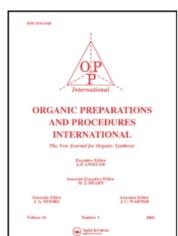
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PREPARATION OF ALKYLTIN POLYFLUOROCARBOXYLATES AND RELATED DISTANNOXANES

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PREPARATION OF ALKYLTIN POLYFLUOROCARBOXYLATES AND RELATED DISTANNOXANES

Bernard R. La Liberte, Helmut F. Reiff, and Wenzel E. Davidsohn

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$$(n-C_4H_9)_2Sn0 + 2RCOOH \longrightarrow (n-C_4H_9)_2Sn(OCOR_2)_2 + H_20$$

 $[(n-C_4H_9)_3Sn]_20 + 2RCOOH \longrightarrow 2(n-C_4H_9)_3SnOCOR + H_20$

$$R = -CF_2CF_2CF_3$$
, $-CF_2CF_2OCOH$, 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:

$$2R_2Sn0 + 2HOCOC_3F_7 \longrightarrow (C_3F_7OCOSnR_2)_20 + H_20$$

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

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

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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.

	Sn0 stretch and CO ₂ out-of-plane bend	SnO ring and CO ₂ rock	Sn0
C ₃ F ₇ OCOSnR ₂ OSnR ₂ OCOC ₃ F ₇	622S \ 596Sh \	485S	303S
C ₃ F ₇ OCOSnR ₂ OSnR ₂ OCOCH ₃	638S) 629Sh)	492S	295 S

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°.

<u>Anal.</u> Calcd. for $C_{24}H_{36}F_{14}O_{5}Sn_{2}$: 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.

	mp	bp	Analysis		
Tin Compounds	(°Ć)	(°C)/mm		Calcd.	Found
R ₃ SnOCO(CF ₂) ₂ CF ₃	62-64	94/0.2	MW*	503 38.20 5.41	525 38.10 5.12
R ₂ Sn[OCO(CF ₂) ₂ CF ₃]OCOCH ₃		108/0.15	MW C	33.30	33.55
[CF ₃ (CF ₂) ₂ OCOSnR ₂] ₂ O	106-107		H MW C	4.19	4.27 31.74
R ₃ SnOCO(CF ₂) ₆ CF ₃	45-47	119/0.2	H MW	4.00 703	4.03
		-	C H	34.16 3.85	33.90 3.60
$R_2 Sn[OCO(CF_2)_6 CF_3]_2$	63-65	137/0.1	MW C H	1059 27.22 1.71	1080 26.92 1.80
R ₂ SnOCOCF ₂ CF ₂ OCO	204-206		MW C H	34.24 4.31	dimer+ 34.00 4.33
R ₃ SnOCOCF ₂ CF ₂ OCOSnR ₃	79-80		MW C H	768 43.78 7.09	755 43.75 7.35
R ₂ SnOCOCF ₂ CF ₂ CF ₂ OCO	188-190		MW C H	33.15 3.85	dimer+ 32.87 3.83
R ₃ SnOCOCF ₂ CF ₂ CF ₂ OCOSnR ₃	125-126.5		MW C	818 42.57	832 42.63
R ₂ Sn[OCOCH ₂ OC ₆ F ₅] ₂	138-139		H MW C	6.65 715 40.31	6.59 704 40.12
R ₃ SnOCOCH ₂ OC ₆ F ₅	84-86		H MW C	3.10 531 45.22	3.07 543 45.21
		L	Н	5.50	5.42

 $R = n-C_4H_9$

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

^{*}MW - Molecular weight

[†]Determined by mass spectroscopy

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Anal. Calcd. for C₁₄H₂₁F₇O₄Sn: 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.

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

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