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Communications

New Latent Organotin Catalysts: Preparation and Mechanism of the Thermal Decomposition of Bis(2-(acyloxy)alkyl)diorganotins

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Summary: New organotin compounds, bis(2-(acyloxy)-alkyl)diorganotins, can be thermally decomposed into diorganotin dicarboxylates. The substituent effects on the reaction parameters are studied, and a possible mechanism for the decomposition is proposed. These tetraorganotins can be regarded as latent catalysts for silicone curing and polyurethane preparation.

The industrial applications of organotin compounds are mainly based on their efficiency as PVC stabilizers and their usefulness for crop protection, wood preservation, and marine antifouling.[1] Another use of these organotins, especially diorganotin dicarboxylates, is as catalysts for silicone curing,[2] polyurethane formation,[3] and esterification[4] because of their high efficiency, low cost, and moderate toxicity. The mechanisms of these tin-promoted reactions have been investigated by several research groups, and catalysts newer and more efficient than the conventional ones for esterification and polyurethane formation have recently been described.[5,6] Such high efficiency of these catalysts may, however, cause inconvenience, for instance, in the curing of silicones, where condensation reactions start as soon as reactants and catalysts are mixed together. The gel point is reached rapidly if the reaction mixtures are not processed in time, which may present a problem to their users. An ideal catalyst would cure silicones instantaneously at oven temperature, whereas at room temperature the pot life of the mixture should be infinite.[7] We present here our approach toward new organotin compounds, inactive at room temperature either for SiOH/SiOR and SiOH/SiH polycondensation or for polyurethane formation, which can be

Table I. Conditions for Complete Thermal Decomposition of (2-(Acyloxy)alkyl)tributyltins

compd	temp, °C	time, h
$Bu_3SnCH_2CH_2OCOCH_3$	135	5
$Bu_3SnCH_2CH_2OCO\text{-}n\text{-}C_{11}H_{23}$	150	5
$Bu_3SnCH_2CH_2OCOCH(C_2H_5)(C_4H_9)$	150	7

Table II. Parameters for the Thermal Decomposition of Bis(2-(acyloxy)alkyl)dibutyltins

compd	R^1	R^2	temp, °C	time,[a] h	k(120 °C), 10^4 s^{-1}
1	H	H	110	3	*b*
2	CH_3	H	140	3	2.5
3	$n\text{-}C_{11}H_{23}$	H	140	5	0.24
4	$CH(C_2H_5)(C_4H_9)$	H			0.07
5	$4\text{-}CF_3C_6H_4$	H			163
6	C_6H_5	H	110	2	25
7	$4\text{-}CH_3OC_6H_4$	H			22
8	$4\text{-}CH_3C_6H_4$	H			4
9	CH_3	C_6H_5			*b*
10	CH_3	CH_3	80	0.3	435
11	CH_3	CF_3			0.01

[a] Time necessary for the complete decomposition of the latent catalyst at the given temperature. [b] Unstable compound at room temperature.

transformed at will by a short heating into diorganotin dicarboxylates serving as highly effective catalysts.

Tetraorganotins, known to be very poor catalysts, were chosen as inactive organotins likely to be transformed into diorganotin dicarboxylates. To perform the transformation tetraorganotin–catalyst, an intramolecular reaction was thought to be of better use since the complexity of industrial mixtures and the low concentration of the catalyst probably would make a bimolecular process much more questionable. Among possible transformations we chose a β-elimination reaction. Although this is often an undesirable process because of the induced instability of hetero-substituted organometallic compounds,[8] this reaction has successfully been applied in organic chemistry for the stereospecific preparation of functional olefins from β-hydroxylated triphenylstannanes.[9] Moreover, this process is not limited to such compounds and there is an earlier report that esters of β-hydroxy-substituted triorganotins decompose on heating to give triorganotin carboxylates and olefins.[10] We first reproduced Noltes' results, which were originally described with triethyl- and triphenyltin derivatives, using tributyltins, more interesting

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compounds for industrial purposes, and various ester groups:

$$CH_2=CHOCOR^1 \xrightarrow{Bu_3SnH} Bu_3SnCH_2CH_2OCOR^1 \xrightarrow{\Delta}$$
$$Bu_3SnOCOR^1 + CH_2=CH_2$$
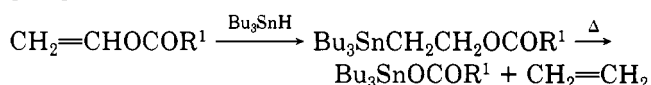
As shown in Table I, hydrostannation products indeed decomposed, and very interestingly, the decomposition conditions were dependent on the nature of the ester groups. This is a very promising finding if such a property could be transferred to the generation of dialkyltin dicarboxylates.

Dialkyltin dihydrides were allowed to react with vinyl esters to prepare the starting materials. Hydrostannation of alkenes with dialkytin dihydrides has not often been used in organotin chemistry, and it has been shown that the reaction sometimes gives somewhat unexpected results.[11] In our case UV irradiation was of better use than 2,2'-azobis(2-methylpropionitrile) (AIBN) initiation. By this way, the adducts were prepared in high yield[12] (>90% as indicated by ^1H and ^{119}Sn NMR spectroscopy). Because of their low stability, these compounds could not be purified either by distillation or by column chromatography and were used as crude products. In the thermal decomposition they were indeed quantitatively transformed into the expected diorganotin dicarboxylates:

$$Bu_2Sn(CH_2C(R^2)HOCOR^1)_2 \xrightarrow{\Delta}$$
$$2R^2CH=CH_2 + Bu_2Sn(OCOR^1)_2$$
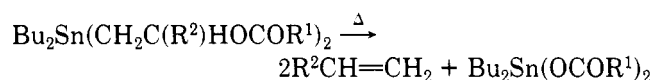
Heating times necessary for the complete decomposition of some latent catalysts are given in Table II. As Table II shows, these data regarding the reactivity of bis(2-(acyloxy)alkyl)dibutyltins do not correspond to the expected data if a nucleophilic attack of the carbonyl on the tin atom through a six-membered ring is the crucial factor. As can be seen, the more nucleophilic the carbonyl is, the more difficult the decomposition is. Therefore, we carried out a systematic study by varying the substituents, R^1 and R^2, and measuring the parameters of the reaction by differential scanning calorimetry (DSC), which gave the following results.

