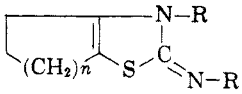
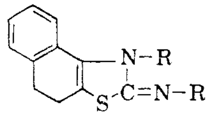
TABLE II



R	n	M.P., °C.	Yield, %	Empirical Formula	Analysis, % Calculated N	Calculated S	Found N	Found S
C_2H_5	1	157	32	$C_{10}H_{16}N_2S\cdot HCl$	12.57	14.38	12.82	14.37
C_2H_5	2	145–147	70	$C_{11}H_{18}N_2S\cdot HCl$	11.35	13.00	11.48	13.26
Cyclohexyl	1	188–190	46	$C_{19}H_{28}N_2S\cdot HCl$	7.98	9.18	8.02	9.00
Cyclohexyl	2	184–186	75	$C_{20}H_{30}N_2S\cdot HCl$	7.65	8.73	7.44	8.56
p-C_3H_7O—C_6H_4	2	104–106	15	$C_{25}H_{30}N_2O_2S$	6.63	7.58	6.64	7.80
p-$i$$C_5H_{11}O$—$C_6H_4$	2	124–125	30	$C_{29}H_{33}N_2O_2S\cdot HCl$	5.44	6.23	5.80	6.00

TABLE III



R	M.P., °C.	Yield, %	Empirical Formula	Analysis, % Calculated N	Calculated S	Found N	Found S
Cyclohexyl	108–109	38	$C_{23}H_{28}N_2S$	7.65	8.76	7.50	8.99
p-$C_3H_7OC_6H_4$	220–223	30	$C_{29}H_{30}N_2O_2S\cdot HBr$	5.09	5.83	5.04	5.79
p-$i$$C_5H_{11}OC_6H_4$	234–235	45	$C_{33}H_{38}N_2O_2S\cdot HBr$	4.62	5.28	4.70	5.07
p-C_4H_9—C_6H_4	223–225	44	$C_{31}H_{34}N_2S\cdot HBr$	5.12	5.87	5.03	5.88

EXPERIMENTAL[9]

Preparation of intermediates. α-Chlorocyclopentanone and α-chlorocyclohexanone were prepared according to the procedure outlined by Kötz,[10] and 2-bromotetralone was prepared according to Wilds.[11] The substituted arylisocyanates and isothiocyanates were prepared by well known methods.[6]

Condensation of 2-amino-4,5-cyclic substituted thiazoles with arylisocyanates and arylisothiocyanates. General procedure. An equivalent amount of arylisocyanate or isothiocyanate was added to the 2-aminothiazole dissolved in 10 times its volume of dry benzene. A vigorous reaction usually occurred leading to copious precipitation of the product. The reaction mixture, after refluxing for a period of time, was filtered, washed with benzene, and recrystallized from ethanol. In preparing the ureas, it was found that only 1 to 2 hr. reflux was necessary, whereas the condensation between the 2-aminothiazoles and the arylisothiocyanates proceeded at a much slower rate, requiring from 12 to 24 hr. of reflux.

Condensation of α-haloketones with symmetrical thioureas. General procedure. The products of this condensation are presented in Tables II and III. For the sake of clarity, the details for the preparation of 3-p-butylphenyl-2-p-butylphenylimino-8,9-dihydro-β-naphthothiazoline hydrobromide will be described. The other compounds in these tables are prepared in similar fashion.

A mixture of 17.0 g. (0.05 mole) of 1,4-bis(p-butylphenyl)-2-thiourea, 11.3 g. (0.05 mole) of 2-bromotetralone, and 200 ml. of absolute ethyl alcohol was refluxed for 6 hr. The clear solution was evaporated to one-tenth its volume and then 300 ml. of dry ether was added with vigorous stirring. After chilling overnight, the fine white powder was collected on a Büchner funnel and washed well with ether. Analytically pure material was obtained by dissolving the powder in a minimum amount of absolute ethyl alcohol and precipitating the product through the addition of ether.

Acknowledgments. We would like to express our gratitude to Mr. Louis Dorfman and his associates for the microanalytical data.

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[9] All melting points are uncorrected.

[10] A. Kötz, *Ann.*, **400**, 53 (1940).

[11] A. L. Wilds, *J. Am. Chem. Soc.*, **67**, 1751 (1945).

