Table II shows a 9% yield of tri-*n*-amyltin pentafluoropropionate from di-*n*-amyldimethyltin and pentafluoropropionic acid; possible explanations include a free radical mechanism or a redistribution reaction.[16]

Experimental

Table I lists 18 reactions of tetraethyltin and a median yield of 60%, in reflux through electrical heating. Purifications of organotin products included several fractional distillations in small or very small equipment, or four double crystallizations from carbon tetrachloride. Tetraethyltin reacted not at all or very slowly with tin(II) fluoride or benzoate, acetyl chloride, ethyltrichlorosilane, phosphorus trichloride, mercuric oxide, copper(I) iodide, thallium(I) formate, silver oxide, silver thiocyanate, or silver iodide.

Known boiling points for the chief organotin products in Table I include[17]: triethyltin chloride, 210°; triethyltin bromide, 224°; triethyltin iodide, 234°; triethyltin acetate, 224° (m.p., 132–134°)[8]; triethyltin trifluoroacetate, 218° (m.p., 122–123°)[8]; diethyltin dichloride, 220° (m.p., 84°).

Seven dealkylations in Table II involve difficult purifications for four reasons: simultaneous removal of one methyl group and either one *n*-amyl or one *n*-butyl group; persistent retention of a little perfluoroacid or hydrogen halide, later removed by vigorous shaking once or twice with a double volume of water for 1 hr.; some free radical reaction or redistribution reaction at least in the formation of tri-*n*-amyltin pentafluoropropionate; also, the presence of dark solid residues.

Gradual addition of pentafluoropropionic acid to di-*n*-amyldimethyltin required a temperature of 45–50° to obtain a single phase. After the reaction, fractional distillation under 1 mm. pressure furnished the following: 11 g. of *n*-amyldimethyltin pentafluoropropionate, with some unchanged di-*n*-amyldimethyltin, mainly at 90° (found: $OCOC_2F_5$, 34.0); 14 g. of di-*n*-amylmethyltin pentafluoropropionate, b.p. mainly 112°, later extracted with water and redistilled to get a 5-g. pure center cut; 10 g. of high cut, b.p. approximately 140°; also, 2 g. of residue later discarded. Two hr. storage of the 11-g. low cut with an extra 1.6 g. of pentafluoropropionic acid at 50°, next extraction with water, and finally two distillations furnished 3.6 g. of center cut *n*-amyldimethyltin pentafluoropropionate. Repeated distillation of the high cut at 1 mm. furnished 4 g. of solid admixed with a little liquid, later pipetted off. Then followed four careful fractional freezings, next crystallization from *n*-butyl chloride, then pressing dry on filter paper, and finally storage in a desiccator; 1.1 g. of solid tri-*n*-amyltin pentafluoropropionate resulted. Determinations of both m.p. and b.p. were in capillaries.

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[16] H. H. Anderson, *J. Am. Chem. Soc.*, **73**, 5804 (1951); also references therein.

[17] E. Krause and A. von Grosse, "die Chemie der metallorganischen Verbindungen," Berlin, Gebruder Borntraeger, 1937.

CONTRIBUTION FROM THE RESEARCH LABORATORIES, UNION CARBIDE PLASTICS COMPANY,
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The Reaction of Carbon Disulfide with Organotin Oxides and Related Substances

BY WALTER T. REICHLE

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When bis-(triphenyltin) oxide is heated with carbon disulfide or carbon oxysulfide, the oxygen is quantitatively replaced by sulfur, yielding pure bis-(triphenyltin) sulfide and carbon oxysulfide and/or carbon dioxide. Similar tin, lead, mercury, and arsenic metalorganic compounds having metal–oxygen–metal or metal–hydroxide bonds also undergo this reaction with carbon disulfide to yield sulfides. Analogous phosphorus, germanium, silicon, and boron compounds do not exchange oxygen for sulfur when heated with carbon disulfide.

