

TIN HETEROCYCLES. SOME PHENOXASTANNIN AND PHENOTHIASTANNIN DERIVATIVES*

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INTRODUCTION

Novel heterocyclic organosilicon, -boron, and -phosphorus compounds have been obtained from the reaction of 2,2'-dilithiodiphenyl ether (I) with diorganodichlorosilanes^{2,3,4}, silicon tetrachloride^{2,3}, diphenylsilane⁵, phenylsilane⁵, n-butyl metaborate⁶, and phenyldichlorophosphine⁷. Also, heterocyclic organosilicon compounds have been obtained from the reaction of 2,2'-dilithiodiphenyl sulfone⁸ (X) with diorganodichlorosilanes⁹. Since, to our knowledge, no heterocyclic compounds containing the C-Sn-C linkage and oxygen or sulfur in the ring had previously been reported, it was of interest to determine if such compounds could be prepared by allowing (I) and (X) to react individually with diorganotin dichlorides and stannic chloride.

The use of dilithium compounds for the preparation of tin heterocycles is not new. Tin heterocycles have been obtained from the reaction of *o,o'*-dilithiobibenzyl with diphenyltin dichloride and stannic chloride¹⁰. A tin analog of fluorene has been obtained from the reaction of 2,2'-dilithiobiphenyl with triphenyltin chloride¹¹. Tin heterocycles in the cyclopentadiene series have been obtained from the reactions of 1,4-dilithiotetraphenylbutadiene with diorganotin dihalides and stannic chloride^{12,13,14}. Tin heterocycles containing the C-Sn-C linkage and nitrogen in the ring have been obtained from the reactions of diorganotin dichlorides and stannic chloride with various N-alkyl-2,2'-dilithiodiphenylamines^{15,16,17}.

RESULTS AND DISCUSSION

The reactions of (I) with diorganotin dichlorides and stannic chloride are summarized in chart 1. The reactions of (X) are summarized in chart 2. The reaction of (I) with dimethyltin dichloride gave 10,10-dimethylphenoxastannin (IV) in only 2% yield. A similar low yield (5%) was obtained when dimethyltin dichloride was allowed to react with (I) which was prepared by allowing 2,2'-dibromodiphenyl ether to react with n-butyllithium^{3,7}. A considerable amount of solid polymer accompanied the formation of (IV). In contrast to the very low yield of (IV), the yield of 10,10-dimethylphenothiastannin 5,5-dioxide (XI) from (X) and dimethyltin dichloride was 18%. When the reaction between (I) and dimethyltin dichloride was carried out in

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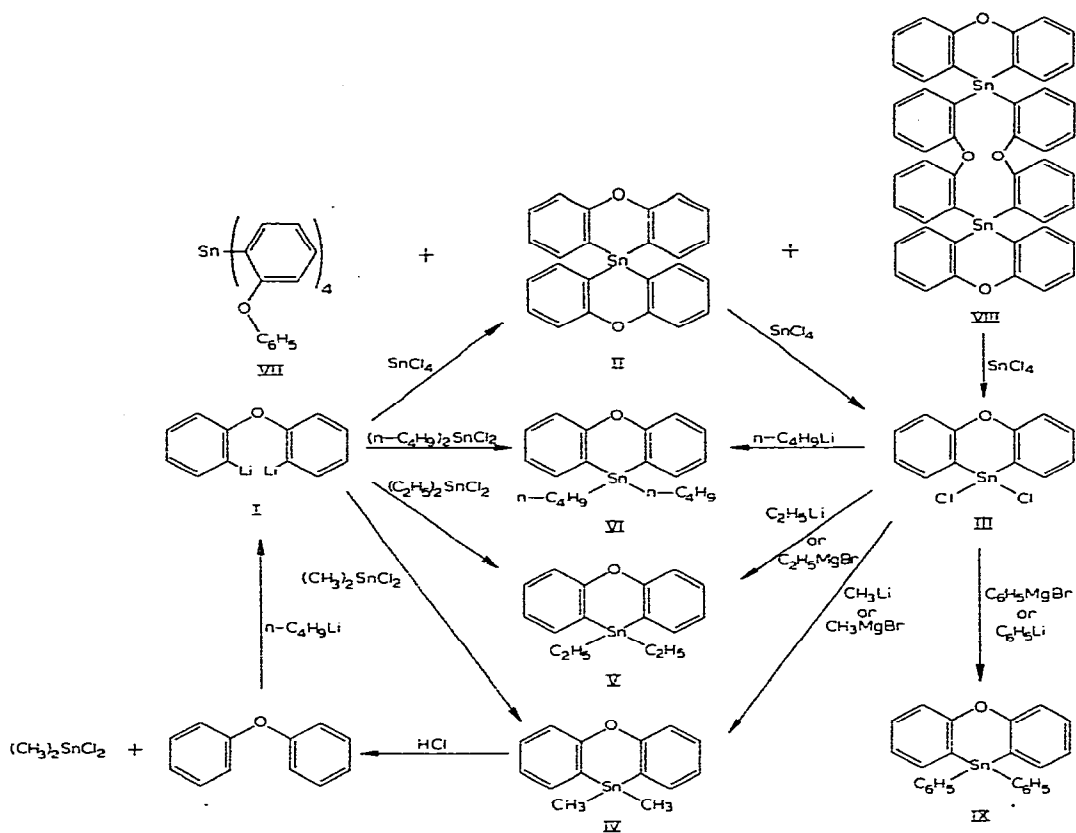


