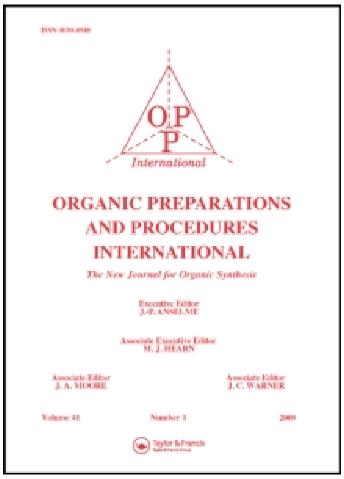

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

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To cite this Article La Liberte, Bernard R. , Reiff, Helmut F. and Davidsohn, Wenzel E.(1969) 'PREPARATION OF ALKYLTIN POLYFLUOROCARBOXYLATES AND RELATED DISTANNOXANES', Organic Preparations and Procedures International, 1: 3, 173 — 176

To link to this Article: DOI: 10.1080/00304946909458375

URL: http://dx.doi.org/10.1080/00304946909458375

ORGANIC PREPARATIONS AND PROCEDURES 1(3), 173-176 (1969)

PREPARATION OF ALKYLTIN POLYFLUOROCARBOXYLATES AND RELATED DISTANNOXANES

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$$(n\text{-}C_4H_9)_2SnO + 2RCOOH \longrightarrow (n\text{-}C_4H_9)_2Sn(OCOR_2)_2 + H_2O$$

$$[(n\text{-}C_4H_9)_3Sn]_2O + 2RCOOH \longrightarrow 2(n\text{-}C_4H_9)_3SnOCOR + H_2O$$

$$R = \text{-}CF_2CF_2CF_3,\ \text{-}CF_2CF_2OCOH,\ \text{etc.}$$

The alkyltin polyfluorocarboxylates have been synthesized, in nearly quantitative yields, by following established methods[1-2] for preparing alkyltin nonfluorocarboxylates.

A stoichiometric investigation of di-*n*-butyltin oxide and heptafluorobutyric acid unexpectedly revealed a 1:1 mole preference which resulted in a quantitative yield of a solid stable distannoxane:

$$2R_2SnO + 2HOCOC_3F_7 \longrightarrow (C_3F_7OCOSnR_2)_2O + H_2O$$

Another related example of a direct distannoxane formation, not reported in the literature,[3] is indicated below:

$$2CH_3OCOCH_2CH_2OCOH + 2R_2SnO \longrightarrow (CH_3OCOCH_2CH_2OCOSnR_2)_2O + H_2O$$

A mixed tin ester was converted to an unsymmetrical distannoxane:

$$R_2Sn(OCOC_3F_7)OCOCH_3 + R_2SnO \longrightarrow F_7C_3OCOSnR_2OSnR_2OCOCH_3$$

Although an analytical sample could not be prepared since the viscous liquid thermally decomposes under reduced pressures, the compound's purity was suitable for infrared study. The two polyfluoro-distannoxanes had the typical, assigned SnO vibrations found in general distannoxanes.[4-5]

	SnO stretch and CO_2 out-of-plane bend	SnO ring and CO_2 rock	SnO
$C_3F_7OCOSnR_2OSnR_2OCOC_3F_7$	622S 596Sh	485S	303S
$C_3F_7OCOSnR_2OSnR_2OCOCH_3$	638S 629Sh	492S	295S

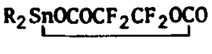
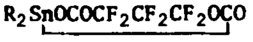
EXPERIMENTAL

Bis(di-*n*-butyl heptafluorobutyryl) Distannoxane: A mixture of di-*n*-butyltin oxide (9.97 g) and heptafluorobutyric acid (8.56 g) in 300 ml of benzene was heated under reflux for one hour. The water of reaction was removed azeotropically and collected in a Dean-Stark trap. The slight excess of di-*n*-butyltin oxide was filtered and the filtrate concentrated, resulting in a crude quantitative yield, mp 99-102°. The product was recrystallized from cold petroleum ether (bp 30-60°); mp 106-107°.

Anal. Calcd. for $C_{24}H_{36}F_{14}O_5Sn_2$: F, 29.30; Sn, 26.15. Found: F, 29.24; Sn, 25.98.

Di-*n*-butyl heptafluorobutyryltin Acetate: A mixture of di-*n*-butyltin oxide (8.56 g), di-*n*-butyltin diacetate (7.01 g) and heptafluorobutyric acid (4.98 g) in 300 ml of benzene was placed on a rotary evaporator and

Table I.

Tin Compounds	mp (°C)	bp (°C)/mm	Analysis		
				Calcd.	Found
$R_3SnOCO(CF_2)_2CF_3$	62-64	94/0.2	MW*	503	525
			C	38.20	38.10
			H	5.41	5.12
$R_2Sn[OCO(CF_2)_2CF_3]OCOCH_3$		108/0.15	MW		
			C	33.30	33.55
			H	4.19	4.27
$[CF_3(CF_2)_2OCOSnR_2]_2O$	106-107		MW		
			C	31.75	31.74
			H	4.00	4.03
$R_3SnOCO(CF_2)_6CF_3$	45-47	119/0.2	MW	703	723
			C	34.16	33.90
			H	3.85	3.60
$R_2Sn[OCO(CF_2)_6CF_3]_2$	63-65	137/0.1	MW	1059	1080
			C	27.22	26.92
			H	1.71	1.80
 $R_2SnOCOCF_2CF_2OCO$	204-206		MW		dimer†
			C	34.24	34.00
			H	4.31	4.33
$R_3SnOCOCF_2CF_2OCOSnR_3$	79-80		MW	768	755
			C	43.78	43.75
			H	7.09	7.35
 $R_2SnOCOCF_2CF_2CF_2OCO$	188-190		MW		dimer†
			C	33.15	32.87
			H	3.85	3.83
$R_3SnOCOCF_2CF_2CF_2OCOSnR_3$	125-126.5		MW	818	832
			C	42.57	42.63
			H	6.65	6.59
$R_2Sn[OCOCH_2OC_6F_5]_2$	138-139		MW	715	704
			C	40.31	40.12
			H	3.10	3.07
$R_3SnOCOCH_2OC_6F_5$	84-86		MW	531	543
			C	45.22	45.21
			H	5.50	5.42

$R = n\text{-}C_4H_9$
*MW - Molecular weight
†Determined by mass spectroscopy

the reaction mixture was concentrated. The clear viscous residue was distilled, yielding 9.2 (92%) of compound; bp 108°/0.15 mm; N_D^{22} 1.4174.

Anal. Calcd. for $C_{14}H_{21}F_7O_4Sn$: F, 26.34; Sn, 23.50. Found: F, 26.11; Sn, 23.12. The integrated NMR spectrum showed that the proton ratio is consistent with the assigned structure.

Acknowledgment

The authors express their sincere appreciation to Dr. T. Shannon and Dr. H. Langer of the Dow Chemical Company, Eastern Research Laboratories, Wayland, Massachusetts, for the molecular weight determinations by mass spectroscopy. We wish to thank Mr. R. Sacher for his assistance in assigning SnO bands found in the infrared analysis.

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The findings in this report are not to be construed as an official position of the Department of the Army.

(Received March 28, 1969)