CYCLIC ESTERS OF THE GROUP IV ELEMENTS

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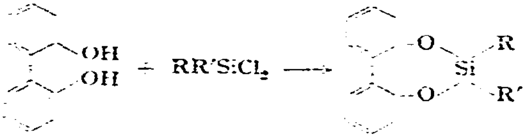
The synthesis of cyclic esters of silicon and tin by direct reaction of a dihydric phenol on elementary silicon or tin metal in the presence of a copper catalyst has been reported[1,2]. This paper describes the preparation of some further examples of this class of compounds by more conventional means.

The most important method of obtaining organosilicon alkoxides and phenoxides involves the treatment of an organosilicon chloride with an alcohol or a phenol, and this method was used to prepare a number of new derivatives of the spiro-esters by reaction of diorganodichlorosilanes with catechol and 2,2'-dihydroxybiphenyl. The product from diphenyldichlorosilane and catechol is extremely unstable hydrolytically

as is the spiro-compound. The corresponding dimethyl derivative has been previously synthesized[3,4], and shown to be monomeric**.

2,2'-Dihydroxybiphenyl was used similarly:



(I) = R = R' = CH_3

(II) = R = CH_3, R' = C_6H_5

(III) = R = R' = C_6H_5

These products seem more hydrolytically stable than the seven-membered spiro-compound. Refluxing in conc. alcoholic potassium hydroxide was necessary for hydrolysis in all cases and gave 2,2'-dihydroxybiphenyl and a polymeric siloxane. Ease of quantitative hydrolysis in this medium varies in the order $Me_2Si > MeC_6H_5Si > (C_6H_5)_2Si$. Experiments on the nitration and bromination of (2,2'-biphenylenedioxy)-dimethylsilane show that ring opening occurs in each case before attack on the biphenylene aromatic system.

The analogous use of organotin chlorides has been the subject of many patents, and is mentioned in reviews of the subject[5]. Reference to the details of these patents,

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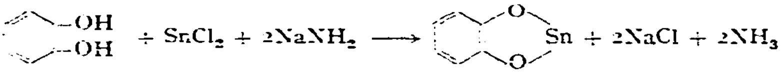
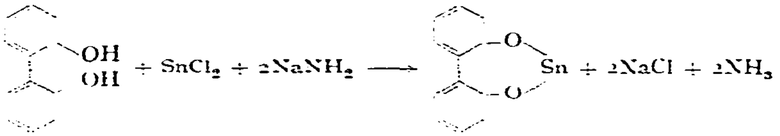
** The *Chem. Abstr.* abstract of reference 3 is in error on this point [*C.A.*, 51 (1957) 8677].

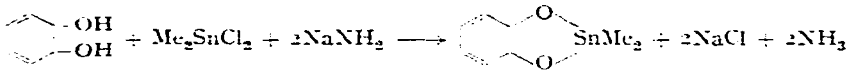
however, shows that reaction is always carried out in the presence of strong base, in some cases in aqueous base known to convert organotin halides into oxides. In a publication repeating a patented synthesis a different route was chosen, but no reason for doing so was given[6]. Sodium alkoxides have been used in all the published preparations of organotin esters from alcohols and organotin halides[7].

The results of our investigations, using dibutyltin dichloride for the most part, force the conclusion that the reaction of diorganotin dichlorides with phenols does not proceed unaided. In addition, hydrogen chloride acceptors such as sodium carbonate or sodium metal are not effective in promoting reaction, nor is the use of high boiling solvents to drive off the hydrogen chloride. Diorganotin dichlorides and also stannous chloride do react with dihydric phenols in the presence of sodamide, however. Sodamide is suspended in ether with the tin compound, and the phenol added in ether solution. Stirring under nitrogen is continued for a prolonged period, during which ammonia evolves slowly. When ammonia evolution ceases the solid is filtered and the product sublimed *in vacuo*. The products obtained previously by the Direct Synthesis method using dihydric phenols on a tin–copper contact mass can be obtained by this independent route:

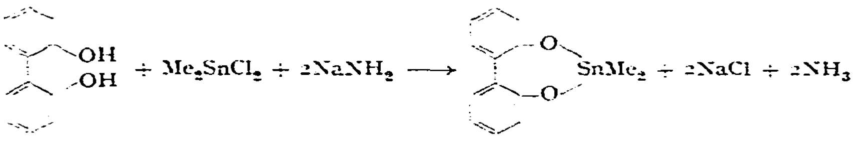




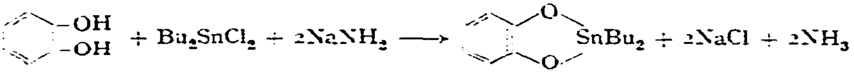
The method can also be employed to obtain alkyl-substituted derivatives of the above compounds. Catechol reacts with a suspension of sodamide with dimethyltin dichloride in ether under nitrogen to give (*o*-phenylenedioxy)dimethyltin:



2,2′-Dihydroxybiphenyl reacts similarly to give (2,2′-biphenylenedioxy)dimethyltin:

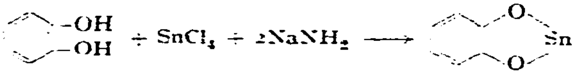


The analogous reaction of catechol with dibutyltin dichloride gives (*o*-phenylenedioxy)dibutyltin:



2,2'-Dihydroxybiphenyl does not react with dibutyltin dichloride in the presence of sodamide, however, even after stirring for 300 hours. The reaction of catechol with diphenyltin dichloride in the presence of sodamide results in cleavage of the phenyl groups, and (o-phenylenedioxy)tin is obtained. The product from diphenyltin dichloride and 2,2'-dihydroxybiphenyl decomposes on sublimation.

The method employing sodamide has the obvious drawbacks of long reaction time and the necessity of anhydrous conditions, but there is the great advantage of ready separation of the product from ammonia and sodium chloride. Sodamide is a strong reducing agent, however, and its action as such is seen in the reaction of catechol with stannic chloride to give (o-phenylenedioxy)tin(II):



Bradley has shown that stannic chloride reacts with the lithium salt of diethylamine to give tetrakis(diethylamino)tin[8], and that this material is rapidly esterified by alcohols[9]. Thus, tertiary Lewis bases were tested in order to determine whether the reaction with sodamide involved intermediate formation of $Sn{-}NH_2$ bonds or was being catalyzed by base. It was found that both pyridine and triethylamine catalyzed the formation of organotin esters from dibutyltin dichloride, but in these cases the separation of organotin ester from the amine hydrochloride formed was more complicated. In reactions using pyridine, the resulting pyridine hydrochloride could be washed from the ether-insoluble organotin ester. Pyridine hydrochloride is said to be insoluble in ether, but very soluble in small amounts of water; the ether used was triply dried over sodium wire, and all reactions were carried out under dry nitrogen; but the hydrochloride was found in the ether layer in every case. Triethylamine hydrochloride, formed by reaction of catechol with dibutyltin dichloride in presence of triethylamine, sublimes along with the (o-phenylenedioxy)dibutyltin product *in vacuo*, but separation can be achieved because of the solubility of the hydrochloride in chloroform. The analogous reaction with 2,2'-dihydroxybiphenyl gives the organotin ester and triethylamine hydrochloride, but both components of this mixture are soluble in chloroform, and no method of separation could be devised. Dimethyl- and diphenyltin dichlorides form white solids with pyridine and triethylamine in ether, and these complexes do not react with diols, presumably because of insolubility. Triphenylphosphine does not act as a catalyst.

The above tin esters and their derivatives are white solids, subliming *in vacuo* at *ca.* 260–340°, insoluble in water, conc. hydrochloric acid or in common organic solvents. Only in the case of (o-phenylenedioxy)dibutyltin is melting observed (272°), and all the solid esters exhibit excellent thermal stability. The esters are soluble in warm donating solvents, such as pyridine, and can be recovered unchanged from the anhydrous liquids. In solution, however, they are rapidly hydrolyzed to give the diol precursor. Hydrolysis also takes place in alcoholic potassium hydroxide, but requires longer periods. Molecular weights corresponding to the monomer were obtained ebullioscopically in "AnalaR" pyridine for (o-phenylenedioxy)dibutyltin and for (2,2'-phenylenedioxy)dimethyltin only. The other esters are too insoluble in pyridine for ebulliscopic molecular weight determination.

The action of catechol on lead chloride in the presence of sodamide gives the same product as that from the Direct Synthesis with a lead–copper contact mass.

STRUCTURE OF THE CYCLIC TIN ESTERS

The properties of these compounds show marked contrast to their silicon analogues. Their hydrolytic stability, low volatility, and insolubility all point to the possibility of their being polymeric materials. But they are soluble in donating solvents such as pyridine, and where sufficiently soluble in that solvent, ebullioscopic molecular weights show the compounds to be monomeric. Molecular weight determinations in pyridine can lead to erroneous conclusions, however, since the state of aggregation in other solvents or in the solid state may be different.