Vinyl Derivatives of the Metals. VII. Preparation of Organotin Esters by Cleavage of Vinyltin Compounds[1,2]

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DIETMAR SEYFERTH[3]

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A large variety of methods has been applied to the preparation of the now commercially useful organotin esters. The oldest, most frequently used and most widely applicable procedure involves the

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[1] Part VI: L. Maier, D. Seyferth, F. G. A. Stone, and E. G. Rochow, *J. Am. Chem. Soc.*, **79**, 5884 (1957).

[2] The majority of the experimental work was carried out by Arnold Saitow as part of a senior research problem at Harvard University.

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reaction of an organic acid with an organotin oxide or hydroxide.[4] Less widely used has been the reaction of silver salts of organic acids with organotin halides, pseudohalides, sulfides, and oxides,[5] the reaction of alkali metal salts of organic acids with organotin halides in aqueous[6a] or nonaqueous[6b] solution, transesterification reactions,[4c] and the reaction of organic esters with organotin oxides.[4e,7] A recent method involves the cleavage of organic groups from tetraorganotin compounds:

$$R_4Sn + RCO_2H \longrightarrow R_3SnO_2CR + RH$$

Thus Sasin and Sasin[8] described the cleavage of tetraethyltin by organic acids, phenols and thiophenols, and mercaptans. The cleavage of the vinyl-tin bond in alkyl(vinyl)tin compounds by organic acids has been reported[9] from this laboratory.

In this note more examples of the latter reaction are presented. It was found in all cases that the vinyl group is cleaved preferentially in tri-*n*-propylvinyltin and dimethyldivinyltin. Ethylene was evolved and the corresponding tri-*n*-propyltin or dimethyltin ester remained behind:

$$(n\text{-}C_3H_7)_3SnCH{=}CH_2 + RCO_2H \longrightarrow (n\text{-}C_3H_7)_3SnO_2CR + C_2H_4$$

$$(CH_3)_2Sn(CH{=}CH_2)_2 + 2\ RCO_2H \longrightarrow (CH_3)_2Sn(O_2CR)_2 + 2\ C_2H_4,$$

thus providing confirmation of previous evidence[9] that the vinyl group is cleaved more readily from a tin atom than are *n*-alkyl groups. Qualitative observation of the rate of reaction of organic and inorganic acids showed that the stronger the acid, the faster was the rate of cleavage. Thus, as has been shown previously,[9] hydrogen bromide reacts rapidly even at −78°. Trifluoro-, trichloro-, and dichloroacetic acids reacted very vigorously at room temperature, yields of 50–70% being obtained in a reaction time of less than one minute. Monohaloacetic acids required a reaction time of from 10 to 20 minutes in order to effect comparable yields, while acetic acid required still longer heating. Mercaptans reacted even more slowly.[9] Similar results have been reported by Lesbre and Dupont[10] in their study of the cleavage of tetraalkyltin compounds by acids of varying strength.

The new compounds prepared in this study, together with their melting points and analytical data, are listed in Table I.

TABLE I

NEW ORGANOTIN ESTERS PREPARED BY CLEAVAGE OF VINYLTIN COMPOUNDS

Formula	M.P., °C.	Carbon, %		Hydrogen, %	
		Calcd.	Found	Calcd.	Found
R in $(n\text{-}C_3H_7)_3SnO_2CR$					
CF_3	94–95	36.60	36.87	5.87	6.16
CCl_3	96–97	32.12	32.41	5.16	5.26
$CHCl_2$	84–85	35.15	35.33	5.90	6.02
CH_2Cl	78–80	38.69	38.46	6.78	6.70
CH_2Br	77–78	34.23	34.36	6.00	6.24
CH_2CN	91–92	43.41	43.50	6.98	6.97
CH_3[a]	100				
$CHBrCH_3$	88–89	36.03	36.27	6.30	6.24
R in $(CH_3)_2Sn(O_2CR)_2$					
CF_3	240–243	19.23	19.07	1.61	1.92
CCl_3	190–191	15.22	15.32	1.28	1.32
$CHCl_2$	226–228	17.77	16.83	1.98	2.26
CH_2Cl	162–165	21.47	21.35	3.00	3.04
CH_2Br	159–160	16.97	17.11	2.36	2.23
dimethylvinyltin monochloroacetate	104–107	26.76	26.89	4.12	4.18
dimethyltin bis-benzenephosphinate	260 (dec.)[b]				

[a] Ref. 3d reports m.p. 99–100°. [b] Decomposes with frothing; the froth resolidifies at 263°. This compound was previously described by D. Seyferth and F. G. A. Stone, *J. Am. Chem. Soc.*, **79**, 515 (1957), but the temperature of decomposition given there was incorrect and should be corrected to read: "melted at 259° with decomposition (frothing and solidification of the froth at 262°)".

