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Preliminary communication

ORGANOTIN COMPOUNDS AS TRANSESTERIFICATION CATALYSTS

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Summary

The relative catalytic activity of 18 organotin compounds in promoting the reaction MeCOOPr + MeOH → MeCOOMe + PrOH is reported and a mechanism suggested.

In the course of converting a series of organotin dihalides into the corresponding bis(isooctylthioglycollates) by reaction 1 in methanol it was found

$$R_2SnX_2 + 2NaSCH_2COOC_8H_{17}\text{-i} \xrightarrow{MeOH} R_2Sn(SCH_2COOC_8H_{17}\text{-i}) + 2NaX \quad (1)$$

that, when R = *o*-methoxyphenyl, inadvertant transesterification had occurred to give the methyl thioglycollate $(o\text{-}MeOC_6H_4)_2Sn(SCH_2COOMe)_2$ [1]. The effectiveness of organotin compounds as esterification catalysts is well known [2] but almost all of the compounds proposed are simple alkyltin compounds* and it has been suggested [4] that the aryl derivatives have reduced catalytic activity.

We studied the transesterification reaction between n-propyl acetate (10 cm^3), excess methanol (90 cm^3) and organotin compound (2.5×10^{-4} mol) boiling the solution under reflux for 3 h and analysing the resultant mixture by gas chromatography. The percentage yields of methyl acetate for each catalyst examined were: $(p\text{-}MeOC_6H_4)_2SnO$ 94, $(C_6H_5CH_2CH_2)_2SnO$ [1] 70, $(o\text{-}MeOC_6H_4)_2SnO$ [1] 63, Ph_2SnO 38, $Bu_2Sn(OCOMe)_2$ 34, Bu_2SnO 24, Me_2SnO 21, $(C_8H_{17})_2SnO$ 18, Ph_2SnCl_2 11, Bu_2SnCl_2 5, $(o\text{-}PhOC_6H_4)_2Sn(OH)_2$ [5] 5, $Ph_3SnOCOMe$ 3, Me_2SnCl_2 3, $(o\text{-}MeOC_6H_4)_2SnCl_2$ 1, Bu_2SnS 0, Ph_2SnS 0, Ph_3SnCl 0, Ph_4Sn 0, no catalyst 0.

As tetraphenyltin and triphenyltin chloride were without activity and because of our original observation, we mainly confined ourselves to R_2SnX_2 compounds. For a particular R group the catalytic activity is in the order $R_2Sn(OCOMe)_2 > R_2SnO > R_2SnCl_2 > R_2SnS$ and, for the R_2SnO compounds decreases in the

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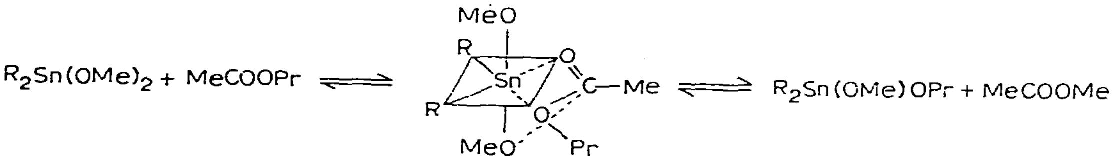
*Butyltin compounds are proposed in recent patents, see e.g. ref. 3.

order R = p-$MeOC_6H_4$ > $PhCH_2CH_2$ > o-$MeOC_6H_4$ > Ph > Bu > Me > C_8H_{17}.

There seems little doubt that the effective catalysts are the alkoxides [6] and the higher activity of the acetates and oxides compared with the chlorides and sulphides reflects the susceptibility of R_2SnX_2 to methanolysis giving $R_2Sn(OMe)_2$. (A similar situation exists with respect to the use of organotin compounds to catalyse the addition of alcohols and phenols to isocyanates [7].) Since both the steric demand and the electronic effects of the R groups appear to be important, an intermediate of the type I is indicated.



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