Introduction

It has been observed that the largely insoluble polydialkyltin oxides[1] dissolve in hot carbon disulfide to yield clear solutions. A closer examination of these solutions showed that the organotin oxygen atoms had been quantitatively replaced by sulfur atoms.

$$[R_2SnO]_n + CS_2 \longrightarrow COS + [R_2SnS]_3$$

Since the yields and product purities appeared high and the reaction conditions fairly mild, it was decided to examine the scope of this reaction using other oxygen-containing metalorganic compounds. These sulfur-containing products have been prepared previously by other methods.

Results

Table I gives the products and yields of twelve organometallic compounds which were found to

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[1] W. T. Reichle, *J. Polymer Sci.*, **49**, 521 (1961).

TABLE I

PRODUCTS AND YIELDS OF REACTIONS OF OXYGEN-CONTAINING METALORGANIC COMPOUNDS WITH CARBON DISULFIDE

Starting Material	Product	% Yield	Remarks
$[(C_6H_5)_3Sn]_2O$	$[(C_6H_5)_3Sn]_2S$	99[a]	
$[(CH_3)_2SnO]_n$	$[(CH_3)_2SnS]_3$	95[a]	
$[(n\text{-}C_4H_9)_2SnO]_n$	$[(n\text{-}C_4H_9)_2SnS]_3$	99[a]	
$[(n\text{-}C_8H_{17})_2SnO]_n$	$[(n\text{-}C_8H_{17})_2SnS]_3$	99[a]	
$[(n\text{-}C_4H_9)_3Sn]_2O$	$[(n\text{-}C_4H_9)_3Sn]_2S$	99[a]	
$[(n\text{-}C_4H_9)_3Sn]_2O$	$[(n\text{-}C_4H_9)_3Sn]_2S$	96[a]	Used COS
$[(C_6H_5)_2SnO]_n$	$[(C_6H_5)_2SnS]_3$	19	
$(C_6H_5)_3PbOH$	$[(C_6H_5)_3Pb]_2S$	79	
C_6H_5HgOH	$(C_6H_5)_2Hg$	30	By-product HgS
$(C_6H_5)_3AsO$	$(C_6H_5)_3AsS$	85	
$(CH_3)_2As(O)OH$	$(CH_3)_3AsS$ +	11	
	$[(CH_3)_2As]_2S$	51	
$CH_3As(O)(OH)_2$	$[(CH_3As]_2S_3$	46	

[a] Crude yields; for details see Experimental.

react with carbon disulfide or carbon oxysulfide. The following compounds did *not* react with carbon disulfide even under very vigorous conditions (250°, 16 hr.): triphenylboroxine, triphenylphosphine oxide, diphenylgermanium oxide (trimer), and phenylstannoic acid, while only undefined gums containing substantially no sulfur could be obtained from triphenylsilanol and triphenyl-(triphenylstannoxyl) silane.[2]

All tin compounds tested, except for the phenylstannoic acid, reacted under varying conditions of time and temperature to produce the corresponding sulfur compounds in high yields and good purities. Generally, metalorganic compounds having metal–hydroxide bonds (triphenyllead hydroxide, dimethylarsenic acid, etc.) react with carbon disulfide to form metal–sulfur–metal bonds. The phenylmercuric hydroxide reacted and subsequently rearranged to form diphenylmercury and mercuric sulfide.[3,4]

$$2C_6H_5HgOH + 2CS_2 \longrightarrow (C_6H_5Hg)_2S + 2COS + H_2S$$

$$(C_6H_5Hg)_2S \longrightarrow HgS + (C_6H_5)_2Hg$$

In some cases reaction conditions had to be so drastic that the sulfur-containing product decomposed. For example, phenylarsenous oxide could be induced to yield all of its oxygen for sulfur only at about 200°. This resulted in a product which contained the beautiful red crystals of arsenic sulfide (As_4S_4)[5] plus sulfur-containing oils which would not yield phenylarsenous sulfide on work-up. At lower reaction temperatures, only incomplete substitution of sulfur for oxygen resulted. In another case, bis-(diphenylarsenous) oxide, the product was an oil which analyzed correctly for the sulfide but could not be induced to crystallize to the known bis-(diphenylarsenous) sulfide.[6] The only arsenic compound which exchanged its oxygen against sulfur readily was the triphenylarsenic oxide.

