reaction product. The high iodine value and low P and Cl results indicated that unreacted olefin is present in the product.

Phosphorylated Pentadecene.[13] Viscous oil. *Anal.* Calcd. for $C_{15}H_{30}POCl$: P, 11.1; Cl, 12.8; iodine value, 0.0. Found: P, 9.07; Cl, 9.15; iodine value, 30.4. This is a crude reaction product. The high iodine value, and low P and Cl results indicated that unreacted olefin is present in the product.

Tricosene-11: Equimolar quantities of olefin, PCl_3, and $AlCl_3$ were used in this reaction. Obtained a viscous oil. Calcd. for $C_{23}H_{46}POCl$: P, 7.65; Cl, 8.77; iodine value, 0.0. Found: P, 7.8; Cl, 4.9; iodine value, 9.0.

The following olefins were obtained as mixtures of free acid and acid chloride. The relative composition is based on % Cl and saponification equivalent determinations. Results are shown in Table III.

With simpler olefins, such as *alpha* olefins and cyclohexene, low yields were obtained as indicated by high iodine values and low P and Cl analyses. Removal of the starting olefins was difficult, since some polymerization had occurred. Cyclohexene is cited as a typical example. The product obtained is a viscous oil with the following analysis: Calcd. for $C_6H_{12}POCl$: P, 18.86; Cl, 21.55; iodine value, 0.0. Found: P, 13.7; Cl, 8.9; iodine value, 41.

General procedure for preparing esters from phosphorylated olefins. The crude phosphorylation product was added dropwise with stirring to a solution containing a 10–20% excess of sodium alkoxide in the corresponding alcohol at 50–60° over a period of about 45 min. The mixture was stirred for 15–30 min. longer. After cooling to room temperature the product was taken up in ether, the phases separated and the ether solution washed with water until the washings were neutral. After drying, the ether and excess alcohol were removed *in vacuo.* Yields of crude ester based on starting olefin varied from 55 to 70% depending on the olefin. If the intermediate acid chloride was purified before use, as can readily be done with the 2,4,4-trimethylpentene phosphorus-acid chloride derivative, yields were nearly quantitative.

Methyl ester of phosphorylated 2,4,4-trimethylpentene-2. Colorless liquid or white solid, m.p. 35–36; b.p. 78°/0.7 mm.

Anal. Calcd. for $C_8H_{16}PO_2CH_3$: sap. equiv., 190.2; P, 16.3; mol. wt., 190.2. Found: sap. equiv., 190.6; P, 17.3; mol. wt. (ebullioscopic in acetone), 201.

CHICAGO 9, ILL.

---

[13] Commercial grade propylene pentamer with 3–4% terminal olefin.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

1,2-Diacyloxyditins: A New Class of Organotin Compound[1]

ALBERT K. SAWYER AND HENRY G. KUIVILA

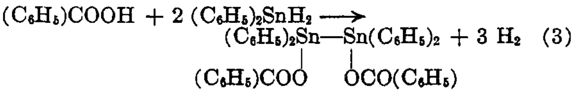
Received May 2, 1961

In the reactions of diphenyltin dihydride with carboxylic acids, 1,1,2,2-tetraphenyl-1,2-diacyloxyditins are formed. With di-*n*-butyltin dihydride and carboxylic acids either this type of ditin or simple di-*n*-butyldiacyloxytin is formed, depending on the acid and the acid/hydride ratio. Quantitative yields of 1,2-diacyloxyditins are also obtained in reactions of di-*n*-butyltin dihydride with di-*n*-butyldiacyloxytins in equimolar ratio. Reactions between bromine and 1,2-diacyloxyditins may be used for quantitative determination of the latter and lead to the formation of disubstituted acyloxybromotins.

