[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DREXEL INSTITUTE OF TECHNOLOGY]

Triethyltin Haloacetates, Halopropionates, and Propenoates

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Table I lists the properties of fourteen new triethyltin haloacetates, halopropionates, and propenoates. All except two of the esters result from the usual preparative method $[(C_2H_5)_3Sn]_2O + 2HOCOCH_2X \rightarrow 2(C_2H_5)_3SnOCOCH_2X + H_2O$. Two esters involve altered preparative methods $[(C_2H_5)_3Sn]_2O + 2CH_3OCOC(CH_3){=}CH_2 \rightarrow 2(C_2H_5)_3SnOCOC(CH_3){=}CH_2 + CH_3OCH_3$ and also $(C_2H_5)_3SnI + AgOCOCH_2OH \rightarrow (C_2H_5)_3SnOCOCH_2OH + AgI$.

Previous investigations on triethyltin esters at this Institute include the preparation of triethyltin esters by two methods: the typical[1,2] $[(C_2H_5)_3Sn]_2O + 2CF_3COOH \rightarrow 2(C_2H_5)_3SnOCOCF_3 + H_2O$ and a recent modification[3] $[(C_2H_5)_3Sn]_2O + 2C_2H_5OCOCH_3 \rightarrow 2(C_2H_5)_3SnOCOCH_3 + C_2H_5OC_2H_5$. The present paper employs acids in twelve preparations and an organic ester in one preparation. Neither of these methods appears suitable for the synthesis of the hydroxyacetate, but the use of a silver salt proves adequate—as in previous[4] organogermanium preparations—$(C_2H_5)_3SnI + AgOCOCH_2OH \rightarrow (C_2H_5)_3SnOCOCH_2OH + AgI$. Transesterifications or ester exchanges often have great usefulness in organosilicon[5] or organogermanium[6] preparations, but appear to have definite limitations in trialkyltin preparations, especially with moderately strong acids, which can yield diesters[7] $(C_2H_5)_3SnOCOCF_3 + 2C_6H_5SH \rightarrow (C_2H_5)_2Sn(SC_6H_5)_2 + C_2H_6 + CF_3COOH$.

An earlier paper shows the position of triethyltin esters in a "conversion series" for the use of silver salts.[8]

This present publication contains, it seems, the first trialkyltin halopropionates and the first trialkyltin propenoates. Earlier papers report the compounds $(C_2H_5)_3SnOCOCF_3$,[1] $(C_2H_5)_3SnOCOCH_2Cl$, and $(C_2H_5)_3SnOCOCHCl_2$[7] as haloacetates; the present paper adds $(C_2H_5)_3SnOCOCH_2F$, $(C_2H_5)_3SnOCOCH_2Br$, and $(C_2H_5)_3SnOCOCH_2I$.

Nearly all the compounds in Table I have limited thermal stabilities, but $(C_2H_5)_3SnOCOC_2F_5$ and $(C_2H_5)_3SnOCO\text{-}n\text{-}C_3F_7$ appear rather stable at their respective boiling points of 216.5° and 224° under 760 mm. pressure. In fact, the combination of limited thermal stability and of fairly high solubility in organic solvents makes the preparation of these compounds painstaking.