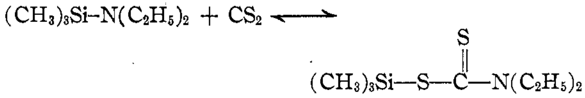
The lead compound reacted under very mild conditions. Triphenyllead hydroxide forms bis-(triphenyllead) sulfide at room temperature in carbon disulfide. Similarly, the reaction of phenylmercuric hydroxide caused the carbon disulfide to reflux.

In summary, this procedure appears to be a satisfactory preparative method only for the tin–sulfur compounds, bis-(triphenyllead) sulfide, and triphenylarsenic sulfide. The reaction conditions are quite critical; too high a reaction temperature may degrade the product.

Discussion of Results

Only two cases could be found in the literature in which an oxygen-containing organometallic compound undergoes reaction with carbon disulfide. Alkylmercuric hydroxides were reported to form the corresponding hydrosulfides[7] and phenylarsenic acid reacted to yield phenylarsenic sesquisulfide.[8] Salerio[9] determined the molecular weight of polydilauryltin oxide in boiling carbon disulfide and found it to be monomeric. He probably prepared the corresponding sulfide.[10a]

Carbon disulfide has similarly been found to react reversibly with the silicon–nitrogen bond,[11] as well as with some transition metal alkoxides.[12–14] The reaction of carbon disulfide with



$$(CH_3)_3Si\text{-}N(C_2H_5)_2 + CS_2 \longleftarrow (CH_3)_3Si\text{—}S\text{—}\overset{\overset{\displaystyle S}{\|}}{C}\text{—}N(C_2H_5)_2$$

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[2] S. Papetti and H. W. Post, *J. Org. Chem.*, **22**, 526 (1957).

[3] E. Dreher and R. Otto, *Ber.*, **2**, 542 (1869).

[4] R. T. McCutchan and K. A. Kobe, *Ind. Eng. Chem.*, **46**, 675 (1954).

[5] C.-S. Lu and J. Donohue, *J. Am. Chem. Soc.*, **66**, 818 (1944).

[6] G. T. Morgan and D. C. Vining, *J. Chem. Soc.*, 782 (1920).

[7] I. A. Koten and R. Adams, *J. Am. Chem. Soc.*, **46**, 2764 (1924).

[8] J. G. Everett, *J. Chem. Soc.*, 1691 (1930).

[9] A. Salerio, *Gazz. chim. ital.*, **81**, 664 (1951).

[10] (a) This sulfide should be trimeric.[10b] The molecular weight of a sample of polydi-*n*-octyltin oxide, which had been found to be 8950 in boiling xylene, was 1600 in boiling carbon disulfide after 4 hr. of refluxing; the indicated molecular weight was still decreasing (1083 calcd. for trimer); (b) W. T. Reichle, *J. Org. Chem.*, **26**, 4634 (1961).

[11] H. Breederveld, *Rec. trav. chim.*, **79**, 1126 (1960).

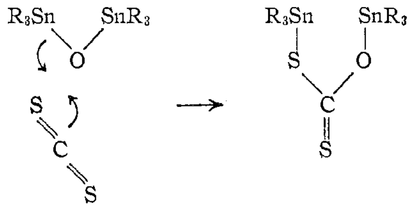
[12] J. V. Dubsky, *J. prakt. Chem.*, **201**, 142 (1916).

[13] M. Nehmé and S. J. Teichner, *Bull. soc. chim. France*, 659 (1960).