In an attempt to prepare diphenyltin dibenzoate by reaction 1, (analogous to reaction 2 observed in earlier work[2]), less than the expected quantity of hydrogen, along with a crystalline product with analysis corresponding to 1,1,2,2-tetraphenyl-1,2-dibenzoyloxyditin was obtained. The structure of the solid product was assigned on the basis of the elemental analysis, the stoichiometry of Equation 3, and the reactions discussed below.

$$2\,(C_6H_5)COOH + (C_6H_5)_2SnH_2 \longrightarrow (C_6H_5)_2Sn(OCO(C_6H_5))_2 + 2\,H_2 \quad (1)$$

$$2\,HCl + (C_6H_5)_2SnH_2 \longrightarrow (C_6H_5)_2SnCl_2 + 2\,H_2 \quad (2)$$



$$2\,(C_6H_5)COOH + 2\,(C_6H_5)_2SnH_2 \longrightarrow \underset{(C_6H_5)COO}{(C_6H_5)_2Sn}\!-\!\underset{OCO(C_6H_5)}{Sn(C_6H_5)_2} + 3\,H_2 \quad (3)$$

In studying the scope of this reaction, carboxylic acids of increasing strength up to trifluoroacetic acid were used with diphenyltin dihydride. The results are shown in Table I. Although in most cases the carboxylic acid was used in excess of that required by reaction 3, the only product isolated was the ditin, and whenever the hydride was used in excess the yield of pure ditin was higher. Although other cases gave nearly the expected amount of hydrogen by reaction 3, trifluoroacetic and trichloroacetic acids gave only about one third of this amount even though all hydride was consumed. It is probable that the trihalomethyl groups were partially reduced by the hydride, as it has been shown that organotin hydrides reduce aliphatic and aromatic halides, the former readily and the latter with more difficulty.[3]

In extending this reaction to di-*n*-butyltin dihydride it became difficult to get crystalline products, and in the case of succinic acid a product

---

[1] Support of this work by the Office of Ordnance Research, U. S. Army, is gratefully acknowledged. Our thanks are also due to Metal and Thermit Corporation for support and gifts of chemicals.

[2] H. G. Kuivila, A. K. Sawyer, and A. G. Armour, *J. Org. Chem.*, **26**, 1426 (1961).

[3] (a) J. G. Noltes and G. J. M. van der Kerk, *Functionally Substituted Organotin Compounds*, Tin Research Institute, Greenford, Middlesex, England, 1958; G. J. M. van der Kerk and J. G. A. Luijten, *J. Applied Chem.*, **7**, 356 (1957). (b) C. A. Rothman and E. I. Becker, *J. Org. Chem.*, **24**, 294 (1959).

TABLE I

REACTIONS OF DIPHENYLTIN DIHYDRIDE WITH RCOOH TO FORM 1,1,2,2-TETRAPHENYL-1,2-DIACYLOXYDITINS

RCOOH	Procedure	Ratio of Acid to Hydride	Yield	Moles H_2/ Mole $(C_6H_5)_2SnH_2$	M.P.	Calculated			Found		
						Sn	C	H	Sn	C	H
Formic	B	0.8	[a]	1.26[b]	[a]						
Acetic	B	0.8	75	1.22[b]	152	35.76	50.66	3.95	35.68, 35.83	50.50	4.12
Monochloroacetic	C	0.8	83	1.57[b]	150	32.40	45.89	3.30	32.61, 32.59	45.84	3.52
	A	2.0	35	1.31	150						
Dichloroacetic	B	0.8	75	1.37[b]	169	29.61	41.95	2.77	29.73, 29.74	42.13	2.77
Trichloroacetic	A	2.0	35	0.55[c]	170	27.27	38.63	2.30	27.29, 27.64	38.88	2.25
Trifluoroacetic	A	2.5	32	0.96	165	30.76	43.57	2.61	30.91, 30.96	43.28	2.42
Benzoic	C	1.5	68	1.52	185	30.13	57.92	3.84	29.75, 30.06	58.13	3.69
o-Chlorobenzoic	C	1.5	47	1.69	161	27.70	53.26	3.29	27.69, 27.76	53.19	3.13
o-Hydroxybenzoic	A	2.0	32	1.29	197	28.95	55.66	3.69	28.68, 28.45	55.53	3.70
Hexanoic	A	2.0	49	1.52	85–87	30.59	55.71	5.46	30.53, 30.34	54.94	5.35
Octanoic	A	2.0	7	1.48	86–88	28.54	57.73	6.06	28.68, 28.59	57.57	6.13

[a] The product after recrystallization from 1) benzene and 2) chloroform melted at 153° (dec.) and had an analysis 1.1% low for Sn. In another run using a ratio of 4.0 the product also melted at 153° (dec.) and had an analysis 1.0% high for Sn. The compound was not obtained analytically pure. [b] Moles of H_2/mole of acid as hydride was in excess. [c] Test showed no unused hydride.

