Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

USE OF THE "INTERFACIAL POLYMERIZATION METHOD" FOR THE PREPARATION OF ORGANOTIN ESTERS

MAX FRANKEL, DAVID GERTNER, DANIEL WAGNER* AND ALBERT ZILKHA
Department of Organic Chemistry, The Hebrew University, Jerusalem (Israel)

(Received November 23rd, 1966)

Various methods have been used for the preparation of organotin esters, such as the reaction of organotin oxides or hydroxides with carboxylic acids or that of organotin halides with organic acid salts. The latter reaction is usually carried out in an inert solvent at reflux temperature[1]. It is the purpose of this paper to describe an efficient, low temperature procedure for the synthesis of organotin esters. This method is based on the principle of the interfacial polymerization technique in which two reactive components are brought into reaction at the interface between two

TABLE 1

TRIBUTYL AND TRIPHENYLTIN ESTERS OF CARBOXYLIC ACIDS

Acid[a]	*M.p. (°C)*	*Yield (%)*
Tributyltin esters		
Succinic	91–3[b]	89
Adipic	104[b]	93
Terephthalic	78[b]	94
Fumaric	128[b]	98
Sebacic	100–1[b]	83.5
Phenylacetic	61–2[b]	100
Crotonic	81–2[b]	88.5
Triphenyltin esters		
Acetic	120–2[c]	91.5
Chloroacetic	160–1[d]	89
Propionic	122–3[e]	95
Benzoic	82–4[c]	89
Succinic	154–5[f]	88
Adipic	166–7[g]	79

[a] In case of dicarboxylic acids, the data given are for the diesters. [b] Same m.p. as reported in the literature[6]. [c] Same m.p. as reported in the literature[7]. [d] Previously reported[8] m.p. 182—3°. Recrystallized from chloroform/ether. (Found: C, 54.10; H, 3.97; Cl, 8.38. $C_{20}H_{17}ClO_2Sn$ calcd.: C, 54.16; H, 3.83; Cl, 7.98%.) [e] Same m.p. as previously reported[9]. [f] Recrystallized from n-propanol. (Found: C, 59.13; H, 4.00; Sn, 29.1. $C_{40}H_{34}O_4Sn_2$ calcd.: C, 58.86; H, 4.16; Sn, 29.1%.) [g] Recrystallized from n-propanol. (Found: C, 59.44; H, 4.50; Sn, 28.2. $C_{42}H_{38}O_4Sn_2$ calcd.: C, 59.75; H, 4.50; Sn, 28.1%.)

---

* Taken in part from the Ph.D. thesis to be submitted by D. W. to the Senate of the Hebrew University of Jerusalem.

TABLE 2

DIALKYLTIN ESTERS OF CARBOXYLIC ACIDS

R	M.p. (°C)	Recrystallized from	Yield (%)	%C found (calcd.)	%H found (calcd.)	%N found (calcd.)	%Cl found (calcd.)	%Sn found (calcd.)
$Bu_2Sn(O_2CR)_2$								
$Cl_2CH^{a,b}$	112–4^c	Isooctane	88					
p-$O_2NC_6H_4{}^{d,e}$	218–9	Benzene	87	46.70 (46.75)	4.47 (4.60)	5.26 (4.95)		20.4 (21.0)
m-$O_2NC_6H_4{}^{d,e}$	120–2	Isooctane	84	46.52 (46.75)	4.72 (4.60)	5.10 (4.95)		20.7 (21.0)
3,5-$(NO_2)_2C_6H_3{}^{d,e}$	187–8	Benzene	89	40.16 (40.32)	3.89 (3.66)	8.29 (8.55)		18.1 (18.1)
o-$ClC_6H_4{}^{b,d}$	84–5	Heptane	83	48.64 (48.56)	4.81 (4.78)		13.54 (13.04)	21.5 (21.8)
C_6H_4-$CH(OH)^{d,e}$	165–6	Methyl ethyl ketone/ petroleum ether	100	53.65 (53.86)	5.64 (5.98)			22.0 (22.2)
p-$H_2NSO_2C_6H_4{}^{d,e}$	225	Chlorobenzene	100	41.56 (41.72)	4.61 (4.74)	4.50 (4.42)		17.8^f (18.8)
$Et_2Sn(O_2CR)_2$								
$C_6H_5{}^{a,b}$	123^g	—	90					
o-$ClC_6H_4{}^{a,b}$	90–1	Petroleum ether	100	45.00 (44.30)	3.54 (3.69)		15.11 (14.52)	24.6 (24.3)
$CHCl_2{}^{a,b}$	123–4	Acetone/n-hexane	88	22.44 (22.19)	2.80 (2.77)		30.94 (32.78)	27.8 (27.4)