Chart 1

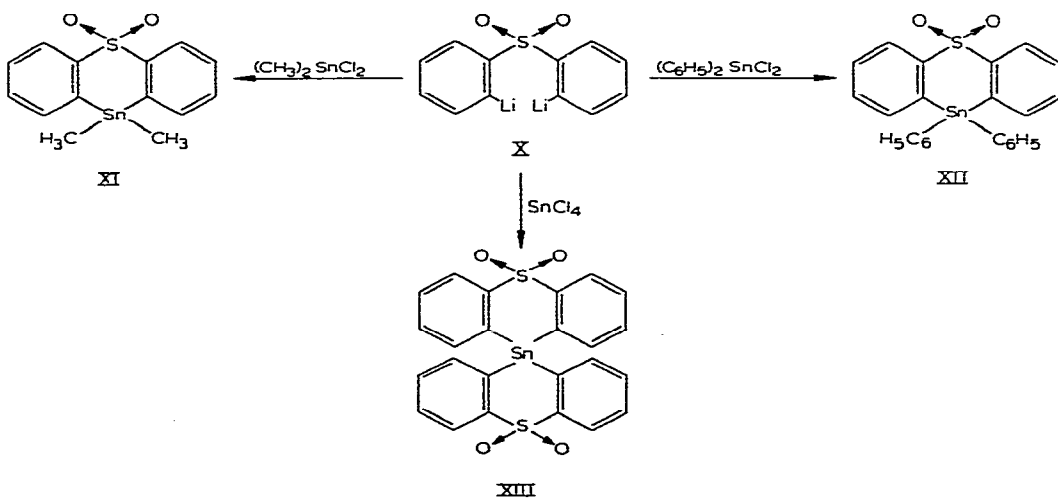


Chart 2

the presence of a relatively large amount of tetrahydrofuran, 10,10'-spirobiphenoxastannin (II) was unexpectedly obtained in 2% yield. Thus, under these conditions, (I) cleaves methyl groups from tin. The reaction of (I) with diethyltin dichloride and di-n-butyltin dichloride under conditions similar to those employed to obtain (IV) gave (V) (0.5% yield) and (VI) (2% yield), respectively.

The reaction of (I) with diphenyltin dichloride under a variety of conditions always resulted in the formation of tetraphenyltin. None of the desired 10,10-diphenylphenoxastannin (IX) could be isolated. In this reaction (I) probably cleaves phenyl groups from tin to give phenyllithium which then reacts with diphenyltin dichloride to give tetraphenyltin. An attempt to form (IX) by allowing (I) to react with triphenyltin chloride¹¹ also resulted in the formation of tetraphenyltin. The reaction of (X) with diphenyltin dichloride, on the other hand, gave the expected 10,10-diphenylphenothiaastannin 5,5-dioxide (XII) in 12% yield.

The structures (IV), (V), (VI), (XI), and (XII) are supported by elemental analyses, infrared data, and NMR data. The presence of a strong band at about 13.2 μ in the infrared spectrum of (IV), (V), (VI), and (XI) and the absence of appreciable absorption in the region 14.08–14.49 μ clearly indicates that these compounds are *ortho*-disubstituted benzene derivatives¹⁸. (XII) had bands in the infrared at 13.09 μ and 14.36 μ indicating the presence of both 1,2-disubstitution and monosubstitution. The NMR spectrum of each compound gave the correct ratio of aliphatic/aromatic protons. The structure for (IV) is further supported by the fact that passage of dry hydrogen chloride gas into a chloroform solution of (IV) gives dimethyltin dichloride and diphenyl ether. However, while these data support the assigned structures they do not necessarily exclude the possibility of polymeric structures or a structure with a twelve-membered ring. The molecular weight data, however, indicate that the assigned structures are correct. Molecular weight determinations indicated that (IV) was a dimer at 37°. At the higher temperature of the Rast procedure, however, dedimerization occurs since values corresponding to the monomer were obtained. Similar results were obtained for (V). Dimerization may be due to intermolecular coordination between tin and oxygen¹⁹. The NMR spectrum of (IV) also indicated the presence of intermolecular coordination between tin and oxygen since two methyl group environments—a singlet at τ 9.69 and a singlet at τ 9.43—were present²⁰. (VI) was dimeric at 37° and also at the higher temperature of the Rast procedure. The assigned structure is still probably correct, however, since (IV), (V), and (VI) were also obtained from the reaction of 10,10-dichlorophenoxastannin (III) with the appropriate organolithium reagent. Therefore, if structures (IV) and (V) are correct, then (VI) must also be correct.