TABLE II

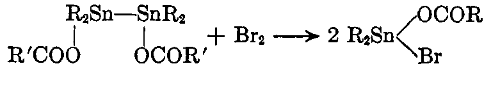
REACTIONS OF DI-*n*-BUTYLTIN DIHYDRIDE WITH RCOOH TO FORM $Bu_2Sn(OCOR)_2$ (A) AND $(Bu_2SnOCOR)_2$(B)

RCOOH	Ratio of Acid to Hydride	Type of Product	Yield,[a] %	% B[b]	Moles H_2/Mole Bu_2SnH_2	M.P.[c]	Calculated			Found		
							Sn	C	H	Sn	C	H
Acetic	2.0	A	90		1.98	8.5–10	33.82			33.75		
	1.14	B	65	68	1.57	−7.0 to −4.0	40.59	41.06	7.24	40.84	40.81	7.51
Monochloroacetic	2.0	A	80.5	Trace	1.94	87–89	28.27	34.32	5.28	28.39	34.24	5.50
Dichloroacetic	2.0	A	16		1.98	112–114	24.29	29.48	4.12	24.36	29.87	4.42
Trichloroacetic	2.0	d	d		1.13	[d]						
Trifluoroacetic	2.0	A	d	Trace	1.99	[d]						
Benzoic	2.0	A	52	9	1.63	68–71	24.98	55.60	5.94	24.77	55.68	6.02
	1.0	B	65	69	1.41	31.5–32.5	33.53	50.88	6.55	33.29	50.72	6.72
o-Chlorobenzoic	0.76	B	60		1.78[f]	65–66.5	30.55	46.37	5.71	30.29	46.41	5.68
p-Chlorobenzoic	0.80	B	15.5		1.69[f]	75–77	30.55	46.54	5.72	30.53	46.41	5.68
Succinic	0.83	A	71	0	[g]	185.5–187.5	34.01			34.10		
Lauric	0.77	B[e]	96[d]		1.66	[e]						

[a] Of sample purified for analysis. [b] In product mixture as determined by bromine analysis. [c] Taken by normal method. [d] Analytically pure product not isolated. [e] Product not isolated but measured by bromine titration. [f] Moles of H_2/mole of acid as hydride was in excess.[g] Not measured. [h] Identified by mixture melting point with authentic sample.

clearly not a ditin, the known[4] tetrameric di-*n*-butyltin succinate, was obtained. With acetic acid and an acid/hydride ratio of 2.0 a 90% yield of di-*n*-butyltin diacetate was obtained along with two moles of hydrogen per mole of hydride. When the acid/hydride ratio was decreased to 1.14, only 1.57 mole of hydrogen per mole of hydride was obtained and a 68% yield of 1,1,2,2-tetra-*n*-butyl-1,2-diacetoxyditin, determined by the consumption of bromine by the reaction product mixture.

To test the validity of the bromine titration by reaction 4 in one case, from an authentic sample



$$\underset{R'COO}{R_2Sn}-\underset{OCOR'}{SnR_2} + Br_2 \longrightarrow 2\,R_2Sn\begin{matrix}OCOR'\\Br\end{matrix} \qquad (4)$$

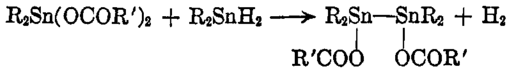
of 1,1,2,2-tetra-*n*-butyl-1,2-diacetoxyditin, which took up 93.4% of the expected bromine, 62% of pure di-*n*-butylacetoxytin bromide was obtained. These and other results are summarized in Table II. When the acid/hydride ratio was 2.0, the product was the simple dialkyldiacyloxytin. Only when this ratio was 1.0 or less was it possible to isolate pure ditin. In the case of succinic acid, although the ratio was as small as 0.83, the product was the simple tetrameric succinate. Loss of hydride occurred with trichloroacetic acid, whereas trifluoroacetic acid showed no such apparent loss. With benzoic acid it was possible to obtain the ditin or the dialkyldiacyloxytin according to whether the acid/hydride ratio was 1.0 or 2.0, respectively.

