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NOTE

ORGANOTIN CHEMISTRY
XIV*. ALKYLATION OF ORGANOTIN SULFIDES

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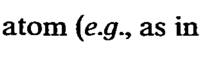
INTRODUCTION

The tin–oxygen bond in organotin compounds is known to have a reactivity different than that of the C–O bond in ethers. Thus, the Grignard reagent is known to cleave Sn–O bonds in organotin oxides resulting in alkylation of organotin compounds[1,2]. This property underlies one preparative method[3] for the synthesis of unsymmetrically substituted alkyl and/or aryl organotin compounds (eqn. 1).

$$(C_4H_9)_2SnO + 2\,CH_2{=}CHMgCl \longrightarrow (C_4H_9)_2(CH_2{=}CH)_2Sn \qquad (1)$$

The generality of this behavior of the Sn–O bond towards an alkylating reagent is further demonstrated by the reduction of bis(tri-n-butyltin) oxide with lithium aluminum hydride to give tri-n-butyltin hydride[4].

Our purpose was to examine the behavior of organotin sulfides toward alkylating reagents. If the behavior of organotin sulfides was similar to that of the oxides, one would have a new method for alkylating organotin compounds. On the other hand, if organotin sulfides behaved differently, one could perhaps selectively alkylate the Sn–O bond in an organotin compound containing both Sn–O and Sn–S bonds on the same tin atom (*e.g.*, as in  $Bu_2Sn\genfrac{}{}{0pt}{}{\diagup O-CH_2}{\diagdown S-CH_2}$). Such behavior would give a selectivity of alkylation that is not available to the organotin chemist. A recent patent disclosure[5] has prompted this report of our work†.

RESULTS AND DISCUSSION

In order to study the behavior of Sn–S bonds under alkylating conditions di-n-butyltin sulfide was treated with butylmagnesium chloride. The reaction was quite exothermic and resulted in the formation of tetra-n-butyltin in a 93% yield. The iden-

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† Since submission of this manuscript, we have become aware of a report on the alkylation and arylation of organotin sulfides with organolithium reagents.

tity of the product was based on its physical constants, gas chromatographic analysis and elemental analysis. Similarly, the reaction between a vinyl Grignard reagent and di-n-butyltin sulfide resulted in the formation of di-n-butyldivinyltin.

This result prompted us to study the scope and limitations of this reaction by varying (*i*) the nature of organotin sulfides, (*ii*) the nature of alkylating reagent and (*iii*) the solvent.

(*i*). *The nature of the sulfide*

In addition to di-n-butyltin sulfide, diphenyltin sulfide was studied as well as the bis(triorganotin) sulfides in the butyl and phenyl series. Butylthiostannoic anhydride was included to complete the butyl series. The reactivity of a mercaptide and a thiophenoxide was also studied. See Table 1 for the results obtained for individual compounds.

TABLE 1

ALKYLATION OF ORGANOTIN SULFIDES

No.	Organotin sulfide	Alkylating reagent	Solvent	Product	Yield (%)	Tin analysis (%)	
						Calcd.	Found
1	$(Bu_3Sn)_2S$	BuMgCl	THF	Bu_4Sn	92	34.19	34.25
2	$[Bu_2SnS]_3$	BuMgCl	THF	Bu_4Sn	93	34.19	34.36
3	$[Bu_2SnS]_3$	ViMgCl	THF	Bu_2Vi_2Sn	92	41.36	40.94
4	$[Ph_2SnS]_3$	PhMgCl	THF	Ph_4Sn	98	27.79	28.42
5	$(Ph_3Sn)_2S$	PhMgCl	THF	Ph_4Sn	98	27.79	28.39
6	$(Ph_3Sn)_2S$	MeMgCl	THF	Ph_3MeSn	89	32.53	33.10
7	$(Ph_3Sn)_2S$	n-C_8H_{17}MgBr	Et_2O	n-$C_8H_{17}Ph_3Sn$	94	25.60	26.00
8	$[BuSn(S)S]_n$	BuMgCl	THF	Bu_4Sn	92	34.19	34.14
9	Bu_2Sn(S-lauryl)$_2$	BuMgCl	THF	Bu_4Sn	90	34.19	33.98
10	Ph_3SnSPh	PhMgCl	THF	Ph_4Sn	93	27.79	27.97
11	$[Ph_2SnS]_3$	PhLi	Benzene/Et_2O	Ph_4Sn	98	27.79	28.12
12	$[Bu_2SnS]_3$	BuLi	Hexane	Bu_4Sn	91	34.19	34.22
13	$(Bu_3Sn)_2S$	$LiAlH_4$	Et_2O	Bu_3SnH	72		[a]

[a] Identity of this product was established by b.p., n_D^{25}, IR and VPC.

(*ii*) *The nature of the alkylating reagents*

A number of different Grignard reagents, including aliphatic, aromatic, and vinylic types were used. Other alkylating reagents such as butyl- and phenyllithium were also studied. Finally, reactions using hydride ion (lithium aluminum hydride) were shown to give the corresponding alkyltin hydride in high yield.

(*iii*). *The solvent*

Ethereal solvents which are commonly used for the generation of Grignard reagents, such as diethyl ether or tetrahydrofuran (THF), were used. Hydrocarbon solvents such as hexane and benzene were equally satisfactory.

EXPERIMENTAL

Melting points of solid products were determined for identification purposes using open capillary tubes with a Mel–Temp apparatus (Laboratory Devices, Cambridge, Mass.). Elemental analyses were performed by Mr. P. Branigan and his associates at M&T Chemicals Inc. Infrared spectra were run on a Beckman IR-8 Infrared Spectrophotometer (Beckman Instruments, Inc., Fullerton, Calif.).

The procedures for alkylation were very similar. All the products obtained were compared with authentic samples. The physical constants of each product; *e.g.* m.p. or b.p., refractive index, and IR spectrum, were in complete agreement with those reported in the literature. The results of all the reactions and the elemental analyses of the products are summarized in the table above. The following procedure for di-n-butyldivinyltin is typical.

Alkylation of di-n-butyltin sulfide with vinylmagnesium chloride

Vinylmagnesium chloride solution (0.425 mole; 225 ml of a 1.89 mole/liter solution in THF) was placed in a one liter three-necked flask provided with a condenser, stirrer, addition funnel, and a nitrogen atmosphere. A solution of di-n-butyltin sulfide (52.8 g, 0.2 mole) in THF (150 ml) was added slowly while stirring over one-half hour. The reaction was quite exothermic. After the addition was completed, the reaction mixture was stirred at ambient temperature for 1 and then heated to reflux temperatures for 2 h. After cooling it was hydrolyzed with 20% citric acid solution. The organic layer was separated, washed with water and dried over anhydrous sodium sulfate. After stripping the solvent, the product was isolated by vacuum distillation; b.p. 114–116°/16 mm (lit.[4] 78–80/2 mm). The yield of product was 51.8 g (0.18 mole, 90%) and had $n_D^{25.5}$ 1.4820 (lit.[4] $n_D^{25.0}$ 1.4824).

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