[a] Reaction carried out at 20°, using methylene dichloride as solvent. [b] The ester was obtained on evaporation of the organic solvent. [c] Same m.p. as previously reported[10]. [d] Reaction was carried out at 0° using petroleum ether as solvent. [e] The ester precipitated out from the reaction mixture. [f] S: calcd. 10.11, found 10.25%. [g] Same m.p. as previously reported[11].

TABLE 3

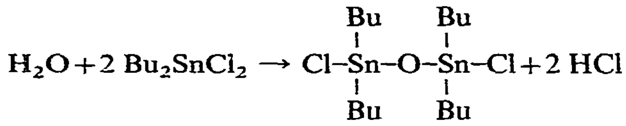
TETRAALKYL DISTANNOXANE ESTERS OF CARBOXYLIC ACIDS

R	M.p. (°C)	Recrystallized from	Yield (%)	Sn–O–Sn Str.Vib. (cm^{-1})	%C found (calcd.)	%H found (calcd.)	%N found (calcd.)	%Cl found (calcd.)	%Sn found (calcd.)
$(Bu_2SnO_2CR)_2O$									
$Cl_2CH^{a,b}$	192		81.5	610	32.64 (32.55)	4.90 (5.15)		18.73 (19.23)	32.3 (32.2)
p-$NO_2C_6H_4^{a,c}$	187	Benzene/heptane	100	638	44.39 (44.26)	5.41 (5.40)	3.60 (3.44)		29.0 (29.2)
m-$NO_2C_6H_4^{a,c}$	148–9	Isooctane	97	630	44.24 (44.26)	5.44 (5.40)	3.61 (3.44)		29.1 (29.2)
3,5-$(NO_2)_2C_6H_3^{a,c}$	204–5	Benzene/isooctane	97	633	40.08 (39.84)	4.67 (4.65)	6.30 (6.19)		26.0 (26.3)
o-$ClC_6H_4^{a,b}$	81–2	n-Hexane	91	630	45.28 (45.43)	5.48 (5.55)		9.37 (8.94)	29.0 (30.0)
$C_6H_5CH(OH)^{a,c}$	190	Methyl ethyl ketone/ petroleum ether	99	623	49.12 (49.01)	6.16 (6.38)			30.3 (30.0)
p-$NH_2SO_2C_6H_4^{a,c}$	250–2		98	620	41.02 (40.84)	5.10 (5.44)	3.41 (3.17)		26.3^d (26.9)
$(Et_2SnO_2CR)_2O$									
$C_6H_5^{e,b}$	213–4^f		88						
o-$ClC_6H_4^{e,b}$	171–2	Acetone	100	629	38.87 (38.81)	4.17 (4.11)		10.79 (10.45)	35.4 (34.9)
$CHCl_2^{e,b}$	164–5	n-Hexane	87	630	23.22 (23.03)	3.40 (3.52)		22.91 (22.65)	38.0 (38.0)

[a] Reaction was carried out at 0°, using petroleum ether as solvent. [b] The ester was obtained on evaporation of the solvent. [c] The ester precipitated from the reaction mixture. [d] S: found 8.05%, calcd. 7.28%. [e] Reaction was carried out at 20°, using methylene chloride as solvent. [f] Same m.p. as previously reported[12].

immiscible solvents[2,3]. The reactive organotin compounds used were trialkyl- or triaryltin chlorides, dialkyltin dichlorides and tetraalkyldichlorodistannoxanes, each of which, dissolved in an inert organic solvent, was added, at temperatures between 0–20°, under stirring to an aqueous solution of the alkali metal salt of the respective organic acid, dissolved in water. The reaction is very fast, being practically complete within about 1 or 2 minutes, as indicated by the amount of chloride ion liberated into the aqueous phase. The organotin esters either precipitated out from the reaction mixture or were recovered in high yields (80–100%) after evaporation of the organic layer (*cf.* Tables 1, 2, 3). By this method organotin esters of various structures were synthesized, some of which were already prepared by different procedures[1], while others are described here for the first time.