The reaction of (I) with stannic chloride gave 10,10'-spirobiphenoxastannin (II) in 7% yield. The reaction of (X) with stannic chloride gave 10,10'-spirobiphenothiaastannin 5,5,5',5'-tetroxide (XIII) in 15% yield. Two additional products isolated in the reaction of (I) were tetrakis(*o*-phenoxyphenyl)tin (VII) and a compound, m.p. 352–353°, which we have tentatively assigned structure (VIII). Structure (VIII) was deduced from its elemental analysis, experimental molecular weight, and infrared spectrum. The infrared spectrum contained a strong band at 13.20 μ indicative of an *ortho*-disubstituted benzene derivative and lacked a band in the monosubstitution region. Further confirmation of structure (VIII) awaits an unambiguous synthesis and degradative studies.

Both 10,10'-spirobiphenoxastannin (II) and compound (VIII) gave 10,10-dichlorophenoxastannin (III) in good yield (57% and 74%, respectively) on reaction with stannic chloride at about 200°. The conversion of (II) into (III) by reaction with stannic chloride was expected since stannic chloride is known to convert R_4Sn compounds into compounds of the type R_2SnCl_2 ²¹. This reaction was first employed in the tin heterocycle field by Kuivila and Beumel¹⁰. The formation of (III) in good yield was fortunate since it enabled the preparation of the previously elusive 10,10-diphenylphenoxastannin (IX). The reaction of (III) with phenylmagnesium bromide afforded (IX) in 28% yield. The reaction of (III) with the appropriate Grignard reagents afforded (IV) (35% yield) and (V) (17% yield). The yields were lower when organolithium reagents were employed. Surprisingly, (VI) could not be obtained by the Grignard route. However, it was obtained in 7% yield when n-butyllithium was employed.

Incidental to the above work, a new phenoxasilin derivative², 10,10-diethylphenoxasilin, was obtained by allowing (I) to react with diethyldichlorosilane.

EXPERIMENTAL

General comments

Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected. All reactions were carried out in an atmosphere of prepurified nitrogen. Elemental analyses and Rast molecular weight determinations were performed by Dr. G. Weiler and Dr. F. B. Strauss, Microanalytical Laboratory, Oxford, England. Tin analyses and thermoelectric molecular weight determinations (carried out at 37° by the method of Tomlinson²²) were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N.Y. The infrared data were obtained using KBr pellets with a Perkin-Elmer Infracord. The far infrared data were obtained using KBr pellets with a Perkin-Elmer Model 21 double beam infrared spectrophotometer which was fitted with a cesium bromide prism and purged with nitrogen. The ultraviolet data were obtained with a Bausch and Lomb Spectronic 505 spectrophotometer using chloroform as solvent. The NMR spectra were determined with a Varian Model A-60 NMR spectrometer using deuteriochloroform as solvent and tetramethylsilane as the internal standard.

10,10-Dimethylphenoxastannin (IV)

To a solution of 10.0 g (0.059 mole) of diphenyl ether in tetrahydrofuran (45 ml) and diethyl ether (59 ml) was added a n-hexane solution of n-butyllithium (77 ml, 0.12 mole). The mixture was heated under reflux for 5 h and then dimethyltin dichloride (12.96 g, 0.059 mole) in diethyl ether (90 ml) was added over 1 h. The mixture was refluxed for 17 h, hydrolyzed with water (3 ml), and filtered. The solid residue was stirred with water (200 ml) and collected on a filter to give 2.56 g of polymer, m.p. >400°.

Distillation of the solvent from the filtrate left an oil which partially solidified upon being cooled and stirred with petroleum ether (b.p. 30–60°). Recrystallization of the solid from 2-butanone gave 0.40 g (2%) of (IV), m.p. 257.5–259°. Repeated recrystallizations from 2-butanone gave the analytical sample, m.p. 259–260°. [Found: C, 53.13; H, 4.25; Sn, 37.56; mol. wt., 298, 307 (Rast), 590 (dioxane), 592 (2-butanone),

610 (benzene), 635 (carbon tetrachloride). $C_{14}H_{14}OSn$ calcd.: C, 53.05; H, 4.45; Sn, 37.45%; mol.wt., 316.95.] IR: 3.29 (aromatic CH), 3.35 and 3.43 (CH_3), 6.38, 6.83, and 6.98 (aromatic C=C), 7.93, 8.21 (aromatic COC), 8.35, 8.62, 8.95, 9.42, 11.38, 12.40, 13.13 (1,2-disubstitution), and 13.80 μ ; far IR: 15.39, 15.99, 17.09, 18.54, 19.09, 22.53, 23.13, and 26.57 μ ; NMR: τ 9.69 and 9.43 [$Sn(CH_3)_2$] and 2.4–3.5 (multiplet, aromatic CH); ratio of aromatic/aliphatic protons, 1.43 (theoretical, 1.33); UV: 250 $m\mu$ (ϵ 4030) and 282 $m\mu$ (ϵ 2380).