(1) The decomposition is monomolecular or pseudomonomolecular.

(2) The longer and the more branched R^1 is, the more difficult the decomposition is. With aryl substituted R^1, the more electron-withdrawing the substituent is, the faster the reaction is.

(3) The nature of R^2 is also critical. When R^2 is C_6H_5, the decomposition is so rapid that no adduct can be obtained. When R^2 is CH_3, the reaction is faster than with R^2 being H. When R^2 is CF_3, the decomposition is the most difficult.

These data give an insight into the mechanism of the β-elimination. It appears that the rate of the reaction depends on the ability of R^2 to stabilize a partially developing positive charge on the carbon at the β-position and also on the ability of R^1 to stabilize a partially developing negative charge on the ester moiety. These results suggest a desynchronized six-membered[13] transition state in which the β-carbon–oxygen bond is broken more than the tin–oxygen bond is established, in agreement with the investigations made on the pyrolysis of 1-arylethyl acetates:[15]
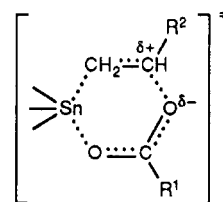
Here the ease of the heterolytic cleavage of the β-carbon–oxygen bond is linked to the β-effect of the tin atom,[16] i.e., stabilization of a positive charge at the β-position through $(\sigma$-p$)\pi$ conjugation.

Most of these compounds have shown excellent activity as latent catalysts, activated at will by moderate heating, when applied to industrial reactions, e.g. the cross-linking of silicone oils and the preparation of polyurethanes.[17] For instance, in the case of a SiOH/SiOR condensation, the pot life at room temperature in the presence of compound 10 was 200 times longer than in the presence of the usual catalyst $Bu_2Sn(OCOCH_3)_2$. However, the gel time at 110 °C was only 2 times longer. In the case of the 1,4-butanediol–isophorone isocyanate condensation, the pot life in the presence of compound 2 was 9 times longer than with $Bu_2Sn(OCOCH_3)_2$, while the gel time at 100 °C was 2 times longer.

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(12) Preparation of bis(2-(acyloxy)alkyl)dibutyltins: A solution of enol ester (10 mmol) and 2.34 g of Bu_2SnH_2 (10 mmol) in dry deaerated cyclohexane (5 mL) was irradiated under nitrogen (Philips HPK 125) in a Pyrex thermostated cell. Compound, irradiation temperature (°C), irradiation time (h): 2, 20, 3; 3, 30, 4; 4, 30, 8.5; 5, 60, 4.5; 6, 20, 4.5; 7, 30, 4; 8, 30, 1.5; 10, 0, 7; 11, 30, 2.5. The solvent was then removed in vacuo (temperature below 20 °C). ^1H NMR (60 MHz, CCl_4, δ): 2, 4.2 (4 H, m), 1.95 (6 H, s), 1.7–0.9 (22 H, m); 3, 4.25 (4 H, m), 2.2 (4 H, t), 1.9–0.9 (64 H, m); 4, 4.3 (4 H, m), 2.4–0.9 (52 H, m); 5, 8.2 (4 H, d), 7.75 (4 H, d), 4.7 (4 H, m), 1.5–0.9 (22 H, m); 6, 8.0 (4 H, m), 7.4 (6 H, m), 4.5 (4 H, m), 1.5–0.9 (22 H, m); 7, 7.9 (4 H, d), 6.8 (4 H, d), 4.4 (4 H, m), 3.75 (6 H, s), 1.5–0.9 (22 H, m); 8, 7.9 (4 H, d), 7.1 (4 H, d), 4.45 (4 H, m), 2.3 (6 H, s), 1.5–0.9 (22 H, m); 10, 5.15 (2 H, m), 1.95 (6 H, s), 1.8–0.9 (28 H, m); 11, 5.50 (2 H, m), 1.68 (3 H, s), 1.66 (3 H, s), 1.5–0.9 (22 H, m). ^{119}Sn NMR (74.63 MHz, C_6D_6, δ): 2, –19.8; 3, –20.0; 4, –20.9; 5, –21.3; 6, –20.9; 7, –20.7; 8, –20.7; 10, –24.9; 11, –13.3 (0.5 Sn, m), –13.5 (0.5 Sn, m), $^4J_{Sn-F}$ = 5 Hz.

(13) The stability of the latent catalysts is considerably lowered in the presence of nucleophiles (H_2O, MeOH, CH_3CN, ...). For instance, at 25 °C, when mixed with H_2O (8% w/v) in acetone as solvent, 2 was decomposed after 14 days whereas an anhydrous solution of 2 in acetone was unchanged under the same conditions. The reaction is thus sensitive to nucleophilic catalysis,[14] which suggests that the carbonyl could act intramolecularly as a nucleophile (even if a nucleophilic attack was not the determining event of the reaction) and supports a cyclic geometry for the transition state.

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