As the major product of the reaction appeared to depend on the acid/hydride ratio, it seemed possible that the reaction proceeds according to the following two steps:

$$R_2SnH_2 + 2\,R'COOH \longrightarrow R_2Sn(OCOR')_2 + 2\,H_2 \qquad (5)$$

---

[4] T. M. Andrews, F. A. Bower, B. R. LaLiberte, and J. C. Montermoso, *J. Am. Chem. Soc.*, 80, 4102 (1958).



$$R_2Sn(OCOR')_2 + R_2SnH_2 \longrightarrow \underset{R'COO}{R_2Sn}—\underset{OCOR'}{SnR_2} + H_2 \quad (6)$$

The fact that the simple dialkyldiacyloxytins are formed in some cases suggests the occurrence of the first step. This occurs specifically with di-*n*-butyltin dihydride and acetic acid. The second step was brought about by mixing di-*n*-butyltin diacetate and di-*n*-butyltin dihydride in equimolar amounts. A 91% yield of the expected product along with the expected volume of hydrogen was obtained. This step was also demonstrated in reactions of di-*n*-butyltin dihydride with di-*n*-butyltin dibenzoate and di-*n*-butyltin succinate, respectively.

Experiments were carried out in order to determine whether the course of the reaction varied in a systematic way with the strength and type (aromatic or aliphatic) of acid used. The results are presented in Table III. Reactions were carried out with different ratios of acid to hydride using acetic and benzoic acids. Only one ratio was used with the other acids.

TABLE III

REACTIONS OF DI-*n*-BUTYLTIN DIHYDRIDE WITH RCOOH IN DIOXANE TO FORM $Bu_2Sn(OCOR)_2$ (A) AND $(Bu_2SnOCOR)_2$ (B)

RCOOH	Ratio of Acid to Hydride	% of A	% of B	Moles of H_2/ Moles of Bu_2SnH_2
Formic	2.5	100	2	2.12
	1.25	48.3	51.3	1.74
Acetic	1.25	9	82	1.41
	1.25	11	80	1.41
	2.50	54	36	1.62
Monochloroacetic	1.25	50	38	1.57
Dichloroacetic	1.25	33	3.5	0.71
Trichloroacetic	1.25	9	3.8	0.24
Trifluoroacetic	1.25	12	53	0.79
Benzoic	1.25	26	69	1.55
	2.50	80	13	1.78
o-Chlorobenzoic	1.25	47.3	48.5	1.65
p-Methylbenzoic	1.25	39	64	1.72

There is little regularity in the figures, as can be seen by comparing results obtained with an acid/hydride ratio of 1.25. Acetic acid gives 82% of ditin; the stronger acid, chloroacetic, gives more monotin than ditin, whereas the still stronger acid, trifluoroacetic, gives more ditin than monotin. Doubling the ratio of acid to hydride has the anticipated effect of increasing the proportion of monotin with acetic and benzoic acids.

The observations are consistent with a sequence involving reactions 5 and 6. The nature of the product is determined by the concentrations of the reactants and by the relative rates for the various steps. As diphenyltin dihydride is prone to give only the ditin regardless of the variation of acid concentration within the limits used, it may be concluded that, for this hydride, reaction 6 has a considerably larger rate constant than does reaction 5. This holds over a change in acid strength over five powers of ten. In the case of di-*n*-butyltin dihydride, on the other hand, the rate constants are more nearly equal. It is possible to change the product composition from predominantly ditin (in the case of benzoic acid) to predominantly monotin merely by doubling the acid concentration. The lack of a consistent variation in product composition with acid strength suggests that although reaction 5 is accelerated as the acid strength is increased, reaction 6 is not.[5] Steric effects, not dependent on acid strength, might well be more important in reaction 6 than in reaction 5.

Although an extensive study of their reactions remains to be made, some characteristics of diacyloxyditins were noted. All of the tetraphenyldiacyloxyditins except that derived from hexanoic acid decomposed at the melting point or at some temperature between about 175° and 200°, frequently with evolution of gas. The decomposition products from 1,1,2,2-tetraphenyl-1,2-diacetoxyditin were examined. A 68% yield of tetraphenyltin was isolated from one decomposition experiment, along with a 25% yield of tin (II) acetate. Thus the main reaction in this case is disproportionation, although other reactions appear to accompany it. The butyl analogs did not appear to undergo decomposition at their melting points.