10,10-Diethylphenoxastannin (V)

To a solution of 17.0 g (0.10 mole) of diphenyl ether in diethyl ether (170 ml) and tetrahydrofuran (130 ml) was added a n-hexane solution of n-butyllithium (125 ml, 0.20 mole). The mixture was refluxed for 5 h and then 24.77 g (0.10 mole) of diethyltin dichloride in diethyl ether (200 ml) was added. After 16 h at reflux, the mixture was hydrolyzed with water (4 ml) and filtered. The residue was stirred with an excess of water and collected on a filter to give 6.92 g of polymer, m.p. $>400^\circ$.

The filtrate was dried, and the solvent was removed by distillation. The oil which remained was distilled to give 8.40 g of liquid, b.p. $90\text{--}163^\circ/10$ mm. The residue was mixed with acetone (10 ml), and the mixture was cooled for about one week. The solid which deposited was collected on a filter and washed with acetone leaving 0.65 g of solid, m.p. $110\text{--}132^\circ$. Recrystallization from 2-butanone afforded 0.16 g (0.5%) of (V), m.p. $159\text{--}160^\circ$. Repeated recrystallizations from 2-butanone gave the analytical sample, m.p. $161\text{--}162^\circ$. [Found: C, 55.94; H, 5.21; Sn, 35.69; mol.wt., 305 (Rast), 547 (2-butanone). $C_{16}H_{18}OSn$ calcd.: C, 55.70; H, 5.26; Sn, 34.41%; mol.wt., 345.] IR: 3.30 (aromatic CH), 3.43 and 3.51 (C_2H_5), 6.40, 6.87, and 7.00 (aromatic C=C), 7.28 (CH_3), 7.96, 8.21 (aromatic COC), 8.63, 8.98, 9.46, 9.89, 10.35, 11.35, 12.43, 13.27 (1,2-disubstitution), 13.80, and 14.80 μ ; far IR: 15.34, 19.29, and 22.63 μ ; NMR: τ 8.87–8.98 and 8.58–8.66 [multiplets, $Sn(C_2H_5)_2$] and 2.4–3.7 (multiplet, aromatic CH); ratio of aliphatic/aromatic protons, 1.26 (theoretical, 1.25); UV: 246 $m\mu$ (ϵ 9140), 272 $m\mu$ (ϵ 3290), 281 $m\mu$ (ϵ 3510), and 288 $m\mu$ (ϵ 3280).

10,10-Di-n-butylphenoxastannin (VI)

To a solution of 17.0 g (0.10 mole) of diphenyl ether in diethyl ether (300 ml) was added a n-hexane solution of n-butyllithium (125 ml, 0.20 mole). The mixture was heated under reflux for 72 h and then 30.38 g (0.10 mole) of di-n-butyltin dichloride in diethyl ether (230 ml) was added over 70 min. The mixture was refluxed for 18 h, hydrolyzed with water (200 ml), and filtered to give 12.5 g of polymer, m.p. $>400^\circ$.

The organic layer was separated from the filtrate, dried, and distilled leaving a yellow oil which gave on further distillation 5.0 g of a yellow liquid, b.p. $80\text{--}164^\circ/0.02$ mm.

The residue was mixed with acetone (10 ml) and cooled for several weeks after which the solid which deposited was collected on a filter and washed with acetone to give 2.14 g of solid, m.p. $108\text{--}114^\circ$. Recrystallization from 2-butanone gave 0.97 g (2%) of (VI), m.p. $118\text{--}119^\circ$. [Found: C, 59.87; H, 6.48; mol.wt., 768 (Rast), 725 (2-butanone). $C_{20}H_{26}OSn$ calcd.: C, 59.88; H, 6.53%; mol.wt., 401.11.] IR: 3.30 (aromatic CH), 3.45 and 3.54 (C_4H_9), 6.40, 6.88, and 7.00 (aromatic C=C), 7.28 (CH_3), 7.96, 8.23 (aromatic COC), 8.64, 8.98, 9.30, 9.47, 11.40, 12.40, 13.15 (1,2-disubstitution), 13.80, 14.35, and 14.79 μ ; far IR: 15.39, 16.54, 16.84, 21.83, 22.73,

and 23.28 μ ; NMR: τ 8.5–9.5 [multiplet, $\text{Sn}(\text{C}_4\text{H}_9)_2$] and 2.4–3.7 (multiplet, aromatic CH); ratio of aliphatic/aromatic protons, 2.32 (theoretical, 2.25); UV: 245 $\text{m}\mu$ (ϵ 8160), 272 $\text{m}\mu$ (ϵ 2880), 281 $\text{m}\mu$ (ϵ 3090), and 288 $\text{m}\mu$ (ϵ 2880).

10,10'-Spirophenoxastannin (II) and (VIII)

(a) *From (I) and stannic chloride.* To a solution of 40.0 g (0.236 mole) of diphenyl ether in tetrahydrofuran (180 ml) and diethyl ether (234 ml) was added a *n*-hexane solution of *n*-butyllithium (308 ml, 0.472 mole). The mixture was refluxed for 5 h and then 31.28 g (0.12 mole) of stannic chloride in benzene (200 ml) was added over 2 h. After 12 h at reflux, the mixture was hydrolyzed with water (12 ml) and filtered. The solid residue was stirred with water (200 ml) and collected on a filter to give 18.7 g of an infusible solid.