TABLE I

PROPERTIES OF TRIETHYLTIN HALOESTERS AND PROPENOATES

Compound	M.P., °C.	OCOR		Tin		Mol. Wt.		Yield, %[a]
		Calcd.	Found	Calcd.	Found	Calcd.	Found	
$(C_2H_5)_3SnOCOCH_2F$	155–156	27.2	27.3	42.0	41.8	282.9	—	30
$(C_2H_5)_3SnOCOCH_2Br$	99.5	40.2	40.5	34.6	34.8	343.8	361	50
$(C_2H_5)_3SnOCOCH_2I$	94.5	47.4	47.9	30.4	30.6	390.8	384	60
$(C_2H_5)_3SnOCOCH_2CH_2Cl$	87.5–88	34.3	33.9	37.9	38.3	313.4	310	70
$(C_2H_5)_3SnOCOCHClCH_3$	90.5–91	34.3	34.2	37.9	38.1	313.4	303	70
$(C_2H_5)_3SnOCOCH_2CH_2Br$	84.5	42.5	42.7	33.2	33.4	357.9	—	60
$(C_2H_5)_3SnOCOCHBrCH_3$	88–89	42.5	42.8	33.2	32.9	357.9	345	40
$(C_2H_5)_3SnOCOCHBrCH_2Br$	99.5–100	52.9	53.1	27.2	27.0	436.8	—	70
$(C_2H_5)_3SnOCOCF_2CF_3$[b]	94.5	44.2	44.5	32.2	32.2	368.9	384	40
$(C_2H_5)_3SnOCO\text{-}n\text{-}C_3F_7$[c]	75.5	50.8	51.1	28.3	28.8	418.9	420	40
$(C_2H_5)_3SnOCOCH{=}CH_2$	116–117	25.6	25.6	42.9	43.5	276.9	—	70
$(C_2H_5)_3SnOCOC(CH_3){=}CH_2$	75.5	29.2	29.1	40.8	40.9	291.0	—	30
$(C_2H_5)_3SnOCOCH{=}CHC_6H_5$	107–108	41.7	41.8	33.6	33.5	353.0	—	55
$(C_2H_5)_3SnOCOCH_2OH$	106.5–107	26.7	26.8	42.3	42.0	280.9	—	25

[a] Yield upon first crystallization. [b] B.p. (760 mm.) of pentafluoropropionate is 216.5°. [c] B.p. (760 mm.) of heptafluoro-*n*-butyrate is 224°.

Analyses in Table I include the direct determination, perhaps for the first time, of the ester group in organotin esters by titration with sodium hydroxide in ethanol.

EXPERIMENTAL

Starting materials included pure $[(C_2H_5)_3Sn]_2O$[1] and $(C_2H_5)_3SnI$, C_2F_5COOH and $n\text{-}C_3F_7COOH$ obtained from

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(1) G. S. Sasin, *J. Org. Chem.*, **18**, 1142 (1953).

(2) P. Kulmitz, *J. prakt. Chem.*, **80**, 60 (1860).

(3) H. H. Anderson, *J. Org. Chem.*, **19**, 1766 (1954).

(4) H. H. Anderson, *J. Org. Chem.*, **20**, 900 (1955).

(5) H. H. Anderson and G. M. Stanislow, *J. Org. Chem.*, **18**, 1716 (1953).

(6) H. H. Anderson, *J. Am. Chem. Soc.*, **74**, 2371 (1952).

(7) G. S. Sasin and R. Sasin, *J. Org. Chem.*, **20**, 387 (1955).

(8) H. H. Anderson and J. A. Vasta, *J. Org. Chem.*, **19**, 1300 (1954).

Peninsular Chemicals Co., Gainesville, Fla., and redistilled, Eastman Kodak white label haloacids, highly toxic, center-fraction CH_2FCOOH prepared from $NaOCOCH_2F$ and concentrated H_2SO_4, propenoic acid distilled free of inhibiting hydroquinone, methyl methacrylate with inhibitor left present, and $AgOCOCH_2OH$ made from $AgNO_3$, $NaOCOCH_2OH$, and a little excess $HOCH_2COOH$ in aqueous solution.

Analytical methods included determination of tin as SnO_2 after treatment of the organotin compound with mixed fuming nitric and fuming sulfuric acids, determination of molecular weights in camphor solution when the compound had sufficient thermal stability, and direct determination of the OCOR group through titration with ethanolic sodium hydroxide. This last procedure may be part of a future publication upon analytical methods.

Determination of corrected melting points in Table I employed an Anschutz thermometer with the tiny bulb immersed in the melted compound or more frequently employed the customary capillary method without recovery of the compound. Three to five recrystallizations sufficed to produce a compound of constant melting point.

Reactions with acids. Typically, 2.35 g. (11.0 milliequivalents) of $[(C_2H_5)_3Sn]_2O$ and 10.0 milliequivalents of the haloacid were combined and heated for 10 min. at 100° if the haloacid decomposed easily, but up to 60 min. at 100° if the haloacids were relatively stable. Some water formed; pipetting separated most of the water and Na_2SO_4 accepted the rest. The material was crystallized from small volumes of an organic solvent such as n-C_4H_9Cl or petroleum ether (30–60°) until the melting point became constant; often the use of a salt-ice bath was necessary in crystallization. At the melting point or slightly above it $(C_2H_5)_3SnOCOCH{=}CH_2$ decomposed somewhat. Formation of two immiscible layers in the preparation of $(C_2H_5)_3SnOCOCH_2F$ probably was responsible for the low yield of ester.