EXPERIMENTAL

All melting points are uncorrected.

Tin analyses were carried out by the method of Gilman and Rosenberg.[6] Other analyses were performed by the Galbraith Microanalytical Laboratories, Knoxville, Tenn.

A nitrogen atmosphere was used to protect solutions containing hydride.

Melting points of the ditins were carried out using a preheated bath. The tetra-*n*-butyl-1,2-diacyloxyditins appear to melt without decomposition.

All yields reported are for analytically pure products.

Preparation of diphenyltin dihydride and di-n-butyltin dihydride. Diphenyltin dihydride was prepared by the reduction of diphenyltin dichloride with lithium aluminum hydride in ether.[3,7] The ether solution, after drying over calcium chloride, was treated in one of three ways according to the desired use:

Procedure A. The ether solution (about 0.4*M*) or portions of it were used directly for reactions with acids.

Procedure B. The ether solution was concentrated by aspirator to about a fifth of its original volume and this concentrate was used for reactions with acids. This was desirable in case the reaction went slowly in dilute solutions.

Procedure C. The solution was concentrated to constant weight by aspirator and cooled to −80°, whereupon the hydride solidified. This minimized decomposition when the

---

[5] Kinetic studies by P. L. Levins in these laboratories have shown that the reactions of acids with tri-*n*-butyltin hydride obey the Brönsted catalysis law.

[6] H. Gilman and S. D. Rosenberg, *J. Am. Chem. Soc.*, **75**, 3592 (1953).

[7] A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 2692 (1947).

hydride had to be stored before use. The hydride was removed from the bath and allowed to warm to room temperature and the required amount was weighed and used directly or dissolved in a small amount of anhydrous ether.

Di-*n*-butyltin dihydride was prepared by essentially the same method as above. The ether solution was concentrated and the concentrate distilled, b.p. 50–52°/0.5 mm.; 83–86% yield.

Typical reactions involving diphenyltin dihydride by procedure A. Reaction of diphenyltin dihydride with hexanoic acid. To approximately 120 ml. of an ether solution containing 0.0500 mole of diphenyltin dihydride, obtained by Procedure A above, was added 0.100 mole of hexanoic acid. Evolution of gas started within a few minutes and was 90% complete in about 8 hours. Concentration of the solution gave 14.8 g., (77%), m.p. 58–72°, of colorless, crystalline, impure 1,1,2,2-tetraphenyl-1,2-dihexanoyloxyditin. Recrystallization from petroleum ether (b.p. 40–60°) resulted in a final recovery of 9.55 g. (49%) m.p. 85–87°. This compound appeared to melt without decomposition, nor was decomposition observed when the temperature was raised to 175°.

By Procedure B. Reaction of diphenyltin dihydride with dichloroacetic acid. To approximately 25 ml. of an ether solution containing 0.050 mole of diphenyltin dihydride was added 0.040 mole of dichloroacetic acid. Evolution of gas started within a few minutes and was over 97% complete in three hours. Colorless crystals, which had formed during the reaction, were filtered off, giving 13.66 g. (85%) of impure 1,1,2,2-tetraphenyl-1,2-bis-dichloroacetoxyditin. Recrystallization of 3.00 g. from chloroform resulted in a final recovery of 2.81 g. (75%), m.p. 169° dec. When the melting point was taken in the usual fashion, sintering started at 158° with melting at 169° accompanied by gas evolution and formation of a brown-black residue.

By Procedure C. Reaction of diphenyltin dihydride with o-chlorobenzoic acid. Diphenyltin dihydride (7.16 g., 96% pure), (0.025 mole) prepared by Procedure C above, was mixed with 5.85 g. (0.375 mole) of *o*-chlorobenzoic acid and 35 ml. of anhydrous ether. Measurement of gas volume showed the reaction to be 50% complete in 2 hours and 100% complete in 20 hours. The precipitate (11.44 g.) of impure 1,1,2,2-tetraphenyl-1,2-bis-*o*-chlorobenzoyloxyditin was recrystallized from chloroform giving 8.91 g. (83%), m.p. 161°. The analytical sample was obtained by recrystallization from acetone giving 5.04 g., (47%), m.p. 161°. When placed in a preheated bath, it melted to a clear liquid at 161–162° without gas evolution and with the immediate formation of a colorless solid which gradually turned gray as the temperature was raised.