Recent reports by Van der Kerk *et al.* indicate that similar properties are exhibited by tin–nitrogen compounds where nitrogen atoms are coordinated intermolecularly to neighboring tin atoms, each tin atom becoming five-coordinated[10]. There are strong indications that the same type of polymeric structure is also present in tin–oxygen compounds, such as the acetates[11], and stannoxanes[12,13] and similar arguments can be used to explain the absence of carbonyl absorption in the infrared spectra of *sym*-tetraphenyldiaroyloxyditins[14]. Effects of this nature are probably seen in stannic alkoxides[15], and affect the crystal structure of stannous oxide[16]. In this light our results are better understood. The hydrolytic stability and low volatility of these compounds can be explained on the Sn $\leftarrow$ O coupling model, with strong Lewis bases like pyridine breaking up the Sn $\leftarrow$ O coordination and dissolving the compounds. It is interesting that this p_π–d_π coupling in tin–oxygen compounds is seen to occur *inter*molecularly, in contrast to the *intra*molecular type associated with the siloxanes.

EXPERIMENTAL

Materials

Organochlorosilanes and organotin chlorides were of reagent-grade purity.

Analyses

Carbon, hydrogen and nitrogen were determined by the Microanalytical Department of this Laboratory. Tin was analysed by the method previously described for silicon[1] except that no hydrofluoric acid treatment was used. Molecular weights were determined by three methods: compounds freely soluble in methylene dichloride were measured by a differential vapor pressure thermistor method[17]. Other solid compounds were mixed with M.A.R. camphor and the Rast procedure was followed. For certain of the tin compounds an ebullioscopic method employing pyridine was applied[18]. Moisture-sensitive materials were handled in a nitrogen-filled glove box of the usual type with phosphorus pentoxide as the drying agent. The refractive index of (2,2'-biphenylenedioxy)dimethylsilane was measured on an Abbe-refractometer. Infrared spectra were recorded on Perkin–Elmer Model 21 and infrared spectrometers with rock salt and potassium bromide optics. Samples were mulled in Nujol and examined between plates.

Esterification reactions

(o-Phenylenedioxy)diphenylsilane. Diphenyldichlorosilane (1/8 mole) was added dropwise to a briskly stirred solution of catechol (1/8 mole) in refluxing dry ether under nitrogen and the mixture was stirred until HCl evolution was complete (*ca.* 3 h).

Solvent was stripped at reduced pressure and the resulting white needles recrystallized from petroleum ether. Final purification was accomplished through repeated slow sublimations *in vacuo* at 100–110°. The compound (m.p. 162.2–163.5°) was very sensitive to moisture. Quantitative hydrolysis regenerated catechol. (Found: C, 74.7; H, 5.0; Si, 9.5. $C_{18}H_{14}O_2Si$ calcd.: C, 74.5; H, 4.8; Si, 9.65%.) Samples recrystallized from petroleum ether gave monomeric molecular weights in methylene dichloride, but some sublimed samples were shown to be dimeric.

(2,2′-Biphenylenedioxy)dimethylsilane. Dimethyldichlorosilane (1/4 mole) was added dropwise to a rapidly stirred solution of 2,2′-dihydroxybiphenyl (1/4 mole) in dry benzene under nitrogen at 55–60°, and stirring was continued at 55° for one hour, and then at reflux for 30 min to expel all the HCl. The product was then distilled through a nitrogen-filled fractionating column at reduced pressure to recover solvent and unreacted silane. A clear, viscous, water-white, colorless liquid, n^{22} 1.5843, distilled at 172.5–173.5/14.5 mm; it was insoluble in water and dilute base and gave no test with silver nitrate solution, although aqueous ferric chloride developed colour after some time. Hydrolysis in alcoholic potassium hydroxide overnight at 60° regenerated 2,2′-dihydroxybiphenyl quantitatively. (Found: C, 69.5; H, 6.0; Si 11.6. $C_{14}H_{14}O_2Si$ calcd.: C, 69.4; H, 5.8; Si 11.6%.) Molecular weight determinations in methylene dichloride gave 237, 239 and 249 (calcd. 242). A freshly distilled sample of the compound crystallized (m.p. 35.0–35.5°). UV spectra in ethanol gave maxima at 245 and 275 mμ.