In order to find out whether side reactions occurred between the organotin halide and water, these substances were treated with water under the same experimental conditions. With tributyltin chloride and tetrabutyldichlorodistannoxane no reaction appeared to take place even after 1 hour, as concluded from the absence of chloride ions in the aqueous phase. With dibutyltin dichloride, tetrabutyldichlorodistannoxane was obtained in good yield, and the aqueous layer was found to contain chloride ions, the amount of which was in agreement with the following equation:



$$H_2O+2\,Bu_2SnCl_2 \rightarrow Cl\text{–}\overset{Bu}{\underset{Bu}{Sn}}\text{–}O\text{–}\overset{Bu}{\underset{Bu}{Sn}}\text{–}Cl+2\,HCl$$

This reaction is very fast, as indicated by the amount of the chloride ions liberated into the aqueous phase; it appears to be practically complete on mixing the reactants.

In spite of the fast hydrolysis of the organotin dichlorides in water, the reaction between dialkyltin dichlorides and alkali metal salts of carboxylic acids gave esters in high yields, having the structure: $R_2Sn(OOCR')_2$ and not that of tetraalkyl dicarboxy-distannoxanes: $R'CO_2\text{–}SnR_2\text{–}O\text{–}SnR_2\text{–}O_2CR'$. This fact shows that the reaction of organotin halide with carboxylate anion is faster than that with water, even though the concentration of the latter, being the medium for the reaction, is much greater than that of the former. This is in accordance with the nucleophilic constants of carboxylate ions. Thus, *e.g.*, the acetate[4] ion has a nucleophilic constant of 2.72. It may be mentioned here that the reaction between dimethyltin dichloride and some carboxylic acids in the presence of ammonia in aqueous solution was found to yield in many cases tetramethyldiacyloxydistannoxanes[5].

The structure of the dialkyltin dicarboxylates was proved by elemental analyses, and by comparison of their physical properties, including m.p., mixed m.p. and IR spectra, with those of tetraalkyldiacyloxydistannoxanes prepared by the "interfacial" method using $(R_2SnCl)_2O$ as starting material. The most characteristic difference was the appearance of an absorption band near 600 cm^{-1}, known to originate from the Sn–O–Sn bond[5] which appeared only in the compounds prepared from $(R_2SnCl)_2O$ (Fig. 1). Additional evidence for differences in structure was obtained from comparison of the X-ray scattering patterns of the two esters of *o*-chlorobenzoic acid, dibutyltin bis(*o*-chlorobenzoate) and tetrabutylbis(*o*-chlorobenzoyloxy)distannoxane, synthesized from dibutyltin dichloride and tetrabutyldichlorodistannoxane respectively, which were recrystallized under the same condi-