The attempted cleavage of only one vinyl group from dimethyldivinyltin in most cases did not lead to pure dimethylvinyltin ester. Analysis usually indicated that some diester was present as well. Partial cleavage of both vinyl groups was most prevalent with the stronger acids, pure products being obtained only with chloroacetic acid and α-bromopropionic acid.[9]

EXPERIMENTAL*

Starting materials. Tri-n-propylvinyltin, a new compound, was prepared by the following sequence of reactions:

$$4\ n\text{-}C_3H_7MgBr + SnCl_4 \xrightarrow{\text{tetrahydrofuran}} (n\text{-}C_3H_7)_4Sn\quad (81\%)$$

$$3\ (n\text{-}C_3H_7)_4Sn + SnCl_4 \xrightarrow{200°,\ 2.5\ \text{hrs.}} (n\text{-}C_3H_7)_3SnCl\quad (88\%)$$

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[4] (a) A. Cahours, *Ann.*, **114**, 359, 366, 378 (1860); (b) G. S. Sasin, *J. Org. Chem.*, **18**, 1142 (1953); (c) G. S. Sasin and R. Sasin, *J. Org. Chem.*, **20**, 387 (1955); (d) G. J. M. van der Kerk and J. G. A. Luitjen, *J. Appl. Chem.*, **6**, 49 (1956); (e) H. H. Anderson, *J. Org. Chem.*, **22**, 147 (1957).

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

[6] (a) E. G. Rochow, D. Seyferth, and A. C. Smith, Jr., *J. Am. Chem. Soc.*, **75**, 3099 (1953); (c) C. M. Langkammerer, U.S. Patent **2,253,128** (1941).

[7] H. H. Anderson, *J. Org. Chem.*, **19**, 1766 (1954).

[8] R. Sasin and G. S. Sasin, *J. Org. Chem.*, **20**, 770 (1955).

[9] D. Seyferth, *J. Am. Chem. Soc.*, **79**, 2133 (1957).

[10] M. Lesbre and R. Dupont, *Compt. rend. 78e Congr. Socs. Savantes Paris et Depts., Sect. Sci.*, 429 (1953); *cf. Chem. Abstr.*, **49**, 15729 (1955).

* Analyses were performed by the Schwarzkopf Microanalytical Laboratories, Woodside 77, N. Y. Melting points were determined using a Hershberg melting point apparatus.

TABLE II

Vinyltin Compound	Millimoles	Acid: R in RCO_2H	Millimoles	Reaction Time, Min.	Recrystallized From	Ester	Yield, %
$(n\text{-}C_3H_7)_3SnCH{=}CH_2$	12.4	CF_3	12.4	$< 1^a$	30–60° Petroleum ether	$n\text{-}Pr_3SnO_2CCF_3$	64.4
	3.64	CCl_3	3.64	$< 1^a$	30–60° Petroleum ether	$n\text{-}Pr_3SnO_2CCl_3$	53.8
	3.64	$CHCl_2$	3.64	$< 1^a$	30–60° Petroleum ether	$n\text{-}Pr_3SnO_2CCHCl_2$	65.3
	7.28	CH_2Cl	7.28	30^b	30–60° Petroleum ether	$n\text{-}Pr_3SnO_2CCH_2Cl$	58.1
	3.64	CH_2Br	3.64	10^b	30–60° Petroleum ether	$n\text{-}Pr_3SnO_2CCH_2Br$	60.5
	3.64	CH_2CN	3.64	45^c	30–60° Petroleum ether	$n\text{-}Pr_3SnO_2CCH_2CN$	72.0
	7.28	CH_3	7.28	90^b	30–60° Petroleum ether	$n\text{-}Pr_3SnO_2CCH_3$	16.2
	3.64	CH_3CHBr	3.64	15^b	30–60° Petroleum ether	$n\text{-}Pr_3SnO_2CHBrCH_3$	61.4
$(CH_3)_2Sn(CH{=}CH_2)_2$	4.94	CF_3	9.88	$< 1^a$	CH_2Cl_2-30–60° Petroleum ether	$Me_2Sn(O_2CCF_3)_2$	86.3
	4.94	CCl_3	9.88	$< 1^a$	CH_2Cl_2-30–60° Petroleum ether	$Me_2Sn(O_2CCl_3)_2$	99.5
	4.94	$CHCl_2$	9.88	$< 1^a$	CH_2Cl_2-30–60° Petroleum ether	$Me_2Sn(O_2CCHCl_2)_2$	82.4
	4.94	CH_2Cl	9.88	15^b	CH_2Cl_2-30–60° Petroleum ether	$Me_2Sn(O_2CCH_2Cl)_2$	97.5
	4.94	CH_2Br	9.88	5^b	CH_2Cl_2-30–60° Petroleum ether	$Me_2Sn(O_2CCH_2Br)_2$	97.9
	22.2	CH_2Cl	18.0	90^b	CH_2Cl_2-30–60° Petroleum ether	$Me_2ViSnO_2CCH_2Cl$	80.0
	4.94	$C_6H_5(H)P(O)OH$	9.88	30^b	^{d}	$Me_2Sn[O(O)P(H)C_6H_5]_2$	98.0