The filtrate was dried and distilled leaving an oily solid which was collected on a filter and washed with 2-butanone to give 9.75 g of solid, m.p. 192–215°. This solid was stirred with hot 2-butanone (200 ml), and the mixture was filtered to give 1.05 g of solid, m.p. 340–347°. Recrystallization from chloroform gave 0.85 g (2%) of (VIII), m.p. 351–353°. Repeated recrystallizations from *p*-xylene gave the analytical sample, m.p. 352–353°. [Found: C, 63.51; H, 3.67; Cl, 0.00; Sn, 26.18; mol. wt., 753, 747 (Rast), 1005 (dibromomethane), 1275 (benzene). $\text{C}_{48}\text{H}_{32}\text{O}_4\text{Sn}_2$ calcd.: C, 63.34; H, 3.54; Sn, 26.08%; mol. wt., 910.14.] IR: 3.30 (aromatic CH), 6.39, 6.84, and 6.98 (aromatic C=C), 7.73, 7.91, 8.20 (aromatic COC), 8.62, 8.93, 9.44, 10.53, 11.25, 12.40, 13.20 (1,2-disubstitution), and 13.78 μ ; far IR: 15.94, 16.84, 22.68, 26.67, and 28.57 μ ; NMR τ 2.2–3.5 (multiplet, aromatic CH); UV: 246 $\text{m}\mu$ (ϵ 32,400) and 286 $\text{m}\mu$ (ϵ 18,000).

The filtrate was evaporated to about 140 ml and allowed to cool. Long white needles began to crystallize. Crystallization was allowed to proceed until thin lustrous white flakes of another compound began to appear. The mixture was filtered, and the residue was recrystallized from 2-butanone to give 2.04 g of (II) as long white needles, m.p. 220–221°. [Found: C, 63.33; H, 3.56; Sn, 26.00; mol. wt., 382, 374 (Rast), 463 (benzene), 415 (2-butanone), 593 (dioxane). $\text{C}_{24}\text{H}_{16}\text{O}_2\text{Sn}$ calcd.: C, 63.34; H, 3.54; Sn, 26.08%; mol. wt., 455.07.] IR: 3.29 (aromatic CH), 6.30, 6.85, and 7.00 (aromatic C=C), 7.63, 7.90, 8.20 (aromatic COC), 8.50, 8.61, 8.91, 9.40, 10.50, 11.15, 11.62, 12.80, 12.90, 13.12 (1,2-disubstitution), and 14.05 μ ; far IR: 15.94, 16.79, 19.54, 22.98, and 27.07 μ ; NMR: τ 2.6–3.1 (multiplet, aromatic CH); UV: 252 $\text{m}\mu$ (ϵ 23,400) and 298 $\text{m}\mu$ (ϵ 14,100).

The filtrates were combined, evaporated to dryness, redissolved in 2-butanone, and cooled. The mixture of long needles and lustrous flakes which separated were collected on a filter. The needles were mechanically separated from the mixture and recrystallized from 2-butanone to give an additional 1.1 g of (II), m.p. 220–221°. The lustrous flakes were recrystallized from 2-butanone to give 0.34 g of tetrakis(*o*-phenoxyphenyl)tin (VII), m.p. 234–235° (lit.²³ 234–235°). [Found: C, 72.92; H, 4.42; Sn, 14.54; mol. wt., 653 (benzene). $\text{C}_{48}\text{H}_{36}\text{O}_4\text{Sn}$ calcd.: C, 72.46; H, 4.57; Sn, 14.90%; mol. wt., 795.54.] IR: 3.30 (aromatic CH), 6.28, 6.38, 6.70, 6.83, and 6.98 (aromatic C=C), 8.12 (aromatic COC), 8.62, 8.97, 9.30, 9.50, 9.75, 11.45, 12.45, 13.30 and 14.40 (1,2-disubstitution, monosubstitution), and 13.85 μ ; far IR: 16.14, 17.29, 19.74, 20.43, 22.68, 27.67, and 29.57 μ ; UV: 245 $\text{m}\mu$ (ϵ 23,700) and 277 $\text{m}\mu$ (ϵ 9930).

The filtrates were combined, evaporated to dryness, redissolved in 2-butanone,

and cooled. The needles which separated were collected on a filter to give 0.8 g of (II), m.p. 220–221° [total yield of (II), 7%].

The filtrates were combined and evaporated to dryness, and the residue was recrystallized from 2-butanone to give 0.72 g of (VII), m.p. 234–235° [total yield of (VII), 2%].