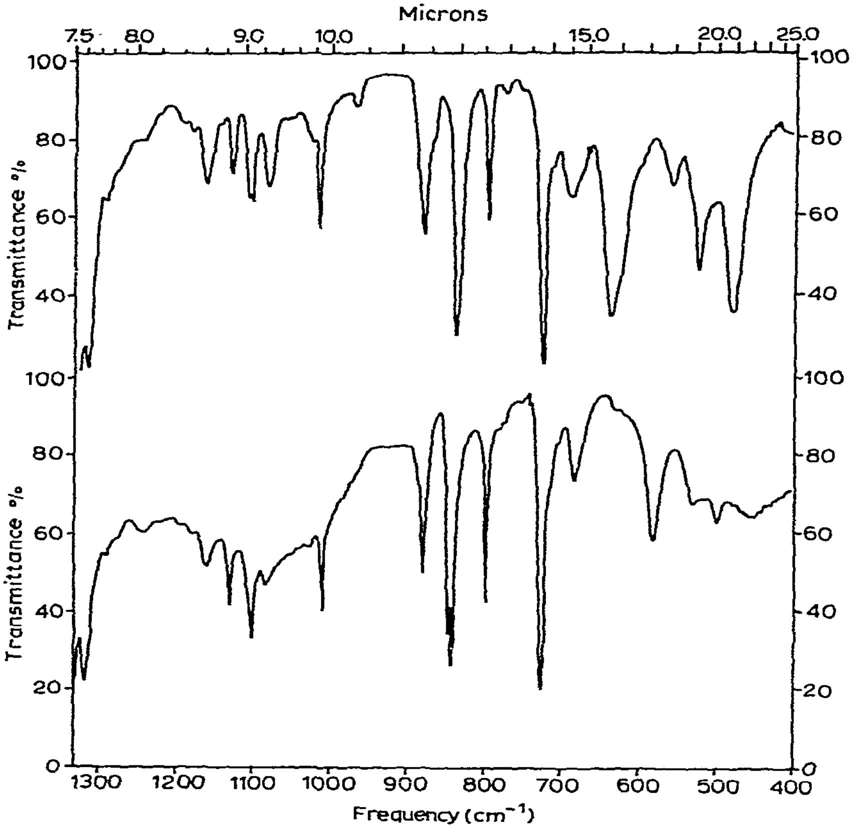


Fig. 1. Infrared spectra of dibutyltinbis(*p*-nitrobenzoate) (below) and tetrabutylbis(*p*-nitrobenzoyloxy)-distannoxane (above).

tions. Without entering into the question of interpretation of these patterns, it is clear that they originate from different compounds.

EXPERIMENTAL

In the following a general procedure for the preparation of the organotin esters is given; the results being summarized in Tables 1, 2, 3.

The respective carboxylic acid (0.01 mole, or excess) was suspended or dissolved in water (30 ml) and neutralized to phenolphthalein with sodium hydroxide (6 *N*). A solution of the organotin halide in methylene dichloride (50 ml) or in petroleum ether (50 ml, 0.01 mole in the case of monocarboxylic acid and 0.02 mole in the case of dicarboxylic acid) was added with strong stirring at 0° or at room temperature. After stirring for 30 min the organic layer was dried and evaporated to yield the almost pure ester. In certain cases (see Tables) the ester separated out from the reaction mixture and was filtered, washed with water and recrystallized.

SUMMARY

The "interfacial polymerization" method was utilized for the preparation of

organotin esters. Trialkyl- or triaryl-tin chlorides, dialkyltin dichlorides and tetraalkyldichlorodistannoxanes, dissolved in an inert solvent, were reacted with an aqueous solution of an alkali metal salt of a mono- or dicarboxylic acid, to yield the organotin esters in high yields.

REFERENCES

1 R. K. Ingham, S. D. Rosenberg and H. Gilman, *Chem. Rev.*, 60 (1960) 459.
2 P. W. Morgan, *Condensation Polymers by Interfacial and Solution Methods*, Interscience, New York, 1965, pp. 1–113.
3 M. Frankel, D. Gertner, D. Wagner and A. Zilkha, *J. Appl. Polymer Sci.*, 9 (1965) 3383.
4 C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, 75 (1953) 141.
5 M. Ohara, R. Okawara and Y. Nakamura, *Bull. Chem. Soc. Japan*, 38 (1965) 1379.
6 P. Dunn and T. Norris, *Australia, Commonwealth, Dept. Supply, Defence Std. Lab., Rept.*, 269 (1964); *Chem. Abstr.*, 61 (1964) 3134.
7 Ref. 1, p. 501.
8 T. N. Srivastava and S. K. Tandon, *Indian J. Appl. Chem.*, 26 (1963) 171.
9 S. Weber and E. I. Becker, *J. Org. Chem.*, 27 (1962) 1258.
10 A. K. Sawyer and H. G. Kuivila, *J. Org. Chem.*, 27 (1962), 610.
11 G. A. Razuvaev, N. S. Vyazankin and O. A. Shchepetkova, *Zh. Obshch. Khim.*, 3 (1961) 3762; *Chem. Abstr.*, 57 (1962) 8597.
12 N. S. Vyazankin, G. A. Razuvaev, O. S. D'yachovskaya and O. A. Shchepetkova, *Dokl. Akad. Nauk SSSR*, 143 (1962) 1348; *Chem. Abstr.*, 57 (1962) 8599.