[a] Mixed at room temp.; exothermic reaction occurred and mixture was not externally heated. [b] Heated on steam bath. [c] Heated in an oil bath at 154°. [d] Washed with ether, hot ethanol, hot water, and methanol.

$$(n\text{-}C_3H_7)_3SnCl + CH_2{=}CHMgBr \xrightarrow{\text{tetrahydrofuran}} (n\text{-}C_3H_7)_3SnCH{=}CH_2 \quad (87\%)$$

$(n\text{-}C_3H_7)_3SnCH{=}CH_2$, b.p. 90° at 8.2 mm., n_D^{25} 1.4776, d_4^{25} 1.131.

Anal. Calcd. for $C_{11}H_{24}Sn$: C, 48.04; H, 8.80; MR_D 68.81. Found: C, 47.83; H, 8.93; MR_D 68.78.

Dimethyldivinyltin was prepared as described previously by us.[11] Dimethyltin oxide was obtained from the basic hydrolysis of dimethyltin dichloride.[12]

Cleavage of tri-n-propylvinyltin. The preparation of tri-*n*-propyltin trifluoroacetate is given as an example of the procedure used.

Trifluoroacetic acid, 1.41 g. (0.0124 mole), and 3.40 g. (0.0124 mole) of tri-*n*-propylvinyltin were mixed in a 25 ml. Erlenmeyer flask. A vigorous exothermic reaction resulted, and in less than 30 sec. the reaction mixture had become a pasty solid. Filtration, followed by recrystallization from 30–60° petroleum ether and drying in an Abderhalden drying pistol, gave 3.09 g. of the desired ester. During the drying process a small amount of the ester sublimed into the colder portion of the tube; this sublimate also melted at 94–95°.

Cleavage of dimethyldivinyltin. The preparation of dimethyltin di(bromoacetate) is given as an example.

To 1.0 g. (4.94 millimole) of dimethyldivinyltin in a 25-ml. Erlenmeyer flask, equipped with an air condenser, was added 1.37 g. (9.88 millimole) of bromoacetic acid. The mixture was heated on the steam bath for 5 min. On cooling a pasty crystalline solid resulted. This was recrystallized from a mixture of dichloromethane and 30–60° petroleum ether and was dried. A yield of 2.05 g. of the desired ester was obtained.

Experimental data for all other preparations are summarized in Table II.

Preparation of dimethyltin dimethacrylate. As an example of the first method mentioned in the introduction, the procedure used to prepare dimethyltin dimethacrylate is given:

To a slurry of 16.5 g. (0.1 mole) of dimethyltin oxide in 200 ml. of methanol was added 17 ml. (0.2 mole) of methacrylic acid. The oxide reacted with the acid when the mixture was warmed on the steam bath. The resulting solution was treated with decolorizing charcoal, filtered, and evaporated. White needles, 26.0 g. (77.6% yield) remained, which were recrystallized from cyclohexane to give pure dimethyltin dimethacrylate, m.p. 140–144°.

Anal. Calcd. for $C_{10}H_{16}O_4Sn$: Sn, 37.2. Found: Sn, 37.3.

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