Reaction of di-n-butyltin dihydride with acetic acid in 1:2 mole ratio. To 4.70 g. (0.0200 mole) of di-*n*-butyltin dihydride was added 2.40 g. (0.0400 mole) of glacial acetic acid. Evolution of gas started within five minutes and was complete in four and one-half hours giving a volume (corrected) of 888 ml. (99%). Distillation of the liquid product gave 6.32 g. (90%) of di-*n*-butyltin diacetate, b.p. 112–114°/1 mm., m.p. 8.5–10.0°, n_D^{26} 1.4692. A mixture melting point with an authentic sample of di-*n*-butyltin diacetate showed no depression.

In order to determine if the solvent had any effect, the reaction was carried out as above except that 25 ml. of anhydrous ether was mixed with the di-*n*-butyltin dihydride before addition of the acetic acid. Gas was evolved more slowly and was complete in 24 hours giving a volume (corrected) of 892 ml. (99.6%). Evaporation of the ether and distillation of the liquid product gave 6.31 g. (90%) of di-*n*-butyltin diacetate, b.p. 110–112°/0.5 mm., m.p. 8.5–9.0°, n_D^{26} 1.4688. A mixture melting point with an authentic sample of di-*n*-butyltin diacetate showed no depression.

Reaction of di-n-butyltin dihydride with acetic acid in 1:1 mole ratio. To 4.70 g. (0.0176 mole) of di-*n*-butyltin dihydride was added 1.20 g. (0.0200 mole) of glacial acetic acid. Evolution of gas started within five minutes and was complete in 10 hours giving a volume (corrected) of 619 ml. Bromine analysis of a sample of the product showed 68% yield of the ditin based on di-*n*-butyltin dihydride. The remaining liquid (5.53 g.) mixed with 12 ml. of anhydrous ether after standing overnight at −70° gave 3.35 g. (65%) of colorless crystals of 1,1,2,2-tetra-*n*-butyl-1,2-diacetoxyditin, m.p. −7 to −4°, n_D^{26} 1.5060. Mixture melting point with an authentic sample showed no depression.

Reaction of di-n-butyltin dihydride with di-n-butyltin diacetate. To 4.70 g. (0.0200 mole) of di-*n*-butyltin dihydride was added 7.20 g. (0.0200 mole) of di-*n*-butyltin diacetate. Evolution of gas started within 10 minutes and was 98% complete in 10 hours. After 18 hours, gas evolution had ceased giving a corrected volume of 410 ml. (92%). A sample of the colorless liquid (11.70 g.) remaining in the flask decomposed on attempted distillation at 1 mm. Recrystallization of the remaining 11.35 g. from 25 ml. of anhydrous ether cooled to −70° gave 10.06 g. (91%) of colorless needles of 1,1,2,2-tetra-*n*-butyl-1,2-diacetoxyditin, m.p. −7.0 to −4.0°, n_D^{26} 1.5068.

In two separate runs 94% of the theoretical amount of bromine in carbon tetrachloride reacted with the ditin.

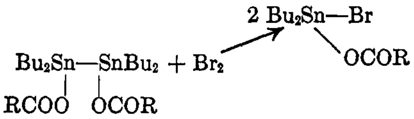
Reaction of di-n-butyltin dihydride with succinic acid. Di-*n*-butyltin dihydride was prepared from 0.100 mole of di-*n*-butyltin dichloride and 0.100 mole of lithium aluminum hydride in 90 ml. of anhydrous ether at 0°. The ether solution was concentrated by aspirator to constant weight and three-tenths of it (containing 0.03 mole of hydride, based on the dichloride used) was mixed with 2.95 g. (0.025 mole) of succinic acid and 25 ml. of anhydrous ether. The mixture was stirred for two and one-half days. Filtration of the product gave 8.00 g. (92%) of impure di-*n*-butyltin succinate melting at 184–185.5°. Recrystallization of 6.00 g. from benzene gave 3.53 g., m.p. 185.5–187°. Concentration of the product yielded 1.14 g., m.p. 186–187.5°. Total recovery was 4.67 g. (71%), m.p. 185.5–187.5°. The analysis (see Table II) corresponded to the product expected from the reaction of one mole of succinic acid per mole of hydride. Its failure to react with bromine showed that the product did not contain tin-tin bonds. A sample of this material was found to have the same infrared spectrum as a sample of tetrameric di-*n*-butyltin succinate prepared by the method of Andrews *et al.*[4] from dibutyltin oxide and succinic anhydride. The mixture melting point of the two substances showed no depression.

