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Abstract

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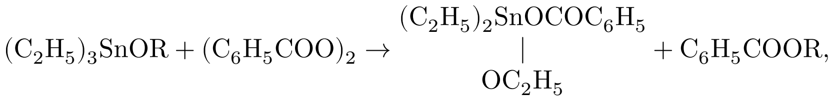
THE REACTION OF BENZOYL PEROXIDE WITH TRIETHYLALKOXYTIN COMPOUNDS

As is known, tetraethyltin, triethyltin halides, and triethyltin benzoate react with benzoyl peroxide only at the temperatures of its decomposition ([1]). The reactions are characterized by a diversity of products, which testifies to the complexity of the reaction mechanism. Benzoyl peroxide reacts quite differently with triethylalkoxytin compounds. In this case, already upon dissolving the peroxide in the organotin substance, a vigorous exothermic reaction is observed, which under milder conditions (in dry benzene under nitrogen at $\simeq 20^\circ$) proceeds according to the equation:

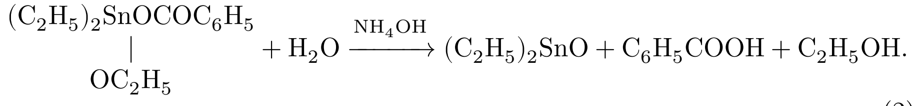


$$(C_2H_5)_3SnOR + (C_6H_5COO)_2 \rightarrow \begin{array}{c}(C_2H_5)_2SnOCOC_6H_5\\ |\\ OC_2H_5\end{array} + C_6H_5COOR, \quad (1)$$

where $R = CH_3,\ C_2H_5,\ C_6H_5CH_2$, cyclohexyl, C_6H_5.

The yields and constants of the benzoic acid esters obtained by reaction (1) are given in Table 1. The second reaction product—diethylethoxytin benzoate (A)—cannot be isolated in the pure state. The structure of this substance, as well as the independence of its structure from the nature of R, is, in our opinion, sufficiently convincingly demonstrated by the following reactions.

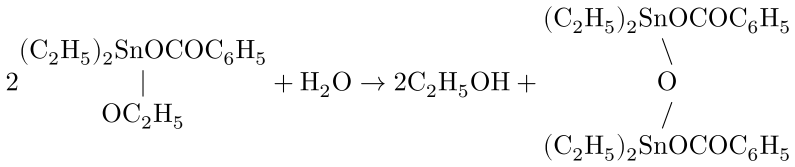
On treatment of the product with concentrated ammonia, in all cases a non-melting and insoluble diethyltin oxide was obtained, converted into diethyltin dichloride with m.p. 82° (from hexane). In addition, benzoic acid with m.p. 121° (from water) and ethanol, identified by the formation of iodoform with m.p. 118°, were isolated from the reaction mixture. Mixed samples of the compounds obtained with pure substances showed no depression of melting points. The yields of diethyltin oxide and benzoic acid are quantitative, corresponding to the equation



$$(C_2H_5)_2\underset{\displaystyle OC_2H_5}{\underset{|}{Sn}}OCOC_6H_5 + H_2O \xrightarrow{NH_4OH} (C_2H_5)_2SnO + C_6H_5COOH + C_2H_5OH.$$

(2)

On recrystallization of product A from 96% alcohol, hydrolysis of the ethoxyl group occurs and diethyltin benzoate oxide (B) is formed, with m.p. 214–215° (from benzene)



$$2\,(C_2H_5)_2\underset{\displaystyle OC_2H_5}{\underset{|}{Sn}}OCOC_6H_5 + H_2O \rightarrow 2C_2H_5OH + \begin{array}{c}(C_2H_5)_2SnOCOC_6H_5\\ \backslash\\ O\\ /\\ (C_2H_5)_2SnOCOC_6H_5\end{array}$$

(B) (3)

The yields of oxide B according to reaction (3) are also given in Table 1. As is seen from Table 1, for all triethylalkoxytin compounds the yield of oxide (B) is rather high and does not depend sharply on the structure of the alkoxy group. Consequently, equation (1) describes the principal direction of the reaction, and compound A is its main tin-containing product. Only in the interaction of benzoyl peroxide with triethylphenoxytin is reaction (1) accompanied—

Table 1

$(C_2H_5)_3SnOR$, mol	Benzoyl peroxide, mol	Benzene, ml	Temp., °C	Duration, h	R in C_6H_5COOR	b.p., °C/mm	n_D^{20}	Yield, %	Yield of diethyltin benzoate oxide (B), %
0.015; $R = CH_3$	0.015	30	20	36	CH_3	195-201	1.5138	81.4	70.7
0.020; $R = C_2H_5$	0.020	40	20	36	C_2H_5	208-211	1.5043	69.0	61.9
0.015; $R =$ cyclohexyl	0.015	30	20	48	cyclohexyl	116-119/2	1.5217[2]	93.3	65.1