(b) *From (I) and dimethyltin dichloride.* To a solution of 21.25 g (0.125 mole) of diphenyl ether in tetrahydrofuran (200 ml) and diethyl ether (260 ml) was added a n-hexane solution of n-butyllithium (156 ml, 0.25 mole). The mixture was heated under reflux for 5 h and then 27.46 g (0.125 mole) of dimethyltin dichloride in tetrahydrofuran (300 ml) was added over 80 min. An additional 100 ml of tetrahydrofuran and 100 ml of diethyl ether was added, and the mixture was refluxed for 12 h, hydrolyzed with water (6 ml), and filtered. The residue was stirred with water and collected on a filter to give 5.4 g of solid, m.p. >400°.

The filtrate was dried and distilled leaving an oil which was stirred with acetone and cooled. The oily solid which separated was collected on a filter and washed with acetone leaving 0.96 g of solid, m.p. 214–219°. Recrystallization from 2-butanone gave 0.58 g (2%) of (II), m.p. 219–220°.

10,10-Dichlorophenoxastannin (III)

(a) *From (II).* A mixture of (II) (1.45 g, 0.0032 mole) and stannic chloride (0.83 g, 0.0032 mole) was heated over a 45-min period to 220°. The mixture was maintained at 220° for 30 min and then at 180–210° for 2 h. The residue was recrystallized from benzene/petroleum ether (b.p. 30–60°) to give 0.71 g (31%) of (III), m.p. 243–244°. [Found: C, 40.35; H, 2.44; Cl, 19.65; Sn, 32.98; mol. wt., 613 (benzene). $C_{12}H_8Cl_2OSn$ calcd.: C, 40.28; H, 2.25; Cl, 19.82; Sn, 33.18%; mol. wt., 357.79.] IR: 3.30 (aromatic CH), 6.37, 6.83, and 6.96 (aromatic C=C), 7.90, 8.18 (aromatic COC), 8.59, 8.90, 9.47, 11.24, 12.45, 13.20 (1,2-disubstitution), and 13.80 μ ; far IR: 15.28, 15.98, 17.13, 19.23, 23.07, and 29.06; NMR: τ 2.2–3.6 (multiplet, aromatic CH); UV: 245 $m\mu$ (ϵ 6500) and 285 $m\mu$ (ϵ 2890). The yields in eight others runs were 61, 63, 63, 36, 57, 47, 31 and 36%.

(b) *From (VIII).* A mixture of (VIII) (1.00 g, 0.0011 mole) and stannic chloride (0.495 g, 0.0019 mole) was heated at 190–210° for 3 h. The residue was recrystallized from benzene/petroleum ether (b.p. 30–60°) to give 0.50 g (74%) of (III), m.p. 239–241°.

10,10-Diphenylphenoxastannin (IX)

Bromobenzene (2.93 ml, 0.028 mole) was added to a mixture of magnesium (0.68 g, 0.028 mole) and diethyl ether (20 ml), and as soon as the reaction started, diethyl ether (50 ml) was added. After the mixture was refluxed for 1 h, 2.00 g (0.00559 mole) of (III) in diethyl ether (50 ml) was added. The mixture was refluxed for 19 h, hydrolyzed with 50 ml of 1% aqueous hydrochloric acid, and filtered to give 1.89 g of solid, m.p. 215–235°. Recrystallization from 2-butanone gave 1.01 g of solid, m.p. 247–250°.

The ether layer was separated from the filtrate, dried, and distilled leaving a solid, m.p. 225–245°. Recrystallization from 2-butanone afforded 0.26 g of solid, m.p. 247–249°.

The two solids were combined and recrystallized from benzene to give 0.31 g of (IX), m.p. 250–251.5°. A second crop (0.37 g) had m.p. 249–251° (total yield 28%).

Repeated recrystallizations from 2-butanone gave the analytical sample, m.p. 251–252°. [Found: C, 65.54; H, 4.53; mol.wt., 648 (Rast), 1060 (dibromomethane). $C_{24}H_{18}OSn$ calcd.: C, 65.35; H, 4.11; mol.wt., 441.08.] IR: 3.28 (aromatic CH), 6.38, 6.75, 6.83, and 6.98 (aromatic C=C), 7.93, 8.20 (aromatic COC), 8.61, 8.94, 9.28, 9.43, 9.62, 9.98, 11.28, 12.35, 13.13 and 14.26 (1,2-disubstitution, monosubstitution), and 13.69 μ ; far IR: 15.24, 15.94, 17.14, 19.19, 22.18, and 26.77 μ ; NMR: τ 2.4–3.6 (multiplet, aromatic CH); UV: 245 $m\mu$ (ϵ 6210) and 282 $m\mu$ (ϵ 3090).

