 2010

Acknowledgement

My utmost gratitude goes to my supervisor, Assoc. Prof. Dr. Lo Kong Mun, whose encouragement, guidance and support from the initial to the final level enabled me to complete this project. My thanks goes to him for reading through the draft of the thesis and advice in the compilation of the thesis. I would like to express my deepest thanks to Prof. Dr. Ng Seik Weng for assistance in solving the crystal structures.

Besides, deepest appreciation to Mr. Chee Chin Fei. His willingness to motivate and guide me contributed tremendously. He has made available his support in a number of ways. Without him I might not be able to carry out the cytotoxicity tests. I am indebted to many of my colleagues, especially Ms. Yap Quai Ling, to support me and gave me a hand while I am in needs. I would like to express my sincere appreciation to Ms. Norzalida Zakaria, Mr. Azizul and Mr. Jasmi for guidance in the recording of the ^{13}C NMR spectra.

An honorable mention goes to my family, especially Mr. Yee See Hoo, and friends for their understandings and encourages me in completing this project. Without helps of the particular that mentioned above, I would face many difficulties while doing this project. I also offer my regards and blessings to all of those not mentioned here who encouraged and helped me in any respect during the completion of the project.

Lastly,I would like to take this opportunity to thank to University of Malaya for providing tutorship and grants to fund this project.

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Abstract

Two series of carboxylic acids namely substituted cinnamic acids with the general formula *p*-*Z*-C_6H_4CH=CHCOOH where *Z* = H, CH_3, OCH_3, NO_2, Cl and diorganodithiocarbamylacetic acid with the general formula R'R"NCS_2CH_2COOH where R', R" = CH_3, C_2H_5, C_4H_9, C_3H_7, morpholinyl and piperidinyl were prepared. Triorganotin carboxylates with the general formula $R_3SnOCOCH$=CHC_6H_4-*Z*-*p* where R = C_4H_9, Cyh and Bz; Z = H, CH_3, OCH_3, NO_2, Cl and $R_3SnOCOCH_2CS_2NR'R"$ where R = Cyh; R' and R" = CH_3, C_2H_5, C_4H_9, C_3H_7, morpholinyl and piperidinyl were prepared by reacting the triorganotin hydroxides with the respective carboxylic acids. These carboxylic acids and their triorganotin derivatives were charaterised by elemental analysis, infrared spectroscopic technique and ^1H and ^{13}C NMR spectrometry. The crystal structures of *p*-nitrocinnamic acid and four triorganotin carboxylate derivatives namely tricyclohexyltin cinnamate (**C6**), tributyltin *p*-chlorocinnamate (**C5**), tribenzyltin *p*-nitrocinnamate (**C14**) and tricyclohexyltin dimethyldithiocarbamylacetate (**D1**) were determined by single crystal X-ray crystallographic technique. The carboxylic acids and triorganotin carboxylates prepared were also investigated for their bromination reactions using various types of brominating agents such as bromine liquid, *N*-bromosuccinimide, pyridinium tribromide and 4,4-dimethylaminopyridinium tribromide. In general, the bromination of the substituted cinnamic acids leads to the formation of bromine addition products such as substituted 2,3-dibromo-3-phenylpropionic acids. The bromination of triorganotin carboxylates by bromine and 4,4-dimethylaminopyridinium tribromide gave the bromine substituted carboxylic acid, *p*-$ZC_6H_4CH(Br)CH(Br)COOH$ as the major product. In the case of bromination of triorganotin cinnamates using *N*-bromosuccinimide and methanol, *p*-Z-

$C_6H_4CH(Br)CH(OCH_3)COOH$ was obtained as the major product. The triorganotin diorganodithiocarbamylacetate were found to be inert towards any brominating agents. The bromination products were characterized by spectroscopic techniques such as ^{1}H, ^{13}C NMR and FT-IR spectroscopies. The X-ray structures of four bromination products namely 2,3-dibromo-3-phenylpropionic acid (**A6**), 2-bromo-3-methoxy-3-(*p*-methoxyphenyl)propionic acid (**A7**), bis(4,4-dimethyl-aminopyridinium)-2,3-dibromo-3-(*p*-chlorophenyl)propionate (**A9**) and tricyclohexyltin 2,3-dibromo-3-phenylprionate (**P4**) were also determined.

In addition, ten selected triorganotin carboxylates, **C4–C10, C14, P4–P6** were investigated for their cytotoxic activities against the human leukemia HL60 cells. In general, the triorganotin carboxylates exhibit comparable cytotoxic activities to that of *cisplatin*.

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List of Abbreviations

Me	$-CH_3$
Bu	$-CH_2CH_2CH_2CH_3$
Bz	$-CH_2C_6H_5$
Cyh	$-C_6H_{11}$
DMF	dimethylformamide
DMSO	dimethylsulphoxide
Et	$-CH_2CH_3$
EtOH	ethanol
Ph	$-C_6H_5$
THF	tetrahydrofuran

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Chapter 2: Experimental Section

Chapter 3: Result and Discussion