Reaction with methyl methacrylate. Methacrylic acid alone would probably polymerize too rapidly for use with $[(C_2H_5)_3Sn]_2O$. Three individual runs consisted of heating 2.60 g. of $[(C_2H_5)_3Sn]_2O$ and 1.30 g. of inhibited $CH_3OCOC(CH_3){=}CH_2$ for 1.5 hr. at 100° and then crystallizing from CCl_4 at $-10°$ to get 0.6–1.0 g. of $(C_2H_5)_3SnOCOC(CH_3){=}CH_2$ without isolation of the CH_3OCH_3. In one run excessive viscous polymeric methyl methacrylate prevented recovery of the organotin ester. Later crystallizations employed mixtures of CCl_4 and petroleum ether (30–60°) first and finally petroleum ether alone.

Reaction with $AgOCOCH_2OH$. No reaction occurred between $[(C_2H_5)_3Sn]_2O$ and 70% aqueous $HOCH_2COOH$. However, 1.8 g. of $AgOCOCH_2OH$ and 2.25 g. of $(C_2H_5)_3SnI$ after 15 min. reflux in 15 ml. of CCl_4 and the usual filtration and washing of silver salts[4,8] finally yielded 0.4 g. of $(C_2H_5)_3SnOCOCH_2OH$ upon crystallization from mixed CCl_4 and n-C_4H_9Cl. Two crystallizations from n-C_4H_9Cl followed.

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Hydrogenolysis of the Nitrogen—Nitrogen Bond of Acylhydrazines with Raney Nickel

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The scope of the reductive cleavage of mono- and diacylhydrazines by Raney nickel in the absence of added hydrogen has been explored. Alkyl substituted monoacylhydrazines and unsubstituted 1,2-diacylhydrazines are cleaved readily. 1,2-Diacylhydrazines, which bear substituents other than hydrogen on the nitrogens, are generally reduced with difficulty or not at all. The nitrogen—nitrogen bonds of 1-acyl-2-alkylidenehydrazines undergo smooth hydrogenolysis, yielding the corresponding amides.

In 1954, Ainsworth[1] showed that the nitrogen—nitrogen bond of simple carboxylic acid hydrazides can be reductively cleaved by refluxing an ethanolic solution of the hydrazide with a large quantity of Raney nickel (Equation 1). More recently this

$$RCONHNH_2 \longrightarrow RCONH_2 + NH_3 \qquad (1)$$

reaction has been extended to a variety of other compounds, including 1,2-diacylhydrazines and some heterocycles which contain a nitrogen—nitrogen bond.[2]

The purpose of the present work was to explore more completely the scope and limitations of this useful reaction, as it applies to acylhydrazines bearing various substituent groups on the nitrogens. A number of the acylhydrazines were those prepared in connection with other recently reported work.[3] Raney nickel W-2[4] was used in most of the experiments. However, a commercial catalyst[5] was used in a few of the experiments for comparison purposes. No significant differences in activity were observed. The results are summarized in Table 1.

Although 1,2-dibenzoylhydrazine was cleaved to benzamide in 3 hr., as reported by Ainsworth,[2] only a trace of acetamide was isolated from the reaction of 1,2-diacetylhydrazine which was recovered largely unchanged after 3 hr. Since acetamide was isolated in good yield from the latter reaction after a 15-hr. reaction period, the longer time was used with all 1,2-diacylhydrazines.

As examples 1 to 3 show, the accumulation of

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(1) C. Ainsworth, *J. Am. Chem. Soc.*, **76**, 5774 (1954).

(2) C. Ainsworth, *J. Am. Chem. Soc.*, **78**, 1636 (1956).

(3a) R. L. Hinman, *J. Am. Chem. Soc.*, **78**, 1645 (1956).

(3b) R. L. Hinman, *J. Am. Chem. Soc.* **79**, 414 (1957).

(4) R. Mozingo, *Org. Syntheses*, **Coll. Vol. III,** 181 (1955).

(5) "Raney Catalyst in Water," Raney Catalyst Co., Chattanooga, Tennessee.