Reaction of di-n-butyltin dihydride with di-n-butyltin succinate. To 1.74 g. (0.050 mole) of di-*n*-butyltin succinate and 1.17 g. of 88% di-*n*-butyltin dihydride (0.0044 mole) was added 10 ml. of benzene and the flask connected for gas collection. Gas evolution started within 5 minutes and continued slowly for 6 hours at which time the reactants were warmed to approx. 75° on a hot plate until gas evolution had ceased (6 hours). The corrected volume of gas was 106 ml. (95%). The product was a very syrupy yellow solution. It was treated to remove solvent at 100° using an aspirator and finally was kept for several hours at 1 mm. Two separate portions of the solid when analyzed with bromine showed 92% and 94% yields of ditin.

Reactions of di-n-butyltin dihydride with RCOOH to form $Bu_2Sn(OCOR)_2$ *(A) and* $(\underset{|}{Bu_2Sn}OCOR)_2$ *(B).* In all of these runs to 0.470 g. of di-*n*-butyltin dihydride of 88% purity (0.00176 mole) was added 0.00220 mole of RCOOH dissolved in 2.00 ml. of freshly distilled dioxane. Gas evolution usually started within 5–10 minutes and was complete within 6–16 hours. When gas evolution had ceased for several hours, the reaction product was titrated with bromine in carbon tetrachloride to the appearance of a persistent yellow color. The results of these experiments are shown in Table III.

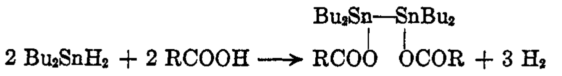
The relative amounts of A and B formed were calculated from the bromine analysis and the total gas produced.

The number of moles of B was calculated from the number of moles of bromine used by the reaction:



$$\underset{\text{RCOO}\quad\text{OCOR}}{\text{Bu}_2\text{Sn—SnBu}_2} + \text{Br}_2 \longrightarrow 2\ \text{Bu}_2\text{Sn}\underset{\text{OCOR}}{\overset{\text{Br}}{<}}$$

The number of moles of gas produced during the formation of B was calculated as equal to 3 times the number of moles of B by the reaction:



$$2\ \text{Bu}_2\text{SnH}_2 + 2\ \text{RCOOH} \longrightarrow \underset{\text{RCOO}\quad\text{OCOR}}{\text{Bu}_2\text{Sn—SnBu}_2} + 3\ \text{H}_2$$

The number of moles of gas formed in producing A was considered equal to the total number of moles of gas minus the number of moles of gas obtained in forming B.

The number of moles of A produced could then be calculated by the equation:

$$\text{Bu}_2\text{SnH}_2 + 2\ \text{RCOOH} \longrightarrow \text{Bu}_2\text{Sn(OCOR)}_2 + 2\ \text{H}_2$$

The percentages of A and B produced are based on di-*n*-butyltin dihydride.

Thermal decomposition of 1,1,2,2-tetraphenyl-1,2-diacetoxyditin. A sample of 1,1,2,2-tetraphenyl-1,2-diacetoxyditin (2.00 g., 0.00301 mole, m.p. 152°) in a test tube was placed in an oil bath preheated to 156° and suction applied (23 mm.). Over a three-hour period, with the oil bath temperature kept between 153 and 161°, colorless needles sublimed and filled the tube above the oil level, and a tan residue (1.73 g.) remained in the bottom of the tube. Treatment of the residue with hot benzene (15 ml.) dissolved 1.56 g. from which on cooling 0.87 g. (68%) of colorless crystals were deposited which were shown to be tetraphenyltin by melting point (224–226°) and mixture melting point with an authentic sample. The sublimate 0.18 g. (25%), m.p. 189–190° was shown to be tin(II) acetate by comparison with an authentic sample prepared from tin(II) hydroxide and acetic acid.[8] During the sublimation at 23 mm. and 180–200° of 10.2 g. of product prepared by the latter method, 5.1 g. (43%) of stannous acetate, was obtained melting clear at 189–190°, and 5.1 g. of yellow-black residue, evidently from decomposition at elevated temperature. The sensitivity of stannous acetate to air was shown by exposing a sample for 17 days to air during which time it changed from colorless to yellow and its melting point changed to 180–183° (with residue). These observations and the literature references to stannous acetate as a yellowish powder, m.p., 182°, point to preparation of an improved product by sublimation.