$(C_2H_5)_3SnOR$, mol	Benzoyl peroxide, mol	Benzene, ml	Temp., °C	Duration, h	R in C_6H_5COOR	b.p., °C/mm	n_D^{20}	Yield, %	Yield of diethyltin benzoate oxide (B), %
0.015; $R = C_6H_5$[3]	0.015	30	20	48	C_6H_5[4]	–	–	87.3	47.2
0.0125; $R = C_6H_5CH_2$[5]	0.0125	30	20	36	$C_6H_5CH_2$	176-180/9	1.5644[6]	79.8	73.3

[1] Obtained by recrystallization from 96% alcohol of the tin-containing reaction product; m.p. 214–216°.
[2] According to (3): b.p. 119°/2 mm; n_D^{25} 1.5200.
[3] Obtained by heating an equimolar mixture of triethylmethoxytin and phenol in benzene in a water bath for 5 h. Yield 77.2%; b.p. 111–127°/1 mm; n_D^{20} 1.5428. According to (3): b.p. 115–126°/1 mm; n_D^{20} 1.5422.
[4] M.p. of the substance and of a mixed sample 68–69°.
[5] Synthesized by heating (5.5 h) an equimolar amount of sodium benzylate and triethyltin chloride in an excess of benzyl alcohol. Yield 30.0%; b.p. 141°/8 mm; n_D^{20} 1.5265. Found, %: C 49.89; 49.54; H 7.59; 7.49. $C_{13}H_{22}SnO$. Calculated, %: C 49.88; H 7.08.
[6] According to (4): b.p. 187°/20 mm; n_D^{20} 1.5687.

is accompanied by the formation of compounds intensely colored cherry-red, which, naturally, is reflected in the yield of oxide B. The structure of oxide B was confirmed by independent syntheses.

The same diethyltin benzoate oxide, with m.p. 216°, was obtained in up to 81.2% of theory upon recrystallization of diethyltin dibenzoate from rectified alcohol. As experiment shows, in this case, simultaneously with recrystallization, hydrolysis of one benzoate group occurs

$$2\,(C_2H_5)_2Sn\,(OCOC_6H_5)_2 + H_2O \rightarrow 2\,C_6H_5COOH + \begin{array}{c}(C_2H_5)_2SnOCOC_6H_5\\ O\\ (C_2H_5)_2SnOCOC_6H_5\end{array} \quad (4)$$

With a yield of 55.0%, diethyltin benzoate oxide was synthesized by dissolving diethyltin oxide in an excess of a boiling alcoholic solution of benzoic acid. M.p. 216–217° (from benzene).

Found, %: C 43.49; H 5.50; Sn 38.52

$C_{22}H_{30}Sn_2O_5$. Calculated, %: C 43.13; H 4.94; Sn 38.79

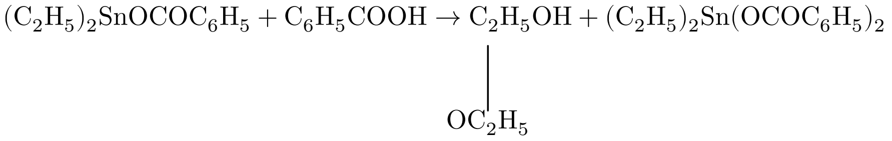
A mixed sample of substance B with the oxides obtained by independent syntheses shows no depression of the melting point.

As already mentioned, the reaction described by equation (1) was carried out under mild conditions. At the same time, separation of the products was carried out by fractionation in vacuo at elevated temperatures, which could have affected the structure of the organotin compound. The fact that product A is formed in the course of the main process (1) and does not undergo changes during fractionation was proved by us using the example of the reaction of the peroxide with triethylbenzyloxytin.