[14] L. H. Little, G. W. Poling, and J. Leja, *Can. J. Chem.*, **39**, 745 (1961).

group Ia alkoxides leads to the well known xanthates. Recently[15] it has been observed that trimethyl siloxytriethyltin forms the carbonate when contacted with carbon dioxide in acetone solution. In the reactions uncovered here, those metal–oxygen bonds reacted most readily which could be expected to be most ionic.[1] For example, triphenyllead hydroxide reacted at room temperature, bis-(triphenyltin) oxide at 90°, while similar germanium or silicon compounds would not react even at 250°. Also, the triphenylarsenic oxide reacted in boiling (46°) carbon disulfide, while the corresponding phosphorus compound was unreactive at 250°. Some further experiments demonstrated that the reaction is not reversible; bis-(tri-*n*-butyltin) sulfide does not yield the oxide on heating with carbon dioxide at 160° in benzene. The ebullioscopic molecular weights of dimethyltin sulfide (trimer) and bis-(triphenyltin) sulfide in carbon disulfide were normal and exhibited no drift with time (up to 48 hr.). Carbon oxysulfide can be used to replace oxygen with sulfur. The use of either carbon disulfide or carbon oxysulfide leads to carbon dioxide and carbon oxysulfide in the first case and carbon dioxide in the second case. This was demonstrated by an infrared examination of the gaseous co-products of these reactions.

Since this reaction bears a certain analogy with the xanthate reaction some attempts have been made to identify the intermediate(s) involved. It would seem reasonable[11,15] for the carbon disulfide to first insert itself between the metal–oxygen bond



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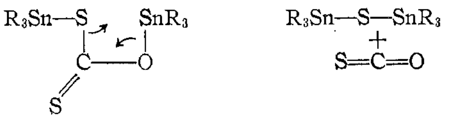
The product then expels carbon oxysulfide



To test this hypothesis the triphenyllead hydroxide–carbon disulfide reaction (carried out at 25°) was carefully freed of solvent on a salt plate in a drybox (at or below 25°) and the resulting solid examined by infrared. The spectrum was superimposable with that of authentic bis-(triphenyllead) sulfide; no bands due to C=S bonds[14] could be found. Several other experiments designed to demonstrate the presence of a xanthate-type intermediate failed to show anything positive.

Experimental

The starting materials were either purchased[1] or prepared by known[16] procedures. The triphenyl-(triphenylstannoxyl) silane was prepared from equimolal quantities of triphenylsilanol, triphenyltin chloride, and triethylamine in benzene. It melted at 142.5–144.0°; lit.[2] m.p. 138–139°. *Anal.* Calcd. for $C_{36}H_{30}OSiSn$: Sn, 19.1; Si, 4.48; mol. wt., 625. Found: Sn, 18.9; Si, 4.89; mol. wt., 622 (ebullioscopic in methyl ethyl ketone).

The reactions conducted above the reflux temperature of carbon disulfide (46°) were carried out in a 300-ml. stainless steel bomb by charging 1–10 g. of the oxide, 150–200 ml. of carbon disulfide, and heating for the indicated period of time. Work-up was carried out by distilling off the volatiles and distilling or recrystallizing the product(s).

Bis-(triphenyltin) oxide was heated for 18 hr. at 95°; crude yield, 99%; m.p. 140.5–141.5°; lit.[17] m.p. 141.5–143.0°. *Anal.* Calcd. for $C_{36}H_{30}Sn_2S$: S, 4.37. Found (crude product)[18]: S, 4.40.

Polydi-*n*-butyltin oxide was heated at 150° for 25 hr.; a liquid product was obtained[10b] (99% crude yield). *Anal.* Calcd. for $C_8H_{18}SnS$: S, 12.1. Found (crude product): S, 12.7.

Polydi-*n*-octyltin oxide was heated at 140° for 20 hr.; a liquid product was obtained[10b] (99% crude yield). *Anal.* Calcd. for $C_{16}H_{34}SnS$: S, 8.49. Found (crude product): S, 9.06.

Bis-(tri-*n*-butyltin) oxide was heated for 16 hr. at 145°; a liquid product was obtained (99% crude yield). *Anal.* Calcd. for $C_{24}H_{54}Sn_2S$: S, 5.23. Found (crude product): S, 5.53.

This oxide also was heated with carbon oxysulfide for 18 hr. at 95°; 96% yield of crude product which distilled at 185–188° (0.6 mm.) (91% yield). *Anal.* Calcd. for $C_{24}H_{54}Sn_2S$: S, 5.23. Found: S, 5.66.

