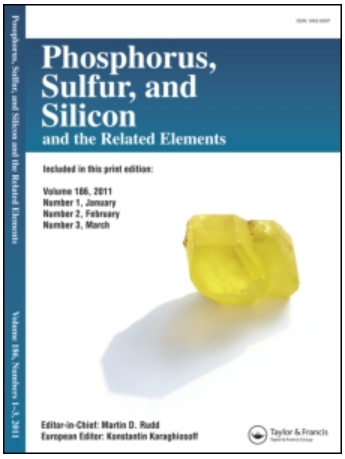


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# On the Properties of n-Butyltin Ox0 Cages and Clusters

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# ON THE PROPERTIES OF n-BUTYLTIN OXO CAGES AND CLUSTERS

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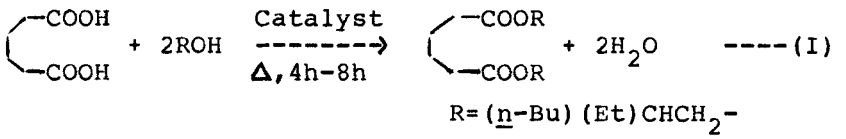
**Abstract** Thermal behaviour and possible uses of the newly characterized monoorganotin cages and clusters (e.g. In catalyzing esterification, polymerization) are discussed.

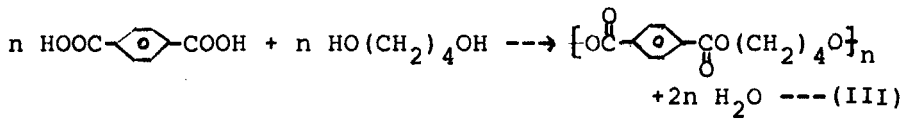
A variety of monoorganotin oxo cages and clusters are now structurally characterized[1,2] and the stage is set for a study of their properties, including catalysis. Otera and coworkers have effectively utilized monobutyl phosphates (structurally not fully characterized) as catalysts for polymerization[3] and for ring opening of oxiranes[4] by alcohols. The objective of the present study is to make use of the new substances as catalysts or polymer precursors, as well as to study their thermal properties.

The esterification catalysts chosen for the first set of investigations include n-BuSnOOH(1), MeSnOOH(2), $[n\text{-BuSnO.O}_2\text{CMe}]_6$(3) and $[\{n\text{-BuSn(OH)(O}_2\text{PPh}_2)_2\}\{n\text{-BuSnCl}_2\text{.O}_2\text{PPh}_2\}_2$(4). The reaction studied is given by equation (I).



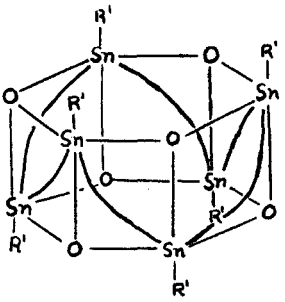

The acid numbers corresponding to each catalyst in a typical run(170-180°C/ 4h) are 41.3(1), 109.3(2), 186.6(3) and 174.3(4) respectively. On conducting several runs, by varying the temperature and time of the reaction, it was found that 1 was the most effective catalyst. A mixture of 1 and 2 was only slightly better. No significant reaction was observed in the absence of catalyst. However preliminary experiments on the esterification reaction

(II)[5] indicate that the effectiveness of the catalysts is

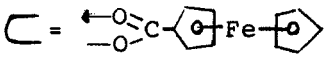


in the order 3 > 1 > 2 > 4; thus there is a possibility of improvement over the patented procedures[6]. Other catalysts that have been used are $Mg(OCH_3)_2$[5], $Sb_2O_3$[5] and $Ti(OR)_4$[6].

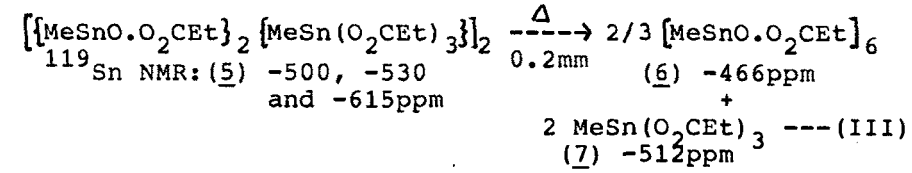
Another possible method for the usage of the new tin compounds involves the incorporation of tin into a polymer system by polymerization/copolymerization or the use of long chain acids. Some useful compounds prepared in this context include $[n\text{-BuSnO.O}_2CC_5H_4FeC_5H_5]_6$ (5) and analogous derivatives of cyanoacetic acid ($NCCH_2COOH$), myristic acid ($CH_3(CH_2)_{12}COOH$) and undecenoic acid ($CH_2{=}CH(CH_2)_8COOH$).

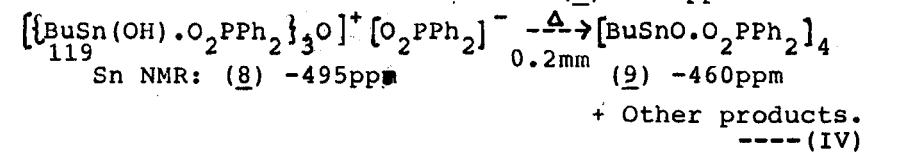


(5): R' = n-Bu



The facile manner in which the Sn-O bonds are rearranged to effect structural transformations[7] is exemplified by reactions (III) and (IV):





The disproportionation of 5 (m.p. 156-157°C, solidifies at 160°C, remelts at 240°C[8]) is also indicated by DSC which shows peaks around 130°C, 162°C and 273°C (the difference may be related to the rate of heating). The transformation shown in equation (IV) takes place near the melting point (range: 198-208°C) of 6 and is also corroborated by DSC in which both a maximum and a minimum are seen in the range 165-195°C. Detailed analysis of the thermal data will probably reveal more features.

In summary, attempts have been made to utilize the structurally characterized monoorganotin cages and clusters albeit with limited success. Future work would involve a comparative study of epoxide polymerization and other organic reactions using the accessible tin derivatives.

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