For this purpose, equimolar amounts of the reactants were dissolved in benzene, mixed in a nitrogen atmosphere, and kept for 24 h at 20°. Then an equimolar amount of benzoic acid was added to the reaction mixture, and the mixture was left for another day at 20°. The ethanol formed in this process was distilled off under reduced pressure as an azeotrope with benzene and was identified as α-naphthylurethane (m.p. 84–85°). Benzyl benzoate was also isolated from the reaction mixture (yield 75.5%; b.p. 165–167° at 10 mm; n_D^{21} 1.5639, which agrees with the data-

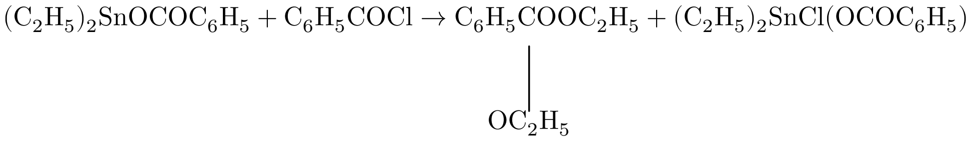
···and diethylolov dibenzoate. Yield 57.7%; m.p. 121–122° (from heptane). A mixed sample with authentic diethylolov dibenzoate shows no depression of the melting point.

The formation of ethanol and diethylolov dibenzoate in the experiment under discussion shows that product A, arising from reaction (1), subsequently reacts with the benzoic acid introduced



$$(C_2H_5)_2\underset{\displaystyle | \atop \displaystyle OC_2H_5}{Sn}OCOC_6H_5 + C_6H_5COOH \rightarrow C_2H_5OH + (C_2H_5)_2Sn(OCOC_6H_5)_2 \qquad (5)$$

In the case where, instead of benzoic acid, an equimolar amount of benzoyl chloride was added to the reaction mixture, the reaction products were benzyl benzoate (yield 44.0%), ethyl benzoate (yield 53.7%), diethyltin dichloride (yield 27.7%, m.p. of the substance and of the mixed sample 81–82°), and diethylolov dibenzoate. Yield 33.4%. Identified by the absence of depression of the melting point of a mixed sample with the pure substance (121–122°). The formation of the last three compounds can be explained only by the interaction of product (A) with benzoyl chloride:



$$(C_2H_5)_2SnOCOC_6H_5 + C_6H_5COCl \rightarrow C_6H_5\underset{\overset{|}{OC_2H_5}}{C}OOC_2H_5 + (C_2H_5)_2SnCl(OCOC_6H_5) \quad (6)$$

$$2(C_2H_5)_2SnCl(OCOC_6H_5) \rightarrow (C_2H_5)_2SnCl_2 + (C_2H_5)_2Sn(OCOC_6H_5)_2 \quad (7)$$

Disproportionation of $(C_2H_5)_2SnCl(OCOC_6H_5)$ according to reaction (7) had already been observed by us earlier (^{1}), and the possibility of reaction (6) was checked on a simpler example:

$$(C_2H_5)_3SnOC_6H_5 + C_6H_5COCl \rightarrow (C_2H_5)_3SnCl + C_6H_5COOC_6H_5 \quad (8)$$

Reaction (8) was carried out by heating an equimolar mixture of the reagents in dry benzene for 2 hours. Yield of triethyltin chloride 91.2%; b.p. 98-102° at 15 mm; n_D^{20} 1.5043. According to data (^{5,6}): b.p. 100-101° at 16 mm; n_D^{20} 1.5055. The second reaction product is phenyl benzoate. Yield 83.0%; m.p. of the substance and of the mixed sample 69-70°.

Thus, there are all grounds to assert that in product A only two ethyl groups are directly bonded to tin. The third ethyl group is bonded to tin through oxygen, which explains the formation of ethanol in reactions (2) and (5) and of ethyl benzoate in reaction (6). Finally, the negative reaction for peroxide oxygen, as well as the presence among the hydrolysis products of benzoic acid (reaction (2)) or of diethylolov benzoate oxide (reaction (3)), indicates the presence of a benzoate group in molecule A.

To explain the pathways of formation of substance A, it should be assumed that triethylalkoxytin compounds react with benzoyl peroxide similarly to sodium ethylate, with subsequent rearrangement of the triethyltin perbenzoate formed into (A). The reaction probably proceeds within the reaction complex, since, for its successful completion, conditions are necessary under which the reagents are separately sufficiently stable.

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CITED LITERATURE

1. G. A. Razuvaev, O. S. D' yachkovskaya et al., DAN, **137**, 618 (1961).

2. R. K. Ingham, S. D. Rosenberg, H. Gilman, Chem. Rev., **60**, 460 (1960).
3. W. J. Swirbely, W. M. Eareckson et al., J. Am. Chem. Soc., **71**, 507 (1949).
4. H. A. Nottorf, C. H. Herr et al., Ind. and Eng. Chem., **39**, 1300 (1947).
5. K. A. Kocheshkov, ZhOKh, **4**, 1359 (1934).
6. C. R. Dillard, E. H. McNeill et al., J. Am. Chem. Soc., **80**, 3607 (1958).

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