Reaction of 1,1,2,2-tetra-n-butyl-1,2-diacetoxyditin with bromine. To 5.85 g. (0.0100 mole) of 1,1,2,2-tetra-*n*-butyl-1,2-diacetoxyditin was added 4% bromine solution in carbon tetrachloride until the bromine color persisted. Evaporation of the solvent on a steam bath followed by vacuum at 0.5 mm. gave 7.39 g. (99.5%) of colorless crystals of di-*n*-butylacetoxytin bromide, melting at 66–67°. Two recrystallizations from light petroleum ether gave the analytical sample 4.61 g. (62%), m.p. 67.0–68.5°.

Anal. Calcd. for $C_{10}H_{21}SnO_2Br$: Sn, 31.92; C, 32.29; H, 5.69; Br, 21.49. Found: Sn, 32.21, 31.98; C, 32.52; H, 5.71; Br, 21.62.

DURHAM, N. H.

---

[8] E. H. Baker, *J. Appl. Chem.*, **3**, 323 (1953).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE UNIVERSITY]

Siloxanes and Silanols Derived from Perphenylated Polysilanes

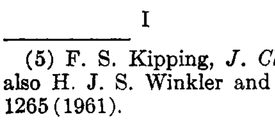
A. W. P. JARVIE, H. J. S. WINKLER, AND H. GILMAN

Received May 5, 1961

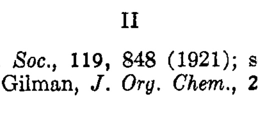
From hydrolysis of 1,4-dichloro- and 1,4-diiodooctaphenyltetrasilane there was isolated a cyclic siloxane containing four silicon atoms and one oxygen atom. This siloxane was obtained from octaphenylcyclotetrasilane by recrystallization from tetralin. The structure of one of the cyclic siloxanes isolated by Kipping[1] was identified as 2,2,3,3,5,5,6-octaphenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane by its synthesis.

Several siloxanes were isolated by Kipping from the hydrolysis of the dihalooctaphenyltetrasilane and the oxidation of either Compound (A), octaphenylcyclotetrasilane, or Compound (B), dodecaphenylcyclohexasilane.[1–4] One of these, designated as octaphenylsilicotetrane oxide, was proposed to be a five-membered ring containing one atom and four diphenylsilylene units.[1] Analytical data and hydrogen values[5] confirmed the suggested structure. This "monoxide" was obtained by hydrolysis of 1,4-diiodooctaphenyltetrasilane.[1] It was also prepared from Compound (A) either by the action of several oxidizing agents[2a] or from attempted halogenations in the presence of either water or oxygen.[1,2a]

Two isomeric oxides with the molecular formula $(C_6H_5)_8Si_4O_2$ were also isolated in many of the reactions discussed above. The tentative structures proposed for these compounds were I and II:



I



II

---

[1] F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 830 (1921).

[2] (a) F. S. Kipping, *J. Chem. Soc.*, **123**, 2590 (1923); (b) F. S. Kipping, *J. Chem. Soc.*, **123**, 2598 (1923).

[3] F. S. Kipping, *J. Chem. Soc.*, 2978 (1927).

[4] The compounds designated by F. S. Kipping as Compound (A) and Compound (B) have been shown to be octaphenylcyclotetrasilane and dodecaphenylcyclohexasilane. See H. Gilman, D. Peterson, A. W. Jarvie, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **82**, 2076 (1960); **83**, 4089 (1961).

[5] F. S. Kipping, *J. Chem. Soc.*, **119**, 848 (1921); see also H. J. S. Winkler and H. Gilman, *J. Org. Chem.*, **26**, 1265 (1961).