10,10-Dimethylphenothiastannin 5,5-dioxide (XI)

To a suspension of 21.8 g (0.1 mole) of diphenyl sulfone in diethyl ether (1000 ml) was added a n-hexane solution of n-butyllithium (160 ml, 0.2 mole) at -35 to -25° over a 4-h period. A solution of dimethyltin dichloride (22.0 g, 0.1 mole) in tetrahydrofuran (75 ml) was then added at -22 to -20° over a 1-h period. The mixture was refluxed for 24 h and then hydrolyzed with water (200 ml). The organic layer was separated, and the water layer was extracted with diethyl ether. The combined organic layers were dried, and the solvent was removed by distillation leaving a residue which yielded 17.8 g of solid, m.p. 105–140°, after being washed with cold methanol. Recrystallization from acetonitrile gave 6.5 g (18%) of (XI) as white crystals, m.p. 164–165°. [Found: C, 46.18; H, 4.02; S, 8.49; Sn, 32.50; mol.wt., 396, 378 (Rast), 330 (2-butanone). $C_{14}H_{14}O_2SSn$ calcd.: C, 46.06; H, 3.87; S, 8.78; Sn, 32.52%; mol.wt., 365.02.] IR: 7.70 and 8.69 μ (SO_2) and 13.17 μ (1,2-disubstitution); far IR: 15.49, 17.04, 17.64, 18.34, 19.19, 19.44, 20.88, 21.83, 23.43, 24.18, 29.02, and 33.06 μ ; NMR: τ 9.30 [$Sn(CH_3)_2$] and 2.2–2.7 and 1.7–2.0 (multiplets, aromatic CH); ratio of aromatic/aliphatic protons, 1.30 (theoretical, 1.33); UV: 246 $m\mu$ (ϵ 9760), 266 $m\mu$ (ϵ 2590), 273 $m\mu$ (ϵ 4470), and 281 $m\mu$ (ϵ 3560).

10,10-Diphenylphenothiastannin 5,5-dioxide (XII)

The procedure was essentially the same as for (XI). From 21.8 g (0.1 mole) of diphenyl sulfone and 34.3 g (0.1 mole) of diphenyltin dichloride there was obtained after recrystallization from acetonitrile 5.9 g (12%) of (XII) as white crystals, m.p. 164–165°. [Found: C, 59.38; H, 3.84; S, 6.71; Sn, 24.52; mol.wt., 433, 447 (Rast), 428 (2-butanone). $C_{24}H_{18}O_2SSn$ calcd.: C, 58.93; H, 3.71; S, 6.56; Sn, 24.27%; mol.wt., 489.15.] IR: 7.62 and 8.69 μ (SO_2) and 13.09 and 14.36 μ (1,2-disubstitution, monosubstitution); far IR: 15.35, 16.15, 16.84, 17.55, 19.44, 20.93, 21.68, 22.33, 23.33 and 29.97 μ ; NMR τ 2.2–2.8 and 1.6–1.8 (multiplets, aromatic CH); UV: 245 $m\mu$ (ϵ 10,800), 266 $m\mu$ (ϵ 6200), 273 $m\mu$ (ϵ 7090), and 281 $m\mu$ (ϵ 5330).

10,10'-Spirobiphenothiastannin 5,5,5',5'-tetroxide (XIII)

The procedure was essentially the same as for (XI) and (XII). From 21.8 g (0.1 mole) of diphenyl sulfone and 13.04 g (0.05 mole) of stannic chloride (added as a n-hexane solution) there was obtained after recrystallization from 2-butanone 4.0 g (15%) of (XIII) as white crystals, m.p. 315–320° decomp. [Found: C, 52.51; H, 2.94; S, 11.47; Sn, 21.70; mol.wt., 1060 (dibromomethane, 37°), 581, 585 (dibromomethane, 65°). $C_{24}H_{16}O_4S_2Sn$ calcd.: C, 52.29; H, 2.93; S, 11.63; Sn, 21.53%; mol.wt., 551.20.] IR: 7.62 and 8.66 μ (SO_2) and 13.00 μ (1,2-disubstitution); far IR: 15.47, 17.00, 17.67, 19.65, 21.03, 21.78, 23.35, 28.45, 29.55, and 31.05 μ NMR: τ 2.0–2.8 and 1.5–1.8 (multiplets, aromatic CH); UV: 247 $m\mu$ (ϵ 16,300), 267 $m\mu$ (ϵ 9620), 274 $m\mu$ (ϵ 12,000), and 282 $m\mu$ (ϵ 10,200).

10,10-Diethylphenoxasilin

To a solution of 6.80 g (0.04 mole) of diphenyl ether in tetrahydrofuran (60 ml) and diethyl ether (138 ml) was added a n-hexane solution of n-butyllithium (58 ml, 0.092 mole). The mixture was heated under reflux for 5 h and then 6.28 g (0.04 mole) of diethyldichlorosilane in tetrahydrofuran (60 ml) was added over 0.5 h. After 14 h at reflux, the mixture was hydrolyzed with water. The organic layer was separated and dried, and the solvent was removed by distillation. Distillation of the residue gave a liquid, b.p. 85–135°/0.04 mm. Redistillation gave 5.38 g (53%) of product, b.p. 111–114°. Redistillation gave the analytical sample, b.p. 112–114°/0.02 mm. [Found: C, 75.52; H, 7.41; Si, 11.02; mol. wt., 263 (Rast), 235 (2-butanone). $C_{16}H_{18}OSi$ calcd.: C, 75.54; H, 7.13; Si, 11.04%; mol. wt., 254.39.] IR: 3.28 (aromatic CH), 3.40 and 3.49 (C_2H_5), 6.15, 6.29, 6.36, 6.70, 6.83, and 7.02 (aromatic C=C), 7.25 (CH_3), 7.69, 7.89, 8.20 (aromatic COC), 8.42, 8.62, 8.83, 9.26, 9.80, 10.39, 10.55, 11.22, 11.60, 12.39, 13.18 (1,2-disubstitution), 13.53, 13.82, 14.03, and 14.43 μ ; far IR: 16.14, 19.24, 21.33, 22.03, 22.83, 24.03, 25.27, and 28.12 μ ; NMR: τ 9.07 and 9.02 [$Si(C_2H_5)_2$] and 2.4–2.9 (multiplet, aromatic CH); ratio of aliphatic/aromatic protons, 1.36 (theoretical, 1.25); UV: 251 $m\mu$ (ϵ 10,700), 289 $m\mu$ (ϵ 3800), and 298 $m\mu$ (ϵ 4260).

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SUMMARY

10,10-Dialkylphenoxastannins, the first examples of heterocycles containing the C–Sn–C linkage and oxygen in the ring, were obtained in low yield from the reaction of 2,2'-dilithiodiphenyl ether (I) with dialkyltin dichlorides and, in higher yield, from the reaction of 10,10-dichlorophenoxastannin (III) with organolithium reagents or Grignard reagents. 10,10-Diphenylphenoxastannin could only be obtained by the organolithium and Grignard route. (III) was prepared in high yield by allowing 10,10'-spirobiphenoxastannin (II) to react with stannic chloride. The reaction of (I) with stannic chloride gave three products: (II), tetrakis(o-phenoxyphenyl)tin, and a novel twelve-membered ring heterocycle containing two tin atoms in the ring (VIII). The reaction of (VIII) with stannic chloride gave a high yield of (III). The first examples of heterocycles containing the C–Sn–C linkage and sulfur in the ring were obtained by allowing 2,2'-dilithiodiphenyl sulfone to react with diorganotin dichlorides and stannic chloride. Infrared, far infrared, ultraviolet, and NMR data are reported for the new heterocycles.

REFERENCES

- 1 E. J. KUPCHIK AND J. A. URSINO, *Chem. Ind. (London)*, (1965) 794.
- 2 K. OITA AND H. GILMAN, *J. Am. Chem. Soc.*, 79 (1957) 339.
- 3 C. H. S. HITCHCOCK, F. G. MANN AND A. VANTERPOOL, *J. Chem. Soc.*, (1957) 4537.
- 4 H. GILMAN AND D. MILES, *J. Org. Chem.*, 23 (1958) 1363.
- 5 H. GILMAN AND W. J. TREPKA, *J. Org. Chem.*, 27 (1962) 1418.
- 6 J. M. DAVIDSON AND C. M. FRENCH, *J. Chem. Soc.*, (1960) 191.

- 7 F. G. MANN AND I. T. MILLAR, *J. Chem. Soc.*, (1953) 3746.
- 8 H. GILMAN AND D. L. ESMAY, *J. Am. Chem. Soc.*, 75 (1953) 278.
- 9 K. OITA AND H. GILMAN, *J. Org. Chem.*, 22 (1957) 336.
- 10 H. G. KUIVILA AND O. F. BEUMEL, Jr., *J. Am. Chem. Soc.*, 80 (1958) 3250.
- 11 R. GELIUS, *Angew. Chem.*, 72 (1960) 322.
- 12 F. C. LEAVITT, T. A. MANUEL, F. JOHNSON, L. U. MATTERNAS AND D. S. LEHMAN, *J. Am. Chem. Soc.*, 82 (1960) 5099.
- 13 E. H. BRAYE, W. HUBEL AND I. CAPLIER, *J. Am. Chem. Soc.*, 83 (1961) 4406.
- 14 H. H. FREEDMAN, *J. Org. Chem.*, 27 (1962) 2298.
- 15 H. GILMAN AND E. A. ZUECH, *J. Am. Chem. Soc.*, 82 (1960) 2522.
- 16 D. WASSERMAN, R. E. JONES, S. A. ROBINSON AND J. D. GARBER, *J. Org. Chem.*, 30 (1965) 3248.
- 17 E. J. KUPCHIK AND V. A. PERCIACCANTE, *J. Organometal. Chem.*, in press.
- 18 R. M. SILVERSTEIN AND G. C. BASSLER, *Spectrometric Identification of Organic Compounds*, Wiley, New York, 1963, p. 60.
- 19 R. C. POLLER, *J. Organometal. Chem.*, 3 (1965) 321.
- 20 W. J. CONSIDINE, G. A. BAUM AND R. C. JONES, *J. Organometal. Chem.*, 3 (1965) 308.
- 21 K. A. KOCHESHKOV, *Ber.*, 62 (1929) 996; 66 (1933) 1661.
- 22 C. TOMLINSON, *Mikrochim. Acta*, 3 (1961) 457.
- 23 R. C. POLLER, *J. Chem. Soc.*, (1963) 706.

J. Organometal. Chem., 10 (1967) 269-278