(2,2′-Diphenylenedioxy)methylphenylsilane. Methylphenyldichlorosilane (1/16 mole) was added dropwise to a stirred solution of 2,2′-dihydroxybiphenyl (1/16 mole) in dry benzene under nitrogen and refluxing was continued for five hours to expel all the hydrogen chloride, and solvent was then stripped from the product. The resulting solid was recrystallized from petroleum ether and ether to fine white crystals (m.p. 101.0–101.2°). (Found: C, 74.9; H, 5.5; Si, 9.3. $C_{19}H_{16}O_2Si$ calcd.: C, 75.0; H, 5.3; Si, 9.2%.) Molecular weight determinations in methylene dichloride gave 290 and 304 (calcd. 304).

(2,2′-Biphenylenedioxy)diphenylsilane. Diphenyldichlorosilane (1/4 mole) was added dropwise to a stirred solution of 2,2′-dihydroxybiphenyl (1/4 mole) in dry benzene under nitrogen at room temperature and the mixture refluxed one hour to expel all the HCl, and then the solvent was stripped at reduced pressure leaving a mass of white needles which sublimed at 100° *in vacuo*. Heating for four hours in alcoholic potassium hydroxide regenerated 2,2′-dihydroxybiphenyl. The compound recrystallized from dry ether to give white needles (m.p. 120.5–121.5°). (Found: C, 78.1; H, 5.3; Si, 7.8. $C_{24}H_{10}O_2Si$ calcd.: C, 78.6; H, 4.9; Si, 7.65%.) Molecular weight determinations in methylene dichloride gave 354 and 370.5 (calcd. 366).

(o-Phenylenedioxy)tin. A solution of catechol (1/9 mole) in ether was added to a rapidly stirred slurry of stannous chloride (1/8 mole) with sodamide powder (1/4 mole) in *ca.* 250 cc. dry ether under nitrogen. Ammonia evolution began after some time, and stirring was continued for *ca.* 48 h. The white solid product was filtered and sublimed *in vacuo* at 300° to give a white material, which gave positive tests for tin(II) with cupferron, mercuric chloride and silver ion. (Found: C, 32.1; H, 1.6; Sn, 52.4. $C_6H_4O_2Sn$ calcd.: C, 31.75; H, 1.8; Sn, 52.3%.) The infrared spectrum of this material was identical with that of the product obtained from the reaction of catechol with tin–copper. No change occurred on addition of catechol to a stirred

solution of stannous chloride and pyridine in refluxing dry ether under nitrogen and only starting material was recovered with some black thermoplastic material which gave a positive test for chloride with silver nitrate.

Stannic chloride (1/8 mole) was added dropwise to a stirred suspension of sodamide (1/2 mole) in refluxing ether under nitrogen. A yellow colour developed. Catechol (1/8 mole) was added dropwise in ether solution, turning the reaction mixture an olive-drab colour. Stirring was continued for 72 h, during which time the slurry turned black. The solid was filtered and sublimed *in vacuo* to 380° to give a white solid whose infrared spectrum was identical to that obtained from catechol with tin–copper or stannous chloride. (Found: C, 31.95; H, 2.09; Sn, 52.8. $C_6H_4O_2Sn$ calcd.: C, 31.75; H, 1.8; Sn, 52.3%.)

Catechol (0.08 mole) reacted with diphenyltin dichloride (0.08 mole) and sodamide (0.17 mole) in refluxing ether under nitrogen during 48 h to give (*o*-phenylenedioxy)-tin. (Found: C, 32.4; H, 1.9. $C_6H_4O_2Sn$ calcd.: C, 31.75; H, 1.8%.)

(2,2'-Biphenylenedioxy)tin. 2,2'-Dihydroxybiphenyl (1/10 mole) in ether solution was added to a rapidly stirred slurry of stannous chloride (1/10 mole) with sodamide powder (1/8 mole) in refluxing dry ether under nitrogen and ammonia evolved during five hours. The white filtrate was sublimed *in vacuo* at 340° to give a white solid, insoluble in water, hot conc. hydrochloric acid, or organic solvents, but slightly soluble in warm pyridine, tetrahydrofuran, and dimethyl formamide and was recovered from these liquids unchanged. Hydrolysis regenerated 2,2'-dihydroxybiphenyl quantitatively. The infrared spectrum was identical to that of the product from 2,2'-dihydroxybiphenyl and tin–copper (Found: Sn, 39.2. $C_{12}H_8O_2Sn$ calcd.: Sn, 39.3%.)

