Journal of Organometallic Chemistry, 173 (1979) C7—C8

Preliminary communication

ORGANOTIN COMPOUNDS AS TRANSESTERIFICATION CATALYSTS

R.C. POLLER and S.P. RETOUT

Department of Chemistry, Queen Elizabeth College, Campden Hill Road, London W8 7AH (Great Britain)

(Received April 9th, 1979)

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

$$R_2SnX_2 + 2NaSCH_2COOC_8H_{17}\text{-i} \xrightarrow{MeOH} R_2Sn(SCH_2COOC_8H_{17}\text{-i})_2 + 2NaX \quad (1)$$

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.

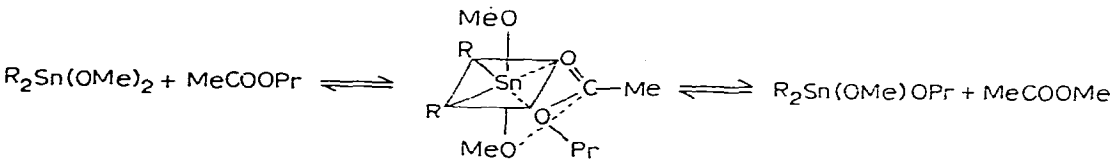
We studied the transesterification reaction between n-propyl acetate (10 cm^3), excess methanol (90 cm^3) and organotin compound (2.5×10^{-4} mol) boiling the solution under reflux for 3 h and analysing the resultant mixture by gas chromatography. The percentage yields of methyl acetate for each catalyst 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

*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.



(I)

References

1 G. Ayrey, F.P. Man and R.C. Poller, unpublished results.
2 A. Ross, Annals N.Y. Acad. Sci., 125 (1965) 107.
3 M. Sato, K. Ichikawa, K. Nakamura, Y. Matsumoto and S. Matsuo, Japan. Kokai 77 39,646; Chem. Abstr., 87 (1977) 13 4692.
4 B.F. Goodrich Co., German Pat., 1,005,947; Chem. Abstr., 54 (1960) 14098.
5 R.C. Poller, J. Chem. Soc., (1963) 706.
6 M. Pereyre, G. Colin and J.-P. Delvigne, Bull. Soc. Chim. France, (1969) 262.
7 A.J. Bloodworth and A.G. Davies, J. Chem. Soc., (1965) 5238.