Bis-(tri-*n*-butyltin) sulfide (10.1 g.) was heated with 50 g. of carbon dioxide (as Dry Ice) in 150 ml. of benzene for 18 hr. at 160° in a 300-ml. bomb. *Anal.* Calcd. for $C_{24}H_{54}Sn_2S$: S, 5.23. Found (crude product): S, 5.04.

Polydiphenyltin oxide was heated for 16 hr. at 160°; 80% crude yield; m.p. 152–175°; lit.[19] m.p. 183–184°. Crystallization from hexane–methylene chloride yielded (19%) crystals, m.p. 181–184°. *Anal.* Calcd. for C_{12}-

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(15) R. Okawara and K. Sugita, *J. Am. Chem. Soc.*, **83**, 4480 (1961).

(16) E. Krause and A. von Grosse, "Chemie der metallorganischen Verbindungen," Verlag Borntraeger, Berlin, 1937.

(17) J. G. Noltes and G. J. M. van der Kerk, *Chem. Ind.* (London), 294 (1959).

(18) Generally the analyses of the crude products are given to demonstrate the fair purity. In each case suitable purification produced a product the analyses of which were in substantial accord with the calculated figures.

(19) I. T. Eskin, A. N. Nesmeyanov, and K. A. Kocheshkov, *J. Gen. Chem. USSR*, **8**, 35 (1938); *Chem. Abstr.*, **32**, 5386 (1938).

$H_{10}SnS$: S, 10.5. Found: S, 10.6. A second crop of solids melted at 152–156°. *Anal.* Calcd. for $C_{12}H_{10}SnS$: Sn, 39.0; S, 10.5. Found: Sn, 39.7; S, 11.8.

A similar run heated at 160° for only 3 hr. gave an 87% yield of an amorphous solid, m.p. 56–64°, which could not be crystallized to the pure sulfide trimer. The analyses indicate a trimeric isomer (linear ?). *Anal.* Calcd. for $C_{12}H_{10}SnS$: Sn, 39.0; S, 10.5, mol. wt. (trimer), 915. Found (crude product): Sn, 39.8; S, 10.9; mol. wt., 865 (ebullioscopic in benzene).

Polydimethyltin oxide was heated for 26 hr. at 140°; crude yield, 95%; m.p. 142–149°; lit.[20] 149°. *Anal.* Calcd. for C_2H_6SnS: S, 17.8. Found (crude product): S, 18.8.

Phenylmercuric hydroxide was mixed with carbon disulfide at room temperature. This brought the mixture to reflux. Filtration and recrystallization isolated a 30% yield of diphenylmercury; m.p. 122.5–123.5° undepressed with authentic material; lit.[21] m.p. 125°.

Triphenylarsenic oxide was refluxed for 1.5 hr. Crystallization gave an 85% yield of triphenylarsenic sulfide, m.p. 163.5–164.5°, lit.[22] m.p. 162°. *Anal.* Calcd. for $C_{18}H_{15}AsS$: S, 9.47. Found: S, 9.17, 9.53.

Dimethylarsenic acid was heated at 150° for 18 hr. Crystallization from hexane gave an 11% yield of trimethylarsenic sulfide; m.p. 181.5°; lit.[23] m.p. 177.5°. *Anal.* Calcd. for C_3H_9AsS: S, 21.05. Found: S, 21.4.

Removal of the solvent from the residue and flash distillation yielded two fractions. One, a liquid, b.r. 80–90° (0.3 mm.) (51% yield), with a very powerful odor, evidently was bis-(dimethylarsenous) sulfide.[24] *Anal.* Calcd. for $C_4H_{12}As_2S$: C, 19.82; H, 4.96; S, 13.22. Found: C, 19.66; H, 4.78; S, 14.05.

The higher boiling fraction, b.r. 135–140° (0.3 mm.), solidified; 25% yield. Crystallization and sublimation gave colorless, odorless needles, m.p. 157.5–163.5°. This substance analyzed approximately for C_2H_6AsSO. *Anal.* Calcd. for C_2H_6AsSO: C, 15.70; H, 3.92; S, 20.90. Found: C, 16.37; H, 4.16; S, 21.03.

Triphenyllead hydroxide was left standing at room temperature in carbon disulfide for 48 hr. Crystallization from benzene–hexene gave a 79% yield of the sulfide, m.p. 139–141°, which was prepared previously[25] but no melting point was given. *Anal.* Calcd. for $C_{36}H_{30}Pb_2S$: C, 47.55; H, 3.30; S, 3.52. Found (purified): C, 48.10; H, 3.25; S, 3.86.

A few drops of the above carbon disulfide solution were placed onto a rock-salt plate and freed of volatiles in a drybox. An infrared spectrum of this was superimposable with that of the crystallized product; no bands due to C=S were in evidence.[14]

Bis-(diphenylantimony) oxide was heated at 115° for 5.5 hr. The resulting oil could not be crystallized. Bis-(diphenylantimony) sulfide melts at 69°.[26] *Anal.* Calcd. for $C_{24}H_{20}Sb_2S$: C, 49.30; H, 3.42; S, 5.48. Found (crude oil): C, 49.02; H, 3.51; S, 7.41.

Phenylarsenous oxide was heated at various temperatures (100–200°, 18 hr.). In no case could a crystalline material be isolated which corresponded to phenylarsenous sulfide (lit. m.p. 152°[27]; calcd. for C_6H_5AsS: S, 17.4). The reaction at 200° gave a 20% yield of red, crystalline arsenic sulfide; m.p. 304–307°; lit.,[28] 307° (β form). *Anal.* Calcd. for AsS: S, 29.9. Found: S, 30.0. The solvent-free residual oils contained 16.8% sulfur.

Bis-(diphenylarsenous) oxide was heated at 140° for 18 hr. This gave an oil (91% yield); lit.[29] m.p. 64–67° for bis-(diphenylarsenous) sulfide. *Anal.* Calcd. for $C_{24}H_{20}As_2S$: C, 58.80; H, 4.09; S, 6.53. Found (crude oil): C, 57.08; H, 4.01; S, 7.18. This oil could not be crystallized to a solid.

Phenylarsenic acid was heated at 150° for 18 hr. Removal of a small amount of solid by filtration and evaporation of volatiles left a 30% yield of a dark pitch which analyzed approximately for phenylarsenic sesquisulfide in analogy with previous work.[8] *Anal.* Calcd. for $C_{12}H_{10}As_2S_3$: C, 36.00; H, 2.50; S, 24.00. Found: C, 33.62; H, 2.05; S, 23.9.

Methylarsenic acid was heated at 145° for 18 hr. Removal of low boiling volatiles and flash distillation (b.r. 95–115° (0.1–0.2 mm.)) gave a 46% yield of methylarsenic sesquisulfide as a viscous orange liquid. *Anal.* Calcd. for $C_2H_6As_2S_3$: C, 8.70; H, 2.17; S, 34.80. Found: C, 8.83; H, 2.45; S, 34.82.

Acknowledgment.—Mr. John J. Mahoney carried out a great deal of the experimental work. The analyses were made by the Geller Laboratories, Bardonia, New York, or the analytical department of this Laboratory under the direction of Mr. John V. Atkinson.

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(20) T. Harada, *Bull. Chem. Soc. Japan*, **17**, 283 (1942); *Chem. Abstr.*, **41**, 4444e (1947).

(21) Reference 16, p. 175.

(22) Reference 16, p. 549.

(23) Reference 16, p. 490.

(24) Reference 16, p. 475.

(25) G. Gruettner, *Ber.*, **51**, 1298 (1918).

(26) Reference 16, p. 616.

(27) Reference 16, p. 513.

(28) N. A. Lange, "Handbook of Chemistry," 8th ed., Handbook Publishers, Inc., Sandusky, Ohio, 1952, p. 204.

(29) Reference 16, p. 517.