(o-Phenylenedioxy)dibutyltin. To a rapidly stirred slurry of dibutyltin dichloride (1/8 mole) with sodamide (1/4 mole) in refluxing ether under nitrogen, a solution of catechol (1/8 mole) in ether was added dropwise and stirring continued with ammonia evolution for 32 h. The grey solid was then filtered and sublimed *in vacuo* at 260° to give a white solid (m.p. 272°) insoluble in common organic solvents, but slightly soluble in warm pyridine, tetrahydrofuran, and dimethylformamide and recoverable unchanged from these solvents. Hydrolysis in alcoholic potassium hydroxide regenerated catechol. Analytical data agreed with the formula $C_{14}H_{22}O_2Sn$. (Found: C, 49.2; H, 6.4; Sn, 35.2. $C_{14}H_{22}O_2Sn$ calcd.: C, 49.05; H, 6.45; Sn, 34.9%.) Molecular weights determined ebullioscopically in pyridine gave 334 (calcd. for the monomer 341).

Catechol (1/10 mole) in ether was added dropwise to dibutyltin dichloride (1/10 mole) with pyridine (1/5 mole) in refluxing ether under nitrogen. A white precipitate which formed almost immediately was filtered from the greenish ether and washed with portions of dry ether. The white solid gave a negative test for chloride with silver nitrate, but the filtrate gave a large amount of silver chloride. The infrared spectrum of this material was identical to that from the synthesis using sodamide. Analysis fit the formula as $C_{14}H_{22}O_2Sn$. (Found: C, 48.7; H, 6.6; Sn, 35.0. $C_{14}H_{22}O_2Sn$ calcd.: C, 49.0; H, 6.45; Sn, 34.9%.)

Catechol (1/20 mole) was treated similarly with dibutyltin dichloride (1/20 mole), but using a catalytic amount of pyridine (1/80 mole), to give (*o*-phenylenedioxy)-dibutyltin in 3.6% yield. Use of twice the molar quantity of pyridine used in the original reaction did not improve the yield there.

Triethylamine (0.067 mole) gave a red solution on addition to dibutyltin dichloride (0.034 mole) in refluxing ether under nitrogen to which addition of catechol (0.034 mole) caused immediate precipitation of white solid. This material after filtration and repeated washing with dry ether gave a positive test for chloride with silver nitrate, and the infrared spectrum, although in other ways similar to (*o*-phenylenedioxy)dibutyltin, contained bands at 2600 and 2500 cm^{-1}. The apparent yield was greater than theoretical, but the material sublimed *in vacuo* at 120° unchanged. Warm chloroform treatment gave a green solution of triethylamine hydrochloride and pure (*o*-phenylenedioxy)dibutyltin.

(o-Phenylenedioxy)dimethyltin. Catechol (1/10 mole) in ether was added to a rapidly stirred slurry of dimethyltin dichloride (1/10 mole) with sodamide (1/5 mole) in refluxing ether under nitrogen and stirring was continued for 48 h while ammonia evolved. The white solid was filtered and sublimed at 280° *in vacuo* to give a white powder which did not melt at 360° (but there was some decomposition in air at 260°) and was insoluble in common organic solvents, but slightly soluble in warm pyridine. (Found: C, 37.5; H, 3.8; Sn, 45.8. $C_8H_{10}O_2Sn$ calcd.: C, 37.4; H, 3.9; Sn, 46.4%.)

(2,2'-Biphenylenedioxy)dimethyltin. 2,2'-Dihydroxybiphenyl (1/10 mole) in ether was added to a rapidly stirred slurry of dimethyltin dichloride (1/10 mole) with sodamide powder (1/5 mole) in refluxing ether under nitrogen, and stirring was continued while ammonia evolved for *ca.* 56 h. The product was filtered and sublimed *in vacuo* at 260° to give a white solid insoluble in common organic solvents, but slightly soluble in warm pyridine, dimethylformamide and tetrahydrofuran and could be recovered unchanged from these solvents. (Found: C, 51.0; H, 4.2; Sn, 35.8. $C_{14}H_{14}O_2Sn$ calcd.: C, 50.4; H, 4.2; Sn, 35.8%.) The molecular weight was determined in pyridine. (Found: 303; calcd. for the monomer: 333.)

With lead chloride. When lead chloride was stirred with sodamide in refluxing dry ether under nitrogen an exothermic reaction set in giving metallic lead. In the presence of catechol, ammonia was evolved slowly to give a grey powder, which after filtration was sublimed *in vacuo* to give benzene and lead oxide at 520°.

ACKNOWLEDGEMENT

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SUMMARY

Five- and seven-membered ring heterocyclic compounds of silicon, tin(II), and tin(IV) have been prepared by esterification of dihydric phenols with organodichlorosilanes, stannous chloride, and organotin dichlorides. Catalysts by strong base is required with the tin compounds, and the products are exceedingly stable, both